

Statistical Physics II.

Janos Polonyi
Strasbourg University
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Statistical physics usually deals with the dynamics of large systems. The interplay of the simple Newton equation for three particles may already produce a very complex motion. Thus one expects no hope to recover any regularity in studying large systems. But what helps is that a negative power of the number of degrees of freedom, N , $\epsilon = N^{-\alpha}$ where α is a fixed positive number plays the role of small parameter in an expansion scheme where the dynamics, obtained in the leading order is remarkably simple. The radius of convergence is rather small for isolated systems and N should be very large to have clean and precise predictions. But open systems may follow simple dynamics even for $N = 1$ because it is the number of degrees of freedom of their environment which enters in simplifying their dynamics.

The simplification mentioned above, universality, holds for certain observables only. To see this point clearer we should distinguish four time scales. τ_{micr} and τ_{rel} denote the microscopic and the relaxation time scales, respectively, characterizing our system. The measurement introduces two other time scales. t_{wait} stands for the waiting time between the preparation of the system and the start of the observation which lasts time t_{obs} . We see universal equilibrium phenomena for $\tau_{\text{micr}} \ll \tau_{\text{rel}} \ll t_{\text{wait}}, t_{\text{obs}}$. These are formally described by the ensembles of equilibrium statistical physics, imaginary closed systems with given probability distribution. The other extremity, $t_{\text{wait}}, t_{\text{obs}} \ll \tau_{\text{micr}}$, is not at all universal and difficult to address. The compromise, $\tau_{\text{micr}} \ll t_{\text{obs}} \ll \tau_{\text{rel}} \ll t_{\text{wait}}$ is called non-equilibrium physics and presents a treatable problem as long as the system we follow within its relaxation time is not too large.

We start our discussion with simpler equilibrium processes and the more involved case of non-equilibrium will be treated later.

I. EQUILIBRIUM ENSEMBLES

The ensemble method to reproduce the observable, average quantities of large systems consists of the construction of formal closed systems obeying certain probability distribution. We shall have a closer look at the origin of the inherent randomness and universal features of the ensembles.

A. Closed systems

Let us consider a system of N classical particles in complete isolation. We further assume that the only conserved quantity is the energy, $H(\mathbf{p}_1, \dots, \mathbf{p}_N, \mathbf{q}_1, \dots, \mathbf{q}_N)$ whose energy is known to us. In lacking of any other information we postulate that the micro states of our system, the points $(\mathbf{p}_1, \dots, \mathbf{p}_N, \mathbf{q}_1, \dots, \mathbf{q}_N)$ in the phase space are distributed in a uniform manner within a given energy shell,

$$P_E(\mathbf{p}_1, \dots, \mathbf{p}_N, \mathbf{q}_1, \dots, \mathbf{q}_N) = \delta(E - H(\mathbf{p}_1, \dots, \mathbf{p}_N, \mathbf{q}_1, \dots, \mathbf{q}_N)). \quad (1)$$

This assumption is not as harmless as it seems at the first sight. The point is that nonlinear coordinate transformations map uniform distribution into nonuniform one. Why do we privilege the Cartesian coordinate system when the basic laws of classical mechanics remain the same in curvilinear coordinates? A possible answer relies on Liouville theorem, stating that the density of states of closed systems is preserved in the phase space during their time evolution. If we impose stationarity on the unknown probability distribution then the form (1) is unique.

The experimental results correspond the average of some observable A over a time span $\tau_{\text{obs}} \ll \tau_{\text{micr}}, \tau_{\text{rel}}$,

$$\langle A \rangle = \lim_{\tau_{\text{obs}} \rightarrow \infty} \frac{1}{\tau_{\text{obs}}} \int_{\tau_{\text{wait}}}^{\tau_{\text{wait}} + \tau_{\text{obs}}} dt' A(t). \quad (2)$$

The ergodic hypothesis states that such a time average agrees with the ensemble average. This assumption allows us to reproduce the observations by ensemble averages.

One furthermore introduces the dimensionless Boltzmann entropy by the definition

$$S_B(E) = \ln \frac{\Omega(E)}{\Omega_0}, \quad (3)$$

where

$$\Omega(E) = \prod_{j=1}^N \int d^3 p_j d^3 q_j \delta(E - H(\mathbf{p}_1, \dots, \mathbf{p}_N, \mathbf{q}_1, \dots, \mathbf{q}_N)) \quad (4)$$

denotes the distribution of the phase space volume as the function of the energy E . The dimension of the argument of the logarithm function is removed by a reference volume Ω_0 in the phase space which is usually chosen to be $(2\pi\hbar)^N$.

As a result, the entropy is well defined up to a constant only. In most of the textbooks one finds the dimensional entropy $k_B \ln \Omega$ but the expressions are simpler when dimensionless entropy is used with temperature

$$k_B T = \frac{1}{\beta}, \quad (5)$$

counted in energy dimension.

We follow the dynamics of few well chosen degrees of freedom in statistical physics and ignore the rest of the system. The probabilistic nature of the resulting laws is the result partially from loosing information. But there is something more than lost information as soon as our phenomena depends on quantum scales. Because Quantum Mechanics comes with internal uncertainties and the corresponding probabilistic features are not related to loss of information. We simply can not possess all information about a quantum system.

Statistical Physics is based on the following postulates:

1. All state accessible by the dynamics and consistent with the known macroscopic averages, of an isolated system in equilibrium is equiprobable. The statistical average over this microcanonical ensemble of uniformly distributed states is supposed to reproduce the averages over the large number of interactions with the ever present environment. The system-environment coupling is supposed to be realized by sufficiently small energy exchanges in order to keep the energy of the system conserved as far as macroscopic resolution is concerned. Notice the nontrivial role the interaction plays: the elements of the ensembles are closed, isolated copies of our system but their uniform distribution is the result of the weak interaction between our system and the environment.
2. The time averages are equivalent with the ensemble averages. This ergodic hypothesis not only opens the way of calculating the measured bulk quantities related to fast, microscopic processes but lends physical, testable importance to the averages and fluctuations of the formal elements in an ensemble.
3. The thermodynamical entropy of an isolated system of energy E is given by Eq. (3). Boltzmann's hypothesis represents a bridge between the microscopic foundation and the phenomenology accumulated in thermodynamics.

The validity of these postulates comes from the success of their application to experimental data.

Example: As a simple example let us consider a system of N independent particles moving in a harmonic potential, given by the Hamiltonian

$$H = \sum_j \frac{\mathbf{p}_j^2}{2m} + \frac{m\omega^2}{2} \sum_j \mathbf{x}_j^2 \quad (6)$$

when the phase space volume available at the energy E is

$$\Omega(E) = \prod_{j=1}^N \int d^3 p_j d^3 q_j \delta \left(E - \sum_{j=1}^N \frac{\mathbf{p}_j^2}{2m} - \frac{m\omega^2}{2} \sum_{j=1}^N \mathbf{x}_j^2 \right). \quad (7)$$

We can use $3N$ dimensional momentum and coordinate variables \mathbf{p} and \mathbf{q} to write

$$\Omega(E) = \int d^{3N} p d^{3N} q \delta \left(E - \frac{\mathbf{p}^2}{2m} - \frac{m\omega^2}{2} \mathbf{x}^2 \right) \quad (8)$$

which gives after the change of integral variable $|\mathbf{p}| \rightarrow K = \frac{\mathbf{p}^2}{2m}$, $|\mathbf{x}| \rightarrow U = \frac{m\omega^2}{2} \mathbf{x}^2$

$$\Omega(E) = C \int_0^\infty dK dU K^{3N/2-1} U^{3N/2-1} \delta(E - K - U) \quad (9)$$

where $C = S_{3N}^2 (4/\omega^2)^{3N/2} / 4$, S_d being the solid angle in dimension d . The integration over U can be carried out yielding

$$\begin{aligned} \Omega(E) &= C \int_0^E dK [K(E-K)]^{3N/2-1} \\ &= C \int_0^E dK e^{(\frac{3N}{2}-1) \ln[K(E-K)]}. \end{aligned} \quad (10)$$

The integrand is proportional to the probability distribution $p(K)$ of the kinetic energy. The down-turned parabola $K(E - K)$ in the logarithm function has a maximum at $K_{max} = E/2$ and the large, $\mathcal{O}(N)$ coefficient of the logarithm function makes a sharp peak in $p(K)$ at K_{max} . Therefore, it is good approximation for large N to approximate the logarithmic function in the exponent by its leading order expansion around its maximum and choosing more convenient lower integration limit,

$$\Omega(E) = C \int_{-E/2}^{E/2} dk e^{(\frac{3N}{2}-1)[\ln \frac{E^2}{4} + \ln(1 - \frac{4k^2}{E^2})]} \approx C e^{(\frac{3N}{2}-1) \ln \frac{E^2}{4}} \int_{-\infty}^{\infty} dk e^{-(\frac{3N}{2}-1) \frac{4k^2}{E^2}} \quad (11)$$

where $k = K - E/2$. Straightforward Gaussian integral gives

$$\Omega(E) = C \left(\frac{E^2}{4} \right)^{\frac{3N}{2}-1} E \sqrt{\frac{\pi}{6N-4}} \sim E^{\mathcal{O}(N)} \quad (12)$$

displaying the extensive nature of the entropy.

One can easily obtain the average value and the fluctuation of the kinetic energy,

$$\begin{aligned} \langle K \rangle &= \frac{\int dk ((\frac{E}{2} + k) e^{-(\frac{3N}{2}-1) \frac{4k^2}{E^2}})}{\int dk e^{-(\frac{3N}{2}-1) \frac{4k^2}{E^2}}} = \frac{E}{2} = \mathcal{O}(N) \\ \langle (K - \langle K \rangle)^2 \rangle &= \frac{\int dk k^2 e^{-(\frac{3N}{2}-1) \frac{4k^2}{E^2}}}{\int dk e^{-(\frac{3N}{2}-1) \frac{4k^2}{E^2}}} = -\frac{1}{6N-4} \frac{\partial}{\partial E^{-2}} \ln \int dk e^{-(\frac{3N}{2}-1) \frac{4k^2}{E^2}} = \frac{E^2}{12N-8} = \mathcal{O}(N) \end{aligned} \quad (13)$$

showing that average fluctuation of the kinetic energy of a single particle is

$$\frac{\sqrt{\langle (K - \langle K \rangle)^2 \rangle}}{N} = \mathcal{O} \left(\frac{1}{\sqrt{N}} \right), \quad (14)$$

the average can safely be replaced by the position of the maximum of the probability distribution in the thermodynamical limit. This is the simplification which emerges in the limit $N \rightarrow \infty$ and leads to simple, deterministic equations for the peak of the probability distributions.

B. Randomness and macroscopic physics

The ergodic hypothesis suggests the presence of some fluctuations in the system, described by the ensembles. There is no problem accepting these fluctuations in the case of an open system. But where do such fluctuations come from in a closed system? We shall see that there are no macroscopic isolated systems, more precisely the impossibility of isolation and macroscopic behavior are equivalent. This is the genuine quantum effect.

Let us consider 1g gas of hydrogen, pressed into $V = 1\text{cm}^3$ and isolated in a box at temperature $T = 100\text{K}$. It contains $N \approx 6 \cdot 10^{23}$ atoms, each having approximately

$$K = \frac{3}{2} k_B T \approx 1.5 \cdot 1.4 \cdot 10^{-16} \cdot 100 \approx 10^{-14} \text{erg} \quad (15)$$

kinetic energy. We use CGS units in this section. Thus the average velocity square is

$$v^2 = \frac{3k_B T}{m} \approx \frac{3 \cdot 1.4 \cdot 10^{-16} \cdot 100}{1.7 \cdot 10^{-24}} \approx 10^{10} \text{cm}^2 \text{s}^{-2} \quad (16)$$

and the average velocity turns out to be $v \approx 10^5 \text{cm s}^{-1}$. The average separation between the atoms is

$$r_0 = \left(\frac{V}{N} \right)^{1/3} \approx 10^{-8} \text{cm}. \quad (17)$$

Therefore, the microscopic time scale, separating two consecutive collision of an atom is

$$\tau_{\text{micr}} = \frac{r_0}{v} \approx 10^{-13} \text{s}. \quad (18)$$

The number of interactions in a second with the environment, the container, is

$$N_e = \frac{1}{\tau_{\text{micr}}} \frac{V^{2/3}}{r_0^2} \approx 10^{29}. \quad (19)$$

Let us assume that a very small fraction, say 10^{-10} , of these collisions are inelastic, this gives us 10^{19} energy changing elementary interactions with the environment per second. Each of them involves approximately $\Delta K = k_B T = 10^{-14}$ erg energy exchange.

Suppose that the gas is in a stationary state, one of the eigenstates of its Hamiltonian which does not include the interaction with the environment, the wall of the container. The importance of the interaction with the environment which generates a non-trivial evolution for this state in time can be measured by the average time needed to reach another stationary state of the gas. In fact, the stationary states are orthogonal and the interaction with the environment is efficient if this time is short compared to the observational time. We shall estimate the inverse of this time, the average energy levels traversed by the gas in one second. The gas changes its energy by approximately $\Delta E = 10^{19} \Delta K$ and the density of the energy levels,

$$\Omega(E) \approx \frac{\Omega_0}{E_1} \left(\frac{E}{E_0} \right)^N, \quad (20)$$

a generalization of the behavior, found for noninteracting oscillators yields

$$N_{tr} = \Omega(E) \Delta E = 10^{19} \Delta K \frac{E_1}{\Omega_0} \left(\frac{E}{E_0} \right)^N \approx 10^{c \cdot 10^{23}}, \quad (21)$$

with $c = \log E/E_0 \gg 1$ as the number of energy levels traversed in a second. Such a double (stretched) exponential is an unusually large number and shows the paramount importance of the interaction with the environment for such a macroscopic amount of gas.

Such a large, double exponential number of collision renders isolation illusory in macroscopic physics. The environment can never be ignored, the apparent isolation of large system is due to the order of magnitude of the observed quantities only. As soon as our observation starts to resolve quantum scales the environment becomes inseparable. This mechanism, the decoherence, which is at the heart of the transition from quantum to classical physics is actually the driving force of the universal, statistical features of systems which are weakly coupled to their macroscopic environment.

C. Heat exchange

The postulates, introduced so far for closed systems are not too realistic and we have to go beyond them and to allow at least energy exchange. For this end we split our system into subsystems and study the effects of the interactions among them. The average distance where the particles making up the system interact is crucial in our simple considerations. The range of interaction should be neither too short nor too long.

- Particles should interact at long enough distances to assure relaxation which drive each subsystem towards its local equilibrium.
- We would like to characterize the subsystem by their energies. These energies are useful only if they are individually conserved. But interactions between the subsystems lead of the exchange of some energy. If this interaction energy is negligible compared to the subsystem energy the latter is approximately conserved. This is certainly the case if the range of the particle interaction is short enough.

A well known, realistic case where this latter condition is not met is gravitation interaction. Gravity is not screened at long distances like the Coulomb interaction and may rule out thermal equilibrium.

Let us now split our system into two subsystems. Relying on the assumptions mentioned above we introduce the Hamiltonians H_j , $j = 1, 2$ of the two systems whose equilibrium before attaching them to each other can be described by two microcanonical ensembles, characterized by the Boltzmann entropies $S_j(E, V) = \ln \Omega_j(E)/\Omega_0$. When the two systems are brought into contact then the total Hamiltonian is supposed to be $H = H_1 + H_2$, by ignoring the numerical value of the interaction energy with respect to the individual energies. What is the probability distribution of the system energies E_j in the common equilibrium state? Let us calculate the probability distribution of the energy of

the total system. The joint system is closed and its equilibrium state can be described by a microcanonical ensemble where the probability is proportional to the accessible phase space volume,

$$\Omega(E) = \Omega_0 e^S = \Delta E \sum_n \Omega_1(n\Delta E) \Omega_2(E - n\Delta E) \quad (22)$$

for sufficiently small ΔE . We assume that the subsystems are sufficiently large thus their individual phase space distribution is strongly peaked. In this case a lower and an upper bound can easily be obtained for the sum of nonnegative contributions. It must at least as large as the largest contribution at the peak and can not be bigger than this contribution multiplied by the number of terms in the sum. Furthermore, it is better to work with the logarithm of such a fast varying terms and we find

$$\ln[\Omega_1(E_{max})\Omega_2(E - E_{max})] < S(E) < \ln \frac{E}{\Delta E} + \ln[\Omega_1(E_{max})\Omega_2(E - E_{max})], \quad (23)$$

for large enough systems where the term $\ln \Delta E/\Omega_0$ can be neglected. Let us estimate the different terms in this inequality. We have $E = \mathcal{O}(N)$ and $\ln \Omega(E) = \mathcal{O}(N)$ according to the estimate (20). Thus $\ln E/\Delta E$ is negligible and we have

$$S(E) = [S_1(E_{max}) + S_2(E - E_{max})] \left(1 + \mathcal{O}\left(\frac{\ln N}{N}\right) \right) \quad (24)$$

and the uncertainty due to the choice of the width of the energy shell is negligible for macroscopic systems. Considering the right hand side as the function of E_{max} we have

$$\frac{\partial S_1(E)}{\partial E} \Big|_{E=E_1} = \frac{\partial S_2(E)}{\partial E} \Big|_{E=E_2} \quad (25)$$

at the maximum. The definition

$$\frac{1}{T} = \frac{\partial S(E)}{\partial E} \quad (26)$$

of the inverse temperature shows that the energies of the subsystems settle where the temperature of subsystems agrees. Since the entropy is a monoton function of the temperature for macroscopic systems the temperature could be used to control the energy. This is realized in such a manner that the reaching of the equilibrium of the energy exchange between two systems is indicated by the agreement of their temperature.

Let us suppose that we are interested in the sub system 1 which is much smaller than the total system. Then $E_1 \ll E_2$, $S_1 \ll S_2$ and the dominance of the available phase space volume (22) by the maximal contribution establishes the approximation

$$\Omega(E) = \Omega_0 e^S \approx \Omega_0 e^{S_2} \approx \Omega(E) e^{-\frac{E_1}{T}} \left[1 + \mathcal{O}\left(\left(\frac{E_1}{E}\right)^2\right) \right]. \quad (27)$$

The dependence of the available phase space on the energy of the observed system is interesting, yielding the non-normalized probability distribution of the canonical ensemble,

$$p(E_1) = e^{-\frac{E_1}{T}} \quad (28)$$

in the thermodynamical limit of the full, isolated system since the available phase space is proportional to the probability. One can construct similar argument for any interaction which can affect an additive quantity and construct an intensive potential for each extensive thermodynamical variable which controls the equilibrium with respect to the exchange of the extensive quantity.

This argument seems too general and raises the question of its limit of applicability. We decided to monitor certain quantities, called thermodynamical variables and ignore the remaining degrees of freedom. Such a restricted description allows us to control a small fraction of the possible interactions only in a deterministic manner. The remaining interactions are responsible of the probabilistic nature of our description and the eventual irreversibility. One can nicely separate these two channels of interactions by considering the thermodynamical variables as expectation values of some random variables. The detailed, deterministic part of our description identifies the possible values, the spectrum of the random variables and the probabilistic features yield the probability distribution. In fact, let us consider the change of the energy

$$E = \langle H \rangle = \sum_n p_n E_n \quad (29)$$

written as

$$\Delta E = \Delta W + \Delta Q, \quad (30)$$

where

$$\Delta W = \sum_n p_n \Delta E_n = \langle \Delta E \rangle = \Delta \langle E \rangle \quad (31)$$

is due to the shift of the energy levels, the part of the energy exchange which is used to change the deterministic, controlled part of the system and will be called work performed by the system. The second term,

$$\Delta Q = \sum_n \Delta p_n E_n = \Delta E - \Delta W, \quad (32)$$

the part of the energy received which is turned into the uncontrolled, "random" components of the system is called heat. Note that Eq. (30) is actually the first law of thermodynamics. Our argument about the origin of temperature as the control of thermal equilibrium is applicable to the heat exchange.

The approximate result (20) for the entropy allows us to establish a simple relation between the temperature and the average energy of a degree of freedom. In fact, we have

$$S(E) = N \ln E \quad (33)$$

up to an energy independent constant which yields together with Eq. (26)

$$\frac{E}{N} = T. \quad (34)$$

The equipartition theorem states that the kinetic energy of a degree of freedom of a harmonic system is

$$\frac{E_{kin}}{N} = \frac{E}{2N} = \frac{T}{2}. \quad (35)$$

D. Information

The postulates enumerated in Section I A are rather unusual. They might be rendered more plausible by introducing the information content of a probability distribution. We start with the intuitive construction of the quantity of our missing information, $I[p]$ by considering a series of independent trials whose outcome $j \in [1, \dots, n]$ follows the probability distribution $p = (p_1, \dots, p_n)$. We shall use discrete random variables for the sake of simplicity. We need probability when information is missing about a deterministic, classical system. In other words, the emergence of probability indicates that we lack some informations. The quantity of the missing information, if well defined, can depend only on the probability distribution. For instance, the probability distribution $p_j = \delta_{j,1}/n$ corresponds to a deterministic situation and no information is missing. Any spreading of such a peaked distribution reflects the loss of some informations.

To be more specific, let us consider the case of a ball which can be placed in one of n equivalent urns. Once the ball is hidden in one of the urns, in each if them with the same probability $p_j = 1/n$, our missing information, I_n , can be obtained by requiring the following properties:

1. $I_{n'} > I_n$ for $n' > n$
2. $I_1 = 0$
3. Composition law: let us place in each of the n urns m smaller urns. Then we miss not only the information concerning the large but the small urn, too,

$$I_{nm} = I_n + I_m. \quad (36)$$

The solution is clearly

$$I = \ln \Omega \quad (37)$$

among the continuous functions where $\Omega = n$ denotes the number of accessible states. This solution is unique up to a multiplicative constant which allows us to choose the base of the logarithm function by convenience. The similarity of Eqs. (3) and (37) suggests that the missing information can be identified with the entropy, at least in the microcanonical ensemble. We shall argue below that this equivalence remains valid in other ensembles, as well.

Let us now make one step further and consider the case of inhomogeneous probability distributions. First we follow a heuristic argument generalizing point 3 above. Assume that a ball placed into one of N positions with equal probability and we regroup the positions into ℓ groups each of them containing n_j positions, $j = 1, \dots, \ell$, $\sum_j n_j = N$. The group j is chosen to place the ball with probability $p_j = n_j/N$. We now seek the missing information $I[p]$ about the positioning of the ball with respect to the groups. This information must be the function of the probability distribution p_j alone. The total information missing because the ball is placed at any position is $I_t = \ln N$. To arrive at $I[p]$ we should take out from I_t the information I_g which is missing due to the different positioning within the groups because we are interested in the group only. The average of the remaining missing information due to the unknown location within the groups is

$$\langle I_g \rangle = \sum_{j=1}^{\ell} p_j \ln n_j \quad (38)$$

according to Eq. (37) and we find

$$I[p] = I_t - \langle I_g \rangle = - \sum_{j=1}^{\ell} p_j \ln p_j. \quad (39)$$

The argument which is closer to the spirit of statistical physics is based on counting the number of available states. Consider a series of N exchangeable (order is irrelevant) numbers, j_1, \dots, j_N , $j_k \in \{1, \dots, n\}$, in such a manner that $P(j_k = j) = p_j$ and define the missing information, the information residing in this series as

$$I[p] = \ln \Omega[p], \quad (40)$$

where the number of possible series which yield the same distribution is

$$\Omega[p] = \frac{N!}{\prod_j (N p_j)!}. \quad (41)$$

We use Stirling's formula, $\ln n! \approx n \ln n - n$, to write the

$$\begin{aligned} I[p] &= N \ln N - N - N \sum_j p_j \ln N p_j + N \sum_j p_j \\ &= -N \sum_j p_j \ln p_j. \end{aligned} \quad (42)$$

Note that the quantities as expectation values are well defined for numerical random variables only. But the information should be possible define for non-numeric variable, eg. for the distribution of the eye or hair color of a given set of people. The missing information per symbol,

$$S[p] = \frac{I[p]}{N} = \sum_j p_j \ln p_j = -\langle \ln p \rangle, \quad (43)$$

is the expectation value of $\ln p$ up to a sign and is well defined for non-numeric random variables, too.

Is it possible to give a more definite, quantitative definition of the information $I[p]$? Let us suppose that we receive a string of bits, each of them is 0 or 1. What is the minimal number of questions to pose in order to find out the actual string? The answer naturally depends on what do we know already about the string. Let us consider now the worst scenario, the absence of any knowledge. The optimal strategy of questions is obviously that one which splits the possibilities into two equal parts, therefore we can reconstruct a binary series of length at most $N = 2^{N_Q}$ by N_Q questions. In the language of statistical physics we have a microcanonical ensemble, $\Omega = 2^{N_Q}$ and each string has the same probability in lacking of other informations. How does this result change if we know the probability distribution of 0 and 1 in the string? The number of strings, compatible with the known probability distribution is given by Eq. (41). By asking N_Q optimized questions we can identify the actual string in this reduced phase space, $2^{N_Q} = \Omega[p]$.

We use now the freedom of choosing a multiplicative factor in Eq. (37) by using the logarithm function with base 2 and write

$$\Omega[p] = 2^{I[p]} = 2^{-N \sum_j p_j \ln_2 p_j} \quad (44)$$

showing that we can recover the missing information by asking

$$\frac{\text{missing information}}{\text{character}} = \frac{I[p]}{N} = S[p] = - \sum_j p_j \ln_2 p_j \quad (45)$$

appropriate questions per bit (Shannon). This quantity can be identified by the information we gather by each optimal question, the logarithm of the accessible volume per symbol.

Few important properties of the missing information are the following.

1. **Lower bound:** $S[p] \geq 0$
2. **Minimizing distribution:** $S[p]$ assumes its minimum, $S[p] = 0$, at $p_j = \delta_{j,k}$, $k \in \{1, \dots, n\}$ where $S[p] = 0$.
3. **Maximizing distribution:** Let us consider a generalization, based on a concave function $F(x) = xf(x)$,

$$F\left(\frac{\sum_j w_j x_j}{\sum_j w_j}\right) \geq \frac{\sum_j w_j F(x_j)}{\sum_j w_j}. \quad (46)$$

Then $S[p] = \sum_j F(p_j)$ reaches its maximum at $p_j = 1/n$. Proof: $w_j = 1$, $x_j = p_j$

$$F\left(\frac{1}{n}\right) \geq \frac{\sum_j F(p_j)}{n} \quad (47)$$

and $\sum_j F(p_j) \leq nF(1/n)$. In particular, $I_{\max}[p] = \ln n$ for $f(x) = -\ln x$.

4. **Additivity:** Let $P = (p_1, \dots, p_n)$ and $Q = (q_1, \dots, q_m)$ two probability distributions for the independent random variables $A = \{a_1, \dots\}$ and $B = \{b_1, \dots\}$. The missing information in these variables is

$$\begin{aligned} S(A \otimes B) &= - \sum_{a,b} p(a)q(b) \ln p(a)q(b) \\ &= - \sum_{a,b} p(a)q(b)(\ln p(a) + \ln q(b)) \\ &= - \sum_a p(a) \ln p(a) - \sum_b q(b) \ln q(b) \\ &= S(A) + S(B). \end{aligned} \quad (48)$$

The property number 3 is valid for any concave function $xf(x)$. The specialty of the choice $f(x) = -\ln x$ is the additivity for factorisable distributions.

5. **Unicity:** The function $S[p] = S(p_1, \dots, p_n)$ is necessarily given by Eq. (42) up to a multiplicative constant if it
 - (a) is continuous for $p_j \geq 0$, $\sum_j p_j = 1$,
 - (b) assumes its maximum at $p_j = 1/n$,
 - (c) satisfies the following composition law: Let us consider the set of n symbol $\{s_1, \dots, s_n\}$, each of them realized with probability $P(s = s_j) = p_j$, regrouped in ℓ subsets,

$$\{s_1, \dots, s_n\} = \{(s_{i_1}, \dots, s_{j_1}), (s_{i_2}, \dots, s_{j_2}), \dots, (s_{i_\ell}, \dots, s_{j_\ell})\}, \quad (49)$$

with $i_1 = 1$ and $j_\ell = n$. The conditional probability for s_i within the subset k is $p_{i|k} = p_i/w_k$, with $w_k = \sum_j p_j$, where the summation is over the elements of the subset. The information represented by a symbol can be obtained as the sum of information corresponding to its subset and the expectation value of the information composed by the conditional probability,

$$S(p_1, \dots, p_n) = S(w_1, \dots, w_\ell) + \sum_{k=1}^{\ell} w_k S(p_{i_k|k}, \dots, p_{j_k|k}). \quad (50)$$

E. Correlations and informations

The relation between two numerical random variable is expressed in terms of correlations. In case of non-numerical variables we need another way of handling correlations. Information proves to be useful in this problem, as well. Let us now return to the the variables $A = \{a_1, \dots\}$ and $B = \{b_1, \dots\}$, introduced above except that they are not independent, their joint probability distribution being $p(a \cap b)$. This probability distribution gives rise the missing informations

$$S(A \otimes B) = - \sum_{a,b} p(a \cap b) \ln p(a \cap b) \quad (51)$$

and the marginal distributions $p(a) = \sum_b p(a \cap b)$, $p(b) = \sum_a p(a \cap b)$ yield

$$S(A) = - \sum_a p(a) \ln p(a), \quad S(b) = - \sum_b p(b) \ln p(b). \quad (52)$$

The mutual information $S(A : B)$ is defined by the equation

$$S(A \otimes B) = S(A) + S(B) - S(A : B) \quad (53)$$

which gives

$$\begin{aligned} S(A : B) &= \sum_{a,b} p(a \cap b) [\ln p(a \cap b) - \ln p(a) - \ln p(b)] \\ &= \sum_{a,b} p(a \cap b) \ln \frac{p(a \cap b)}{p(a)p(b)}. \end{aligned} \quad (54)$$

It satisfies the inequality

$$S(A : B) \geq 0 \quad (55)$$

where the equation holds only if A and B are independent. To prove this it is advantageous to introduce the notation $q(a \cap b) = p(a \cap b)/p(a)p(b)$ which allows us to write

$$S(A : B) = \sum_{a,b} p(a)p(b)q(a \cap b) \ln q(a \cap b). \quad (56)$$

In the next step we need the inequality $q \ln q \geq q - 1$ where the equality is observed for $q = 1$ only. It can be verified by observing that $q(\ln q - 1) + 1$ assumes its minimum at $q = 1$. This inequality assures

$$q(a \cap b) \ln q(a \cap b) > q(a \cap b) - 1 \quad (57)$$

which in turn gives

$$S(A : B) \geq \sum_{a,b} p(a)p(b)[q(a \cap b) - 1] = \sum_{a,b} [p(a \cap b) - p(a)p(b)] = 1 - 1 = 0 \quad (58)$$

with equality for $p(a \cap b) = p(a)p(b)$.

The missing information when the variable b is known,

$$S_b(A) = - \sum_a p(a|b) \ln p(a|b) \quad (59)$$

gives on the average the conditional information

$$S(A|B) = - \sum_b p(b) S_b(A) = - \sum_{a,b} p(a \cap b) \ln \frac{p(a \cap b)}{p(b)}. \quad (60)$$

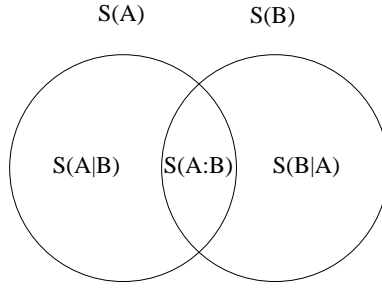


FIG. 1: Wenn diagram for two random variables.

The conditional information, $S(A|B)$ represents the information in $S(A \cap B)$ beyond $P(B)$ since

$$\begin{aligned}
 S(A \otimes B) &= - \sum_{a,b} p(a|b)p(b) \ln p(a|b)p(b) \\
 &= - \sum_{a,b} p(a|b)p(b) \ln p(a|b) - \underbrace{\sum_b \sum_a p(a|b) p(b) \ln p(b)}_1 \\
 &= S(A|B) + S(B).
 \end{aligned} \tag{61}$$

The situation is nicely summarized by the Wenn diagram of Fig. 1.

It is sometime useful to introduce the relative information of two probability distributions corresponding to the same random variable. Let us consider the probabilities $P = \{p(a)\}$ and $P' = \{p'(a)\}$, their relative information is

$$S(P/P') = - \sum_A p(A) \ln \frac{p(A)}{p'(A)}. \tag{62}$$

It is easy to see that $S(P/P') \leq 0$ and the equation holds for $p'(a) = p(a)$ only. To see this we write the relative information as

$$S_{A'}(A) = - \sum_A p'(A) \frac{p(A)}{p'(A)} \ln \frac{p(A)}{p'(A)} \tag{63}$$

and use the inequality (46) for the concave function $-x \ln x$,

$$S_{A'}(A) \leq - \left(\sum_A p'(A) \frac{p(A)}{p'(A)} \right) \ln \left(\sum_A p'(A) \frac{p(A)}{p'(A)} \right) = 0. \tag{64}$$

F. Maximal entropy principle

It is useful to introduce the subjective information, a probability variable represents for us, defined by $I_s[p] = -I[p]$. This definition makes the total information in the subject-object system $I_s + I = 0$ conserved. We can now address the problem of statistical inference, the extraction of an optimal probability distribution from the knowledge of some of its expectation values. Suppose that a random event occurs N -times, $(x(t_1), \dots, x(t_N))$, $x(t_j) \in \{x_1, \dots, x_n\}$ and we measure the average of some functions $f_k(x)$, $k = 1, \dots, m$. What is the best guess for the distribution of the events assuming the knowledge of the averages

$$\frac{1}{N} \sum_j \mathbf{f}(x(t_j)) = \mathbf{F} \tag{65}$$

of our observed quantities? The principle of maximal entropy (MAXENT) finds the probability distribution $p(x|\mathbf{F})$ by minimizing our informations $I_s[p]$ by keeping the constraints

$$\sum_j p_j \mathbf{f}(x_j) = \mathbf{F}. \tag{66}$$

This is obviously equivalent with maximizing the missing information, $I[p]$. Note that due to the convexity of $x \ln x$ the minim will be absolute. Thus this principle is optimal in what it preserves all information without introducing other bias.

The explicit construction of the minimal information distribution is achieved by means of Lagrange multipliers, by maximizing the function

$$S_F = - \sum_j p_j \ln p_j + (1 - \lambda_0) \left(\sum_j p_j - 1 \right) + \boldsymbol{\lambda} (\mathbf{F} - \sum_j p_j \mathbf{f}(x_j)) \quad (67)$$

in the probability distribution $\{p_1, \dots, p_n\}$ and the parameters $\lambda_0, \boldsymbol{\lambda}$. The extremal conditions for p_j fixes the probability distribution,

$$\frac{\partial}{\partial p_j} : 0 = - \ln p_j - 1 - \lambda_0 + 1 - \boldsymbol{\lambda} \mathbf{f}(x_j), \quad p_j = e^{-\lambda_0 - \boldsymbol{\lambda} \mathbf{f}(x_j)}. \quad (68)$$

The maximum for λ_0 yields the partition function

$$\frac{\partial}{\partial \lambda_0} : 1 = e^{-\lambda_0} Z(\boldsymbol{\lambda}), \quad Z(\boldsymbol{\lambda}) = \sum_j e^{-\boldsymbol{\lambda} \mathbf{f}(x_j)} = e^{\lambda_0}, \quad (69)$$

and finally the maximization over $\boldsymbol{\lambda}$ gives the sum rules to express expectation values as the logarithmic derivatives of the partition function,

$$\frac{\partial}{\partial \boldsymbol{\lambda}} : \mathbf{F} = e^{-\lambda_0} \sum_j \mathbf{f}(x_j) e^{-\boldsymbol{\lambda} \mathbf{f}(x_j)} = \frac{1}{Z(\boldsymbol{\lambda})} \sum_j \mathbf{f}(x_j) e^{-\boldsymbol{\lambda} \mathbf{f}(x_j)} = - \frac{\partial \ln Z(\boldsymbol{\lambda})}{\partial \boldsymbol{\lambda}}. \quad (70)$$

The value of the maximal entropy is

$$\begin{aligned} S_{max} &= - \sum_j p_j \ln p_j \\ &= \sum_j e^{-\lambda_0 - \boldsymbol{\lambda} \mathbf{f}(x_j)} [\lambda_0 + \boldsymbol{\lambda} \mathbf{f}(x_j)] \\ &= \lambda_0 + \boldsymbol{\lambda} \mathbf{F}. \end{aligned} \quad (71)$$

What is the relation between the entropy used in MAXENT and in Physics? Entropy is introduced in thermodynamics as a state function, a sum of the heat exchange weighted by the inverse absolute temperature along a reversible path over equilibrium states

$$S = \int \frac{\delta Q}{T}. \quad (72)$$

Another proposal, coming from Boltzmann is given by Eq. (3). Finally, Gibbs proposed the form

$$S = - \int d^{3N} p d^{3N} q P(\mathbf{p}, \mathbf{q}) \ln P(\mathbf{p}, \mathbf{q}) \quad (73)$$

where $P(\mathbf{p}, \mathbf{q})$ denotes the probability density of the system in the phase space. The similarity of this expression with Eq. (42) shows the equivalence of the Gibbs and the information based entropies. The comparison of Eqs. (3) and (40) reveals the identity of the Boltzmann entropy with the previous two. The different ensembles will be introduced below in such a manner that these three entropies become numerically equivalent with the thermodynamical one.

G. Ensembles

All ensembles of Statistical Physics can be obtained by the application of the Maximal Entropy Principle. The closed system of particles, considered in Section I is characterized by its energy E , volume V and particle number N . No other information is available, $m = 0$, thus the MAXENT principle identifies the uniform probability distribution which contains no information beyond the known energy value. The partition function is

$$Z(E, V, N) = \sum_j \delta_{E, H_j} \rightarrow \Omega(E, V, N) = \int \frac{d^{3N} x d^{3N} p}{N! (2\pi\hbar)^{3N}} \delta(E - H(p, x)) \quad (74)$$

according to the second equation in Eqs. (69). In the first, formal expressions we sum over different micro states. In the more detailed expressions the micro states are characterized by continuous variables and the summation turns into integration. Furthermore, the volume element of a micro state is chosen to be $(2\pi\hbar)^3$ to comply with Heisenberg uncertainty relation and the multiplicative factor $1/N!$ is inserted to render the entropy an extensive quantity by identifying micro states obtained by the permutation of the identical particles of the system, to be discussed later. The Gibbs entropy, given by Eq. (71) is

$$S(E, V, N) = - \sum_j p_j \ln p_j \rightarrow \ln \Omega. \quad (75)$$

where the normalization $\sum_j p_j = 1$ was used in the second equation. This relation establishes the numerical equivalence of the Boltzmann and the Gibbs entropies for the microcanonical ensemble.

The natural variable of the Gibbs entropy is the energy and the volume of the system, $S(E, V, N)$. The equivalence of the thermodynamical and the Gibbs entropy will be reached by defining the inverse temperature by

$$\beta = \frac{\partial S(E, V, N)}{\partial E}, \quad (76)$$

cf. Eq. (72). The flow of the energy caused by the change of the volume defines the pressure,

$$\beta p = \frac{\partial S(E, V, N)}{\partial V}. \quad (77)$$

In the view of the fast orthogonalization of the state by the interactions with its environment mentioned in Section IB the microcanonical ensemble, derived for isolated systems is a rather idealized concept. It serves as a starting point to construct more realistic ensembles corresponding to certain open interaction channels between the system and its environments.

Let us first allow energy exchange with the environment. The the energy is not fixed anymore, it is distributed by some probability and we can control its expectation value only. Then the probability distribution for the micro states will be chosen by minimizing its information content by keeping the energy average fixed. We have a single function, $f_1 = H$ to keep fixed, $m = 1$. The corresponding Lagrange multiplier is usually written as $\lambda_1 = \beta = 1/T$ to convert Eq. (70) into the usual relation

$$E = \langle H \rangle = - \frac{\partial \ln Z(\beta, V, N)}{\partial \beta}. \quad (78)$$

The canonical partition function

$$Z(\beta, V, N) = e^{-\beta A(\beta, V, N)} = \sum_j e^{-\beta H_j} \rightarrow \int \frac{d^{3N} x d^{3N} p}{N! (2\pi\hbar)^{3N}} e^{-\beta H(x, p)} \quad (79)$$

is obtained by means of the second equation in Eqs. (69). Therefore,

$$p(E) = \frac{1}{Z} e^{-\beta E} \quad (80)$$

gives the canonical probability distribution of the energy levels. The Gibbs entropy is expressed as

$$S = \beta(E - A) \quad (81)$$

according to Eq. (71).

It is instructive to write

$$\begin{aligned} \Delta S &= \Delta \left(- \sum_n p_n \ln p_n \right) \\ &= - \sum_n (\Delta p_n) \ln p_n \\ &= \beta \sum_n E_n \Delta p_n \\ &= \beta \Delta Q \end{aligned} \quad (82)$$

TABLE I: Legendre transformation of the thermodynamical potentials in the energy representation, starting with $E(S, N, V)$.

| Potential | Legendre transformation | New variable | Transformed function | Alternative form |
|-----------------------|---|--|---------------------------|-----------------------|
| Enthalpy | $-E(S, N, V) \rightarrow H(S, N, p)$ | $p = \frac{\partial(-E)}{\partial V}$ | $H = E + pV$ | $H = TS + \beta\mu N$ |
| Helmholtz free energy | $-E(S, N, V) \rightarrow A(T, N, V)$ | $-T = \frac{\partial(-E)}{\partial S}$ | $A = E - TS$ | $A = -pV + \mu N$ |
| Gibbs free energy | $-A(T, N, V) \rightarrow G(T, N, p)$ | $p = \frac{\partial(-A)}{\partial V}$ | $G = E - TS + pV$ | $G = \mu N$ |
| Grand potential | $-A(T, N, V) \rightarrow \Omega(T, \mu, V)$ | $-\mu = \frac{\partial(-A)}{\partial N}$ | $\Omega = E - TS - \mu N$ | $\Omega = -pV$ |

where the relation $\sum_n \Delta p_m = 1$ was used in the second equation, the canonical probability distribution (80) is used in the second third equation and finally, the last line follows from Eq. (32). This result and the sum rule (78) compared with Eq. (72) yield the equivalence of the thermodynamic entropy and inverse temperature with S and β and identifies A as the Helmholtz free energy.

When both energy and particle exchange are allowed then we keep two expectation values fixed in the minimization of the information of the probability distributions, the energy and the particle number of the system. Thus $m = 2$ and we write $\mathbf{f} = (H, N)$, $\boldsymbol{\lambda} = (\beta, -\beta\mu)$. The corresponding grand canonical partition function is

$$Z(\beta, V, \mu) = e^{\beta p(\beta, V, \mu)V} = \sum_{j, N} e^{-\beta(H_j - \mu N)} \rightarrow \sum_N \int \frac{d^{3N}x d^{3N}p}{N!(2\pi\hbar)^{3N}} e^{-\beta(H(x, p) - \mu N)} \quad (83)$$

and yields the expression

$$S = \beta(E + pV - \mu N). \quad (84)$$

The sum rule

$$E = \langle H \rangle = -\frac{\partial \beta V p(\beta, V, \mu)}{\partial \beta} \quad (85)$$

assures us that the function p introduced in the exponent of the grand canonical partition function of Eq. (83) is indeed the pressure. This result turns Eq. (85) into the fundamental equation of thermodynamics, the Euler equation.

The Gibbs entropy is given in terms of the probability distribution which is different for different ensembles. The identification with the Boltzmann entropy mentioned in the case of the microcanonical ensemble must be extended for the other ensembles. Such an explicit demonstration of the equivalence of the ensembles can be achieved by means of the asymptotic equipartition theorem of information theory. This theorem applies for distributions $p(X)$ which peak with width $\mathcal{O}(1/\sqrt{N})$ in the thermodynamical limit. The prediction of the ensembles naturally differ for finite systems, the unique result is recovered in the thermodynamical limit, $N \rightarrow \infty$ only. Let us chose a probability $0 < p < 1$, introduce a region R of the phase space around the peak of the distribution function $p(X)$ in such a manner that the probability of finding the system in R is p ,

$$\int_{X \in R} dX p(X) = p \quad (86)$$

and define the Boltzmann entropy of this probability distribution as

$$S_B(p) = \ln \frac{1}{\Omega_0} \int_{X \in R} dX \quad (87)$$

where Ω_0 is a reference volume. This entropy can be written as the sum of a p -independent and a p -dependent part. According to the theorem the p -dependent part of this entropy is $o(N)$, ie. the Boltzmann entropy density,

$$\lim_{N \rightarrow \infty} \frac{S_B(p)}{N} = s_B \quad (88)$$

is p -independent. This property allows the identification of the Boltzmann entropy with that which was obtained by Shannon and is consistent with our information of the system.

Observe that when a new interaction channels opens then the maximum of the entropy is parametrized by the corresponding Lagrange multiplier instead of a sharply fixed physical quantity. What happens is that we seek the maximum in terms of a new variable, the derivative of the entropy with respect to the previous one, the physical

quantity in question. Such a reparameterization of the search of an extremal is described by the Legendre transformation, introduced in Appendix A. The natural variables of the partition function Z in Eqs. (69) are the λ , the Lagrange multipliers and Eq. (70) describes the change of variables and the function $-\ln Z$, cf. Eq. (A2). One talks about the energy or entropy representation of the thermodynamical potentials when the entropy $S(E, N, V)$ or energy $E(S, N, V)$ is used as the starting point for the different Legendre transformations. The potentials, listed in Table I are based on the energy representation, starting with the functions $-\beta E(S, N, V)$. The last column of the table follows from the Euler relation (85). The table shows the thermodynamical potentials as they were defined historically. The systematic Legendre transformation would be based on the variable β instead of T and $-\beta$ times the potentials, shown.

H. Second law of thermodynamics

The fundamental laws of Physics, weak interactions left aside, remain unchanged when the direction of time is flipped. Nevertheless, one observes the breakdown of the time reversal invariance, the setting of a time arrow, on different levels:

1. **Radiation:** The retarded solutions of the Maxwell equations seem to be in agreement with our experience, the advanced solutions do not fit to our world.
2. **Thermodynamics:** The second law of thermodynamics,

$$\frac{dS(t)}{dt} \geq 0 \quad (89)$$

prefers the forward going time.

3. **Quantum mechanics:** The phase difference between macroscopically different states is lost during a measurement or observation.
4. **Gravitation:** The space-time singularity of the Big Bang sets the motion of the time in one direction.

Presumably these time arrows are not independent, all of them should come from level 4 where the time is actually constructed. But we now ignore their correlation and consider level 2 only, the breakdown of time reversal invariance as known from thermodynamics. The main point to underline is that this time arrow which is difficult to understand in terms of microscopic, reversible equations of motion, comes from the inevitable interactions of a macroscopic system, with its environment. These interactions, together with the boundary conditions in time, imposed for the environment lead to a preferred direction of time in statistical physics.

Let now consider systems A and B in thermal equilibrium, at temperature T_A and T_B . The probability distributions are chosen by minimizing their free energy $A = E - TS$. Then we bring them into contact with each other by allowing exchange of energy between them. The Liouville theorem states that the evolution of a classical system always preserves the phase space volume and with it the informational entropy. The time evolution is unitary in quantum mechanics and the informational entropy is also preserved. Therefore, the Gibbs-entropy which assumes the value $S(A \cap B) = S(A) + S(B)$ before the contact was established remains a constant of motion.

Let us denote the change of a quantity X before and after the establishment of the contact between the systems by $\Delta X = X_{final} - X_{initial}$. The energy exchange represents heat therefore we have $\Delta E = Q$. The conservation of the full entropy gives $\Delta S_{12} = 0$ what can be written by means of Eq. (53) as

$$\Delta S(A) + \Delta S(B) = \Delta S(A : B). \quad (90)$$

The heat exchange forces the two systems to change their probability distributions, in particular to give up the initial independent equilibrium states. Since $A = E - TS$ was minimized for each system before the contact the states after the contact must obey the inequality

$$\beta Q - \Delta S \geq 0 \quad (91)$$

for both systems which can be written as

$$\beta(A)Q(A) + \beta(B)Q(B) \geq \Delta S(A) + \Delta S(B) = \Delta S(A : B). \quad (92)$$

Energy conservation, $Q(A) + Q(B) = 0$ yields the inequality

$$Q(A) \left(\frac{1}{T(A)} - \frac{1}{T(B)} \right) \geq \Delta S(A : B). \quad (93)$$

The two systems were independent before bringing them into contact hence $S_{initial}(A : B) = 0$, and $\Delta S(A : B) = S_{final}(A : B) \geq 0$. This establishes the second postulate of thermodynamics: (i) The sum of entropies of the two systems is non-decreasing, $\Delta S(A) + \Delta S(B) \geq 0$ and (ii) the inequality (93) assures that heat flows from the warmer to the colder system.

One should keep in mind that the correlations between the two components, A and B are crucial in these considerations. Since the total entropy $S(A \cap B)$ is conserved the system entropies, $S(A)$ and $S(B)$ display non-decreasing nature if and only if $S(A : B)$ is non-decreasing. The entropy increase in a sub-system is always balanced by the same increase of the mutual entropy of the system and its environment. One may say that it is this latter, the ever increasing entanglement among sub-systems which drives the increase of the sub-system entropies. As soon as the mutual entropy decreases the system entropies decrease, as well and the thermodynamical time arrow is flipped. One suspect that by starting with specially rearranged initial conditions where the sub-systems are strongly correlated the mutual information may decrease. What kind of independence is needed in the initial conditions to remain in conform with the second postulate of thermodynamics? It is argued below that the independence we need for the second postulate between a system and its environment is the existence of (thermodynamical) variables which characterise the state of the system in a unique, reproducible manner.

The see how this happens let us assume that our system is in equilibrium with its environment at the initial time t and this equilibrium state can be characterized by Φ , a collection of thermodynamical variables. Furthermore we define macro and micro states. A micro state is a point in the phase space, it denotes a fully identified state of our system, including all information about it. The macro state represents our partial information about the system, it is defined for each set of thermodynamical variables, Φ , and it consists of micro states which are compatible with Φ . The volume of the macro state in the phase space is denoted by $\Omega(\Sigma(\Phi))$. The entropy, or the volume where the probability, given by the maximal entropy principle is concentrated is well defined according to the asymptotic equipartition theorem.

Let us now suppose that the time evolution brings our system, considered isolated from its environment, from the thermodynamical state Φ_i at time t_i into another equilibrium state Φ_f at time t_f in a reproducible manner. Each observation carried out on the system follows the time evolution of a single micro state and reproductibility of the experiment is the claim that any micro state of $\Sigma(\Phi_i)$ evolves into a micro state of $\Sigma(\Phi_f)$. To phrase this in a mathematical statement we introduce the time evolution map, $U_f : \mathbb{R}^{6N} \rightarrow \mathbb{R}^{6N}$ for the points, the micro state in the phase space by the definition $U_{t',t}(x(t), p(t)) = (x(t+t'), p(t+t'))$, where the trajectory $(x(t), p(t))$ is generated by the detailed, elementary equations of motion with couplings to the environment ignored. Reproducibility is the inclusion

$$U_{t_f, t_i}(\Sigma(\Phi_i)) \subset \Sigma(\Phi_f), \quad (94)$$

where $U(\Sigma)$ denotes the image of the phase space region Σ after the time evolution. According to Liouville theorem, based on the equations of motion of the isolated system the volume of the macro state is,

$$\Omega(\Sigma(\Phi_f)) = \Omega(U_{t_f, t_i}(\Sigma(\Phi_i))). \quad (95)$$

The comparison with Eq. (94) yields

$$\Omega(\Sigma(\Phi_i)) \leq \Omega(\Sigma(\Phi_f)). \quad (96)$$

By taking the logarithm of this inequality we arrive at the second law,

$$S(\Phi_i) = \ln \Omega(\Sigma(\Phi_i)) \leq \ln \Omega(\Sigma(\Phi_f)) = S(\Phi_f). \quad (97)$$

In the absence of environment the system dynamics is reversible, the inclusion in (94) would hold for the time reversed system in the opposite direction, as well, leading to $U_{t_f, t_i}(\Sigma(\Phi_i)) = \Sigma(\Phi_f)$ and the conservation of entropy. But the interactions with the environment, the leakage of information, allows that the macro state $\Sigma(\Phi_f)$ becomes "polluted", to contain micro states which are not the result of a possible experiments, starting with Φ_i , without contradicting to our experimental finding, the reproductibility of the transition $\Phi_i \rightarrow \Phi_f$. Therefore the equality in (97) holds for reversible reproducible processes.

Several remarks are in order at this point.

1. The argument presented above is not relying on any specific feature of the thermodynamical variables Φ . What was important is that the set of parameters Φ provides a sufficiently detailed specification of the system for reproducibility. The most natural experimental way to make sure the sufficiency of Φ is to wait until the system "forgets" the special features of its initial condition, in other words to assume that the initial and final states of the second law correspond to equilibrium and use the time honored set of thermodynamical variables as Φ .

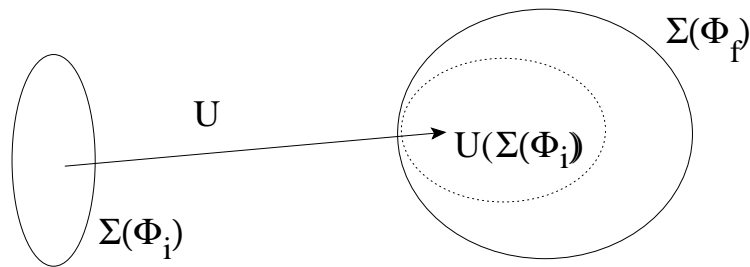


FIG. 2: The second law of thermodynamics: phase space volume of a macro state can not decrease during reproducible changes $\Phi_i \rightarrow \Phi_f$ of the thermodynamic variables.

2. Statistical physics is based on the construction of two levels of the physical world, based on the micro and the macro states. The maximal entropy principle is a bridge between these levels: For each macro state, Φ , we construct the ensemble of micro states, $\Sigma(\Phi)$, as the best representation of our partial information.
 - (a) One finds a fully specified system at the fundamental level of micro states, requiring an inhuman quantity of information to handle. The elementary blocks of the other level, defined by our observations, are the macro states, comprising the the limited informations, gathered by us, observers.
 - (b) The volume $\Omega(\Sigma(\Phi))$ is subjective, i.e. an artificial, a mental construction to characterize the system, based on our partial information. Different experimental setups define different phase-space volumes, in function of what is controlled, “known” experimentally. These volumes are constructed by us and are not obeying Liouville’s theorem. Hence the entropy is an anthropomorphic, auxiliary construction, based on the existence of observers.
 - (c) The maximal entropy principle makes us possible to use our partial information in an optimized and consistent manner. Optimization is provided by removing any preference without actual information possessed, by the maximization of the entropy. Consistency denotes the property that any observers, possessing the same information assign the same entropy and make the same predictions. Thus the probability density and the entropy are objective in this sense and are well defined elements of scientific discussions.
 - (d) The reproducibility as used above stands for a deterministic law. One may interpret the inequality (97) by saying that any deterministic law, imposed on quantities which are fixed by partial informations is always losing information and produces less predictive results.
3. One might think that the second law of thermodynamics, applied to isolated systems, implies a dynamical breakdown of the time inversion invariance. But this interpretation is incorrect on the following counts.
 - (a) The closed system retains its time reversal dynamics and the impression of irreversibility comes rather from our inability to possess all information. What makes the entropy non-decreasing is the loss of information about the non-thermodynamical variables. As soon as we possess all information Φ identifies the system in a unique manner and $\Omega(\Sigma(\Phi)) = (2\pi\hbar)^{3N} = \Omega_0$ becomes a constant of motion.
 - (b) The argument about the non-decreasing of the entropy works in reversed time, too. Once the final state is specified and the time evolution is used to “predict” the corresponding initial state then the entropy is non-increasing in the time which flows backward. The time evolution in phase space preserves the time reversal invariance, it is our partial information about the system, used to designate the macro states, becomes obsolete only.

The thermodynamical time arrow, set by the inequality (89) does not originate from the system, it comes rather from the imposition of the initial conditions for the environment, what we do not know or control.

I. What is entropy after all?

We can now have a more precise view of the entropy. We have seen one part of the picture in Section IF, the proposition of identifying entropy with our missing information. This reproduces equilibrium thermodynamics. The other part is dynamics presented briefly in Section IH, concerns the role of entropy played in the time dependence and we consider now this side more closely. In a process of interaction we trace the energy exchange because the sum

of the energy is conserved. But the amount of energy exchanged is not sufficient to qualify the consequences of the interaction because the given exchange may or may not take place, according to the sign of the change of entropy involved.

Let us start with a closer look on the energy. It is not a directly measurable quantity despite its fundamental use in the formal weaponry of mechanics. It is useful because it is conserved and characterizes the motion. When we intend to perform certain task by an engine then we want to send it onto a certain trajectory in the phase space. The energy is a useful quantity in this process not due to its conservation but rather because it characterizes conveniently the phase space available for the system. When we say that we give some energy to the system then we give a certain "push", come into an interaction with it in such a manner that it is put on the desired phase space trajectory.

The complications start in the thermodynamical or statistical description when we do not wish to follow the complete dynamics in a detailed manner but we still want to keep some control over the phase space. The energy dE exchanged between two systems,

$$dE = \lambda d\mathbf{F} + \delta Q, \quad (98)$$

is split into two parts, corresponding to the macroscopically identifiable forms of the energy and the rest, called heat. Macroscopically identifiable energy is controllable and manipulable. The key point is that the uncontrolled energy exchange channels are less useful because there might be cancellations among unwanted microscopic processes, decreasing the efficiency of our effort of putting the system on a fixed phase space trajectory. For example we can convert electric energy into mechanical work with better efficiency than heat because the disordered motion of the molecules carrying heat leads to strong cancellations whenever the conversion into another form of energy is attempted.

The thermodynamical equation (72), written as

$$\frac{\delta Q}{T} = d \ln \Omega = \frac{d\Omega}{\Omega}, \quad (99)$$

shows that the relative change of the accessible phase is to be compared with the amount of the exchanged, uncontrolled energy. The proportionality constant, the intensive variable controlling the heat exchange is a measure of the efficacy of the phase-space injection. A given amount of energy yields more gain in relative phase space when the energy comes in an ordered manner. Energy, injected in a disordered fashion is less efficient to enlarge the phase space due to the cancellations among the uncontrolled microscopic processes.

Looking from the point of view of tracing the thermodynamical, macroscopic variables then this "leakage" of energy into the new phase-space region represents a loss of information. This loss is naturally increasing as the time passes in whatever direction from the initial state due to the macroscopically undetectable microscopical processes taking place incessantly.

J. Grand canonical ensemble, quantum case

The discussion so far has been confined into the classical regime. But there are several indications that the basic postulates of Statistical Physics can be justified on the quantum level. For instance, the order of magnitude estimate of Section IB relies on the discreteness of the excitation spectrum, a hallmark of Quantum Physics. We shall be satisfied here to outline the generalization of the maximum entropy principle and the equilibrium ensembles for the quantum domain.

The extension of the classical ensembles for quantum systems is made by means of the density matrix whose properties are summarized briefly in Appendix B. A straightforward generalization of the classical Shannon information is Neumann's expression

$$S_G[\rho] = -\text{Tr} \rho \ln \rho. \quad (100)$$

The advantageous feature of this expression is its invariance under unitary transformations, $\rho \rightarrow U\rho U^\dagger$ with $U^\dagger = U^{-1}$, expressing the conservation of the information of a closed system. Let us denote by f_j the observables whose expectation values,

$$\langle \mathbf{f} \rangle = \text{Tr} \mathbf{f} \rho = \mathbf{F}, \quad (101)$$

are known. The list $\{f_j\}$ usually includes all conserved quantity. The maximization of the function

$$S_F = -\text{Tr} \rho \ln \rho + (1 - \lambda_0)(\text{Tr} \rho - 1) + \lambda(\mathbf{F} - \text{Tr} \mathbf{f} \rho) \quad (102)$$

in ρ is achieved by making the infinitesimal variation $\rho \rightarrow \rho + \delta\rho$. To calculate the variation of $\text{Tr}\rho \ln \rho$ we use the identity

$$\begin{aligned}
e^A e^B &= \left(\mathbb{1} + A + \frac{A^2}{2} + \dots \right) \left(\mathbb{1} + B + \frac{B^2}{2} + \dots \right) \\
&= \mathbb{1} + A + B + \frac{A^2 + B^2}{2} + AB + \dots \\
&= \mathbb{1} + A + B + \frac{(A+B)^2}{2} + \frac{1}{2}[A, B] + \dots \\
&= e^{A+B+\frac{1}{2}[A, B]+\dots}
\end{aligned} \tag{103}$$

where the dots stand for multiple commutators, like $[A, [A, B]]$ etc. in the last equation. It allows us to write

$$\begin{aligned}
\delta \text{Tr}[\rho \ln \rho] &= \text{Tr}[\delta\rho \ln \rho + \rho \ln(\rho + \delta\rho) - \rho \ln \rho] \\
&= \text{Tr}[\delta\rho \ln \rho + \rho \ln \rho(1 + \rho^{-1}\delta\rho) - \rho \ln \rho]
\end{aligned} \tag{104}$$

which gives by means of the previously derived identity

$$\begin{aligned}
\delta \text{Tr}[\rho \ln \rho] &= \text{Tr} \left[\delta\rho \ln \rho + \rho \ln \rho + \rho \ln(1 + \rho^{-1}\delta\rho) + \frac{1}{2}\rho[\ln \rho, \ln(1 + \rho^{-1}\delta\rho)] - \rho \ln \rho \right] \\
&= \text{Tr} \left[\delta\rho \ln \rho + \delta\rho + \frac{1}{2}\rho(\ln \rho)\rho^{-1}\delta\rho - \frac{1}{2}\delta\rho \ln \rho \right] \\
&= \text{Tr}[\delta\rho \ln \rho + \delta\rho]
\end{aligned} \tag{105}$$

by using that ρ and $\ln \rho$ commute and by ignoring terms $\mathcal{O}(\delta\rho^2)$. Finally, together with the variation of the parameters λ_0 , $\boldsymbol{\lambda}$ one finds the extremal conditions

$$\begin{aligned}
\frac{\partial}{\partial \rho_{mn}} : 0 &= -(\ln \rho)_{nm} - \lambda_0 \delta_{nm} - \boldsymbol{\lambda} \mathbf{f}_{nm}, \quad \rho = e^{-\lambda_0 - \boldsymbol{\lambda} \mathbf{f}} \\
\frac{\partial}{\partial \lambda_0} : 1 &= e^{-\lambda_0} Z(\boldsymbol{\lambda}), \quad Z(\boldsymbol{\lambda}) = \text{Tr} e^{-\boldsymbol{\lambda} \mathbf{f}} = e^{\lambda_0} \\
\frac{\partial}{\partial \boldsymbol{\lambda}} : \mathbf{F} &= e^{-\lambda_0} \text{Tr} e^{-\boldsymbol{\lambda} \mathbf{f}} \mathbf{f} = -\frac{\partial \ln Z(\boldsymbol{\lambda})}{\partial \boldsymbol{\lambda}}.
\end{aligned} \tag{106}$$

The value of the maximal entropy is

$$\begin{aligned}
S_{F\max} &= -\text{Tr} \rho \ln \rho \\
&= \text{Tr} e^{-\lambda_0 - \boldsymbol{\lambda} \mathbf{f}} [\lambda_0 + \boldsymbol{\lambda} \mathbf{f}] \\
&= \lambda_0 + \boldsymbol{\lambda} \mathbf{F}
\end{aligned} \tag{107}$$

as expected.

The procedure of determining the state of a quantum system by means of available informations is called the quantum inference problem. The naturalness of using the maximisation of the missing entropy in the quantum inference problem hints at possible relations between information theory and quantum mechanics. The attempt to interpret quantum mechanics as a set of rules to treat partial informations in an optimised and systematic manner is made more attractive by Heisenberg's uncertainty relation which excludes the possibility of acquiring full informations about physical systems by observations.

K. Noninteracting particles

We work out now the partition function of the grand canonical ensemble for noninteracting particles, as the an example which already contains some of the usual complications of a quantum many-body system. A basis for a system of N particles can be constructed by a complete set of states $\phi_k(\mathbf{x})$ as

$$\psi(x_1, \dots, x_N) = \mathcal{N}^{-1} \sum_{\pi \in S_N} \xi^{\sigma(\pi)} \phi_{k(1)}(x_{\pi(1)}) \cdots \phi_{k(N)}(x_{\pi(N)}) \tag{108}$$

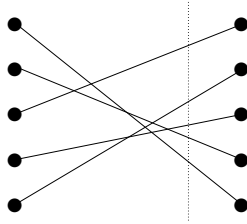


FIG. 3: Graphical representation of the permutation $\left(\begin{smallmatrix} 1,2,3,4,5 \\ 3,5,4,2,1 \end{smallmatrix}\right)$.

where \mathcal{N} is a normalization factor, π denotes a permutation of N objects, ξ is the exchange statistics, $+1$ or -1 for bosons or fermions, respectively and $\sigma(\pi)$ is its parity, defined in the following manner. Any permutation

$$\pi = \left(\begin{array}{c} 1, \dots, N \\ \pi(1), \dots, \pi(N) \end{array} \right) \quad (109)$$

can be visualized as a set of N curves, connecting N dots, representing the N particles as drawn in Fig. 3. Each curve corresponds to a particle and we find a series of crossings, particle exchanges, as the dotted vertical line is moved from the right to the left. Each crossing generates a multiplicative factor ξ in the state (108). It is obvious that the number of crossings is not defined in a unique manner, the continuous deformation of the curves may induce more or less crossings. But it is clear, as well, that such a change of the the number of crossing occurs in pairs only. This argument shows that (i) any permutation can be decomposed into the product of exchanges of neighboring objects and (ii) the number of exchanges ℓ is not unique but its parity, $\sigma(\pi) = \ell(\text{mod}2)$ is well defined. For example, for $N = 3$ we have

$$\begin{aligned} 1 &= \sigma\left(\left(\begin{array}{c} 1,2,3 \\ 1,2,3 \end{array}\right)\right) = \sigma\left(\left(\begin{array}{c} 1,2,3 \\ 3,1,2 \end{array}\right)\right) = \sigma\left(\left(\begin{array}{c} 1,2,3 \\ 2,3,1 \end{array}\right)\right) \\ -1 &= \sigma\left(\left(\begin{array}{c} 1,2,3 \\ 1,3,2 \end{array}\right)\right) = \sigma\left(\left(\begin{array}{c} 1,2,3 \\ 3,2,1 \end{array}\right)\right) = \sigma\left(\left(\begin{array}{c} 1,2,3 \\ 2,1,3 \end{array}\right)\right). \end{aligned} \quad (110)$$

The state (108) has the desired transformation property under particle exchange. To prove this we start with the identity

$$\sum_{\pi \in S_N} F(\pi) = \sum_{\pi \in S_N} F(\pi\pi'). \quad (111)$$

It holds because the map $\pi \rightarrow \pi\pi'$ of S_N for a given $\pi' \in S_N$ is bijective (onto and one-to-one), hence we have the same quantities on both sides summed up in different order. Addition is commutative therefore Eq. (111) follows. This identity allows us write

$$\begin{aligned} \psi(x_{\pi'(1)}, \dots, x_{\pi'(N)}) &= \mathcal{N}^{-1} \sum_{\pi \in S_N} \xi^{\sigma(\pi)} \phi_{k(1)}(x_{\pi\pi'(1)}) \cdots \phi_{k(N)}(x_{\pi\pi'(N)}) \\ &= \xi^{\sigma(\pi')} \psi(x_1, \dots, x_N) \end{aligned} \quad (112)$$

where the equations $\sigma(\pi\pi') = \sigma(\pi) + \sigma(\pi')$, $\sigma(\pi'^{-1}) = \sigma(\pi')$ have been used in arriving at the second line.

We simplify first the notation of the state (108) by means of the Dirac-notation,

$$|\psi\rangle = \mathcal{N}^{-1} \sum_{\pi \in S_N} \xi^{\sigma(\pi)} |k(\pi(1)), \dots, k(\pi(N))\rangle \quad (113)$$

where a state is labeled by the function $k(j)$, $j = 1, \dots, N$. We can render a state more recognizable in the second step by placing particles in the same state beside each other by an appropriate permutation, eg. $|1122213\rangle = \xi|1112223\rangle$. The phase of the state is determined by using an arbitrary but fixed order of the quantum number k . The occupation number $n(k)$ is defined for each quantum number k as the number of particles found in the one-particle state k ,

$$|k(1), \dots, k(N)\rangle \rightarrow |n(k_1), n(k_2), \dots\rangle = |n(k)\rangle, \quad (114)$$

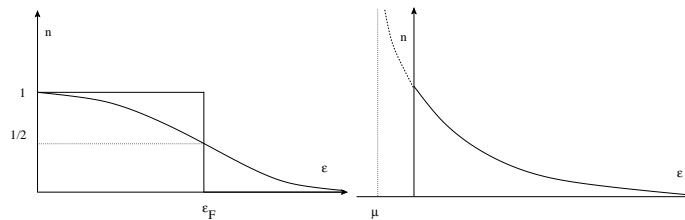


FIG. 4: Fermi-Dirac and Bose-Einstein distribution functions.

eg. $|1112223\rangle \rightarrow |3, 3, 1, 0 \dots\rangle$. The momentum \mathbf{p} is a preferred quantum number for free particles and $\psi_{\mathbf{p}}(\mathbf{x}) = e^{\frac{i}{\hbar}\mathbf{p}\mathbf{x}}$. Additive quantum numbers can easily be constructed, such as the particle number

$$Q|n(\mathbf{p})\rangle = N[n]|n(\mathbf{p})\rangle, \quad N[n] = \sum_{\mathbf{p}} n(\mathbf{p}) \quad (115)$$

and the energy

$$H|n(\mathbf{p})\rangle = E[n]|n(\mathbf{p})\rangle, \quad E[n] = \sum_{\mathbf{p}} n(\mathbf{p})\epsilon(\mathbf{p}), \quad \epsilon(\mathbf{p}) = \frac{\mathbf{p}^2}{2m}. \quad (116)$$

The partition function

$$\begin{aligned} Z = e^{\beta pV} &= \sum_{\{n(\mathbf{p})\}} e^{-\beta(E[n] - \mu N[n])} \\ &= \sum_{\{n(\mathbf{p})\}} e^{-\beta \sum_{\mathbf{p}} n(\mathbf{p})(\epsilon(\mathbf{p}) - \mu)} \\ &= \prod_j \sum_{n(\mathbf{p}_j)} e^{-\beta n(\mathbf{p}_j)(\epsilon(\mathbf{p}_j) - \mu)} \\ &= \prod_j \begin{cases} \frac{1}{1 - e^{-\beta(\epsilon(\mathbf{p}_j) - \mu)}} & \text{bosons} \\ 1 + e^{-\beta(\epsilon(\mathbf{p}_j) - \mu)} & \text{fermions} \end{cases} \end{aligned} \quad (117)$$

gives rise the pressure

$$\beta p = \begin{cases} - \int \frac{d^3 p}{(2\pi\hbar)^3} \ln[1 - e^{-\beta(\epsilon(\mathbf{p}_j) - \mu)}] & \text{bosons} \\ \int \frac{d^3 p}{(2\pi\hbar)^3} \ln[1 + e^{-\beta(\epsilon(\mathbf{p}_j) - \mu)}] & \text{fermions} \end{cases} \quad (118)$$

in the thermodynamical limit. The expectation value of the particle number,

$$\langle\langle N \rangle\rangle = \frac{1}{\beta Z} \frac{\partial Z}{\partial \mu} = \sum_j \begin{cases} \frac{e^{-\beta(\epsilon(\mathbf{p}_j) - \mu)}}{1 - e^{-\beta(\epsilon(\mathbf{p}_j) - \mu)}} & \text{bosons} \\ \frac{e^{-\beta(\epsilon(\mathbf{p}_j) - \mu)}}{1 + e^{-\beta(\epsilon(\mathbf{p}_j) - \mu)}} & \text{fermions} \end{cases} = \sum_j n(\mathbf{p}_j) \quad (119)$$

identifies the average occupation number

$$n(\epsilon) = \frac{1}{e^{\beta(\epsilon - \mu)} - \xi} \quad (120)$$

as a function of the single particle energy, cf. Fig. 4.

II. PERTURBATION EXPANSION

A rudimentary version of the perturbation expansion for the partition function will be presented briefly. It is assumed in this scheme that the system Hamiltonian can be written as a sum of the free and the interactive terms, the former dominating the latter.

Some caution is needed in using the word “interaction, specially in quantum physics. A special feature of statistical physics is that one always needs some interactions between the observed system and its environment. In fact, this interactions should be weak enough to be able to consider the system and to leave the influence of the environment for the choice of certain ensemble. In the same time, it should be strong enough to generate relaxation and equilibrium for the system. What we mean by an ideal gas is a system of particles having no interactions among themselves but still interacting with the thermal, chemical, etc. baths in their environment.

Interaction of two subsystems is handled in classical physics by introducing a part of the total energy which depends on the degrees of freedom of both sub-systems. As long as this contribution is negligible compared to the rest the interaction is considered weak. Take now a gas of non-interacting point particles in a solid vessel where the interactions of the particles with their environment, the vessel wall, are described by some elastic, energy conserving, particle-vessel wall collision dynamics. In the limit of infinitely massive vessel the interaction energy between the particles and the vessel tends to zero, indicating the insufficiency of the interaction energy as measure of the importance of the interaction in the dynamics.

The tradition view of interactions, based on the interaction energy proves to be even less useful in the quantum domain. When two indistinguishable particles form a common system then the (anti)symmetrization of their state introduces correlations, known as exchange interactions as long as their wave-functions overlap in three-space even if the particles are strictly non-interactive. These correlations may make the eigenvalues of the total Hamiltonian complicated, non-additive functions of the single-particle quantum numbers. Such states which can not be factorized as a simple product of vectors corresponding to the two sub-systems are called entangled. The distinguished feature of correlations observed in entangled state are non-locality and selectivity. The former stands for the insensitivity of the correlations on the separation of the particles. The latter can be explained in case of three particles, A, B and C entangled with each other. The insensitivity of the correlations of entangled state on the separation explains that the correlation between A and B may differ substantially from that of A and C even if B and C are close to each other, both of them being far from A.

The correlations due to the (anti)symmetrization of states of indistinguishable particles can approximatively be described by using the classical description extended a suitable chosen interaction potential. This method is described first below, followed by the perturbative treatment of genuine interactions, represented by some interaction energy in the Hamiltonian.

A. Exchange correlations for free particles

The non-interacting particles are correlated when they are indistinguishable. For example the Pauli exclusion principle generates repulsion when the wave functions of the fermions with the same spin overlap. Such kind of exchange correlations can be treated perturbatively when the system is approximately classical which happens to be the case at high temperature.

The partition function is given as the trace of the density matrix. Instead of a direct calculation of the matrix elements of the density matrix we shall rely an a surprising and useful relation between quantum mechanics and quantum statistical mechanics, namely that the density matrix of a canonical ensemble can be obtained by continuing analytically the propagator for imaginary time. To see this relation we start with a free particle whose propagator,

$$G(\mathbf{x}, \mathbf{y}; t) = \langle \mathbf{x} | e^{-\frac{i}{\hbar} H_0} | \mathbf{y} \rangle, \quad (121)$$

is constructed by going over momentum space,

$$\begin{aligned} G(\mathbf{x}, \mathbf{y}; t) &= \langle \mathbf{x} | e^{-\frac{it}{2m\hbar} \mathbf{p}^2} | \mathbf{y} \rangle \\ &= \int \frac{d^3 q}{(2\pi)^3 \hbar^3} \underbrace{\langle \mathbf{x} | e^{-\frac{it}{2m\hbar} \mathbf{p}^2} | \mathbf{q} \rangle}_{\langle \mathbf{x} | \mathbf{q} \rangle e^{-\frac{it}{2m\hbar} \mathbf{q}^2}} \langle \mathbf{q} | \mathbf{y} \rangle \\ &= \int \frac{d^3 q}{(2\pi)^3 \hbar^3} e^{-\frac{it}{2m\hbar} \mathbf{q}^2 + \frac{i}{\hbar} \mathbf{q}(\mathbf{x}-\mathbf{y})} \\ &= \left(\frac{m}{2\pi i \hbar t} \right)^{3/2} e^{\frac{im}{2\hbar} (\mathbf{x}-\mathbf{y})^2}. \end{aligned} \quad (122)$$

The single particle density matrix can be found by Wick rotation, $t \leftrightarrow -i\hbar\beta$, where $\beta = 1/k_B T$. In fact, such a transformation changes the heat equation

$$\partial_t p = D\Delta p \quad (123)$$

into the Schrödinger equation

$$i\hbar\partial_t\psi = -\frac{\hbar^2}{2m}\Delta\psi \quad (124)$$

and the density matrix $\rho(\beta) = e^{-\beta H}$ into the time evolution operator $U(t) = e^{-\frac{i}{\hbar}tH}$. In particular, the transition probability for Brownian motion, satisfying the heat equation is

$$\langle \mathbf{x} | e^{-\frac{\beta}{2m}\mathbf{p}^2} | \mathbf{y} \rangle = \lambda_T^{-3} e^{-\frac{\pi}{\lambda_T^2}(\mathbf{x}-\mathbf{y})^2}, \quad (125)$$

where

$$\lambda_T = \sqrt{\frac{2\pi\hbar^2}{mk_B T}} \quad (126)$$

denotes the thermal de Broglie wave length satisfying $\hbar^2/2m\lambda_T^2 = k_B T/2\pi$. The matrix elements of the density matrix for N distinguishable particles are therefore

$$\langle \mathbf{x}_1, \dots, \mathbf{x}_N | e^{-\frac{\beta}{2m}\mathbf{p}^2} | \mathbf{y}_1, \dots, \mathbf{y}_N \rangle = \lambda_T^{-3N} e^{-\frac{\pi}{\lambda_T^2} \sum_j (\mathbf{x}_j - \mathbf{y}_j)^2}. \quad (127)$$

The physical states of equivalent particles are (anti)symmetrized with respect to their exchange,

$$|\mathbf{x}_1, \dots, \mathbf{x}_N\rangle \rightarrow \frac{1}{\sqrt{N!}} \sum_{\pi \in S_N} \xi^{\sigma(\pi)} |\mathbf{x}_{\pi(1)}, \dots, \mathbf{x}_{\pi(N)}\rangle \quad (128)$$

and the density matrix for equivalent particle is

$$\langle \mathbf{x}_1, \dots, \mathbf{x}_N | e^{-\frac{\beta}{2m}\mathbf{p}^2} | \mathbf{y}_1, \dots, \mathbf{y}_N \rangle = \sum_{\pi\pi'} F(\pi, \pi') \quad (129)$$

where

$$F(\pi, \pi') = \xi^{\sigma(\pi)+\sigma(\pi')} \frac{1}{N!\lambda_T^{3N}} e^{-\frac{\pi}{\lambda_T^2} \sum_j (\mathbf{x}_{\pi(j)} - \mathbf{y}_{\pi'(j)})^2}. \quad (130)$$

An important property of the function $F(\pi, \pi')$ is that it remains invariant under the simultaneous permutations of the coordinates,

$$F(\pi\pi'', \pi'\pi'') = F(\pi, \pi') \quad (131)$$

which follows from the identity

$$\sum_j (\mathbf{x}_{\pi(j)} - \mathbf{y}_{\pi'(j)})^2 = \sum_j f_j = \sum_j f_{\pi''(j)} = \sum_j (\mathbf{x}_{\pi(\pi''(j))} - \mathbf{y}_{\pi'(\pi''(j))})^2 \quad (132)$$

containing the sum of the same terms in different order on the two sides, cf. Eq. (111). We choose $\pi'' = \pi'^{-1}$ and find

$$\sum_{\pi\pi'} F(\pi, \pi') = \sum_{\pi\pi'} F(\pi\pi'^{-1}, \mathbb{1}) = N! \sum_{\pi} F(\pi, \mathbb{1}) \quad (133)$$

where the last equation holds because it contains the sum of the same terms in different order on the two sides. We find finally the canonical partition function

$$\begin{aligned} Z_N &= \text{Tr} e^{-\beta H_0} \\ &= \frac{1}{N!\lambda_T^{3N}} \sum_{\pi} \xi^{\sigma(\pi)} \int d^{3N}x e^{-\frac{\pi}{\lambda_T^2} \sum_j (\mathbf{x}_{\pi(j)} - \mathbf{x}_j)^2} \end{aligned} \quad (134)$$

where the multiplicative factor $1/N!$ is to compensate that for each non-degenerate set of coordinates, $\mathbf{x}_j \neq \mathbf{x}_k$ the same (anti)symmetric state appears $N!$ times in the integration.

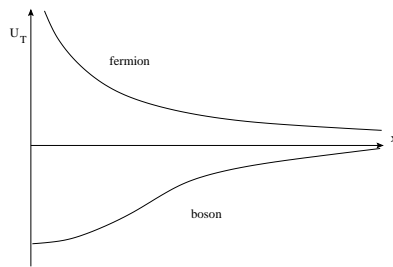


FIG. 5: The qualitative feature of the statistical potential.

It is instructive to consider the high temperature limit, $\lambda_T \rightarrow 0$, when the average interparticle distance becomes large compared with the thermal wave length, $V/N \gg \lambda_T^3$ and one expects that the particles behave classically. The dominant contribution to the partition function is then $\pi = \mathbb{1}$, the next order corresponds to permutations consisting of a single exchange of two particles, the n -th order being the sum over permutations which exchange n particles,

$$Z_N = \frac{1}{N! \lambda_T^{3N}} \int d^{3N} x \left[e^{-\frac{\pi}{\lambda_T^2} \sum_j (\mathbf{x}_j - \mathbf{x}_j)^2} + \xi \sum_{i < j} e^{-\frac{2\pi}{\lambda_T^2} (\mathbf{x}_i - \mathbf{x}_j)^2} + \dots \right]. \quad (135)$$

Let us re-express the factor λ_T^{3N} in front of the the sum by the Gaussian integral over the momenta write the integral over the momenta,

$$Z_N = \frac{1}{N! (2\pi\hbar)^{3N}} \int d^{3N} x d^{3N} p e^{-\beta \sum_j \frac{p_j^2}{2m}} \left[1 + \xi \sum_{i < j} e^{-\frac{2\pi}{\lambda_T^2} (\mathbf{x}_j - \mathbf{x}_i)^2} + \dots \right]. \quad (136)$$

The first term,

$$Z_N^{(0)} = \frac{1}{N! (2\pi\hbar)^{3N}} \int d^{3N} x d^{3N} p e^{-\beta \sum_j \frac{p_j^2}{2m}}, \quad (137)$$

dominates the partition function and shows the approach of the classical behavior with increasing temperature. To see the role of the next order we write

$$Z_N = \frac{1}{N! (2\pi\hbar)^{3N}} \int d^{3N} x d^{3N} p e^{-\beta \left[\sum_j \frac{p_j^2}{2m} + \sum_{i < j} U_T(\mathbf{x}_i - \mathbf{x}_j) + \dots \right]} \quad (138)$$

where the statistical potential

$$U_T(\mathbf{x}) = -k_B T \ln \left(1 + \xi e^{-\frac{2\pi}{\lambda_T^2} \mathbf{x}^2} \right) \quad (139)$$

has been introduced. It represents a repulsive force for fermions, arising from the Pauli exclusion principle and an attractive force for bosons.

It is possible to recover all orders in the series by factorizing the permutations as

$$\pi = \underbrace{(i_1, j_1) \cdots (i_{m_2}, j_{m_2})}_{m_2 \text{ two-cycles}} \underbrace{(k_1, \ell_1, m_1) \cdots (k_{m_3}, \ell_{m_3}, m_{m_3})}_{m_3 \text{ three-cycles}} \cdots \quad (140)$$

where $\sum_\ell \ell m_\ell = N$. The contribution of the ℓ -cycle to the partition functions is

$$C_\ell = \prod_{j=1}^{\ell} \int \frac{d^3 x_j}{\lambda_T^3} e^{-\frac{\pi}{\lambda_T^2} [(\mathbf{x}_1 - \mathbf{x}_2)^2 + (\mathbf{x}_2 - \mathbf{x}_3)^2 + \dots + (\mathbf{x}_\ell - \mathbf{x}_1)^2]} \quad (141)$$

The integration can be carried out successively by means of the following identity for Gaussian integrals,

$$\begin{aligned}
\int \frac{d^3 y}{(2\pi\sqrt{\tau_1\tau_2})^3} e^{-\frac{(\mathbf{x}-\mathbf{y})^2}{2\tau_1}-\frac{(\mathbf{y}-\mathbf{z})^2}{2\tau_2}} &= \frac{e^{-\frac{\mathbf{x}^2}{2\tau_1}-\frac{\mathbf{z}^2}{2\tau_2}}}{(2\pi\sqrt{\tau_1\tau_2})^3} \int d^3 y e^{-\frac{\mathbf{y}^2}{2}\left(\frac{1}{\tau_1}+\frac{1}{\tau_2}\right)+\mathbf{y}\left(\frac{\mathbf{x}}{\tau_1}+\frac{\mathbf{z}}{\tau_2}\right)} \\
&= \frac{1}{(2\pi\tau_1\tau_2)^{3/2}} \left(\frac{\tau_1\tau_2}{\tau_1+\tau_2}\right)^{3/2} e^{-\frac{\mathbf{x}^2}{2\tau_1}-\frac{\mathbf{z}^2}{2\tau_2}+\frac{1}{2\left(\frac{1}{\tau_1}+\frac{1}{\tau_2}\right)}\left(\frac{\mathbf{x}}{\tau_1}+\frac{\mathbf{z}}{\tau_2}\right)^2} \\
&= \frac{1}{[2\pi(\tau_1+\tau_2)]^{3/2}} e^{-\frac{\mathbf{x}^2}{2\tau_1}-\frac{\mathbf{z}^2}{2\tau_2}+\frac{\tau_1^2\mathbf{x}^2+\tau_2^2\mathbf{z}^2+2\mathbf{x}\mathbf{z}}{2(\tau_1+\tau_2)}} \\
&= \frac{1}{[2\pi(\tau_1+\tau_2)]^{3/2}} e^{-\frac{(\mathbf{x}-\mathbf{z})^2}{2(\tau_1+\tau_2)}}, \tag{142}
\end{aligned}$$

showing that the elimination of a coordinate leaves behind the same kind of integral. Applying such an elimination $\ell - 1$ times we find

$$\begin{aligned}
C_\ell &= \prod_{j=1}^{\ell} \int \frac{d^3 x_j}{(2\pi\frac{\lambda_T^2}{2\pi})^{3/2}} e^{-\frac{1}{2\lambda_T^2}[(\mathbf{x}_1-\mathbf{x}_2)^2+(\mathbf{x}_2-\mathbf{x}_3)^2+\dots+(\mathbf{x}_\ell-\mathbf{x}_1)^2]} \\
&= \int \frac{d^3 x_1}{(2\pi\frac{\ell\lambda_T^2}{2\pi})^{3/2}} e^{-\frac{1}{2\lambda_T^2}(\mathbf{x}_1-\mathbf{x}_1)^2} \\
&= \frac{V}{(\ell\lambda_T^2)^{3/2}} \tag{143}
\end{aligned}$$

The canonical partition function is

$$\begin{aligned}
Z_N &= \frac{1}{N!\lambda_T^{3N}} \sum_{\pi} \xi^{\sigma(\pi)} \int d^{3N} x e^{-\frac{\pi}{\lambda_T^2} \sum_j (\mathbf{x}_{\pi(j)}-\mathbf{x}_j)^2} \\
&= \frac{1}{N!} \sum_{\pi} (\xi C_\ell)^{m_\ell} \tag{144}
\end{aligned}$$

The number of permutations corresponding to a given decomposition, ie. set of numbers $\{m_\ell\}$ satisfying $\sum_\ell \ell m_\ell = N$ is $N!/\prod_\ell m_\ell! \ell^{m_\ell}$. In fact, there are $N!$ permutations altogether and the permutation of the cycles and the performance of a cyclic permutation on the symbols in a cycle preserves the decomposition. We have finally

$$\begin{aligned}
Z_N &= \frac{1}{N!} \sum'_{\{m_\ell\}} \frac{N!}{\prod_\ell m_\ell! \ell^{m_\ell}} (\xi C_\ell)^{m_\ell} \\
&= \sum'_{\{m_\ell\}} \prod_\ell \frac{1}{m_\ell!} \left(\frac{\xi C_\ell}{\ell}\right)^{m_\ell} \tag{145}
\end{aligned}$$

where the prime on the sum is the reminder of the constraint $\sum_\ell \ell m_\ell = N$. The grand canonical partition function is therefore

$$\begin{aligned}
Z &= \sum_{N=0}^{\infty} z^N Z_N \\
&= \prod_\ell \sum_{\{m_\ell\}} \frac{1}{m_\ell!} \left(\frac{z^\ell \xi C_\ell}{\ell}\right)^{m_\ell} \\
&= e^{\xi \sum_\ell \frac{z^\ell}{\ell} C_\ell}, \tag{146}
\end{aligned}$$

and we have a series representation of the pressure of the ideal gas,

$$\frac{pV}{T} = \xi \sum_\ell \frac{z^\ell}{\ell} C_\ell = \xi \frac{V}{\lambda_T^3} \sum_\ell \frac{z^\ell}{\ell^{5/2}}. \tag{147}$$

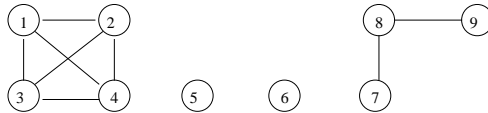


FIG. 6: A ninth order Meyer graph.

B. Interacting classical systems

Let us now consider a system of particles described by the classical Hamiltonian

$$H = \sum_j \frac{\mathbf{p}_j^2}{2m} + \sum_{i<j} v_{ij}, \quad (148)$$

where

$$v_{ij} = V(\mathbf{x}_i - \mathbf{x}_j). \quad (149)$$

denotes a genuine interaction, described by a pair potential. The canonical partition function is

$$\begin{aligned} Z_N &= \frac{1}{N!} \prod_j \int \frac{d^3 p_j}{(2\pi)^3 \hbar^3} d^3 x_j e^{-\beta H} \\ &= \frac{1}{N! \lambda_T^{3N}} \int d^{3N} x e^{-\beta \sum_{i<j} v_{ij}}. \end{aligned} \quad (150)$$

We introduce the function f_{ij} by the expression

$$1 + f_{ij} = e^{-\beta v_{ij}} \quad (151)$$

and write the partition function as a series

$$\begin{aligned} Z_N &= \frac{1}{N! \lambda_T^{3N}} \int d^{3N} x \prod_{i<j} (1 + f_{ij}) \\ &= \frac{1}{N! \lambda_T^{3N}} \int d^{3N} x \left[1 + \sum_{i<j} f_{ij} + \sum_{i<j, k<\ell} f_{ij} f_{k\ell} + \dots \right] \end{aligned} \quad (152)$$

where each contribution is represented by a Meyer graph. A numbered graph for n particles consists of n numbered bubbles, some of them connected by lines. The corresponding mathematical expression contains integration for n coordinates and the integrand is the product of f_{ij} , one factor for line connecting two bubbles. The ninth order graph of Fig. 6 stands for the contribution

$$\int d^3 x_1 \cdots d^3 x_9 f_{12} f_{13} f_{14} f_{23} f_{42} f_{43} f_{87} f_{89}. \quad (153)$$

The partition function is the sum over all different graphs,

$$Z_N = \frac{1}{N! \lambda_T^{3N}} \sum [N \text{ particle graphs}] \quad (154)$$

To simplify the expressions one considers connected graphs, clusters, which do not fall into the product of two independent factors and define the ℓ -cluster integral as

$$b_\ell = \frac{1}{\ell! \lambda_T^{3\ell-3} V} \sum [\ell \text{ particle connected graphs}] \quad (155)$$

where the coefficient is chosen in such a manner that b_ℓ is dimensionless and converges in the thermodynamical limit where the integration over the coordinates of a connected graph produces a volume factor. The first few cluster

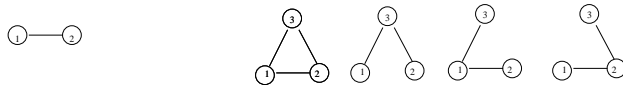


FIG. 7: The second and third order Meyer graphs.

integrals,

$$\begin{aligned}
b_1 &= \frac{1}{V} \int d^x = 1 \\
b_2 &= \frac{1}{2!\lambda_T^3 V} \int d^3 x_1 d^3 x_2 f_{12} = \frac{1}{2\lambda_T^3} \int d^3 x f(\mathbf{x}) \\
b_3 &= \frac{1}{3!\lambda_T^6 V} \int d^3 x_1 d^3 x_2 d^3 x_3 [\text{three particle graphs of Fig.7}]
\end{aligned} \tag{156}$$

with

$$f(\mathbf{x}) = e^{-\beta V(\mathbf{x})} - 1 \tag{157}$$

and shown in Fig. 7.

Any graph can be factorized into the product of its connected components. Let us denote the number of ℓ -particle connected components in a graphs by m_ℓ . This partition of N particles satisfies the relation $\sum_{\ell=1}^N \ell m_\ell = N$. For a given set $\{m_\ell\}$ we have to sum over different distributions of the particles in the bubbles of the graph. There are altogether $N!$ ways of distributing the particles but the connected components can be exchanged and within a connected component the particles can be redistributed without producing new graphs. Therefore there are $N!/\prod_\ell m_\ell! (\ell!)^{m_\ell}$ different distribution of the particles corresponding to the same graph and the contribution of the graph with a given set $\{m_\ell\}$ is

$$\int d^{3N} x e^{-\beta \sum_{i<j} v_{ij}} = \frac{N!}{\prod_\ell m_\ell! (\ell!)^{m_\ell}} \prod_\ell (V \ell! \lambda_T^{3\ell-3} b_\ell)^{m_\ell} = N! \lambda_T^{3N} \prod_\ell \frac{1}{m_\ell!} \left(\frac{V}{\lambda_T^3} b_\ell \right)^{m_\ell}$$

and we find the canonical partition function

$$Z_N = \sum'_{\{m_\ell\}} \prod_\ell \frac{1}{m_\ell!} \left(\frac{V}{\lambda_T^3} b_\ell \right)^{m_\ell}. \tag{158}$$

The grand canonical partition function is free of the constraint on the particle number and reads as

$$\begin{aligned}
Z &= \sum_N z^N Z_N \\
&= \prod_\ell \sum_{\{m_\ell\}} \frac{1}{m_\ell!} \left(\frac{V}{\lambda_T^3} z^\ell b_\ell \right)^{m_\ell} \\
&= e^{\frac{V}{\lambda_T^3} \sum_\ell z^\ell b_\ell}
\end{aligned} \tag{159}$$

where $z = e^{\beta\mu}$. We have finally the expressions

$$\frac{p}{T} = \frac{1}{\lambda_T^3} \sum_\ell z^\ell b_\ell \tag{160}$$

and

$$n = \frac{N}{V} = \frac{\partial}{\partial \mu} p = \frac{dz}{d\mu} \frac{\partial}{\partial z} p = \beta z \frac{\partial}{\partial z} p = \frac{1}{\lambda_T^3} \sum_\ell \ell z^\ell b_\ell \tag{161}$$

for the pression and the density.

The resummed cluster expansion provides results with arbitrary precision for sufficiently dilute gas but is unable to handle phase transitions eventually occurring at higher densities. It is useful to organize the expansion using explicitly the density as small parameter. The equation of state in such a virial expansion is

$$\frac{pV}{NT} = \frac{\sum_{\ell} z^{\ell} b_{\ell}}{\sum_{\ell} \ell z^{\ell} b_{\ell}} = \sum_{\ell=1}^{\infty} a_{\ell} (\lambda_T^3 n)^{\ell-1} \quad (162)$$

The second equation allows us to write

$$\begin{aligned} \sum_{\ell} z^{\ell} b_{\ell} &= \sum_{\ell} \ell z^{\ell} b_{\ell} \sum_{\ell'=1}^{\infty} a_{\ell'} (\lambda_T^3 n)^{\ell'-1} \\ &= \sum_{\ell} \ell z^{\ell} b_{\ell} \sum_{\ell'=1}^{\infty} a_{\ell'} \left(\sum_{\ell''} \ell'' z^{\ell''} b_{\ell''} \right)^{\ell'-1} \end{aligned} \quad (163)$$

and the identification of the coefficients of the same powers of the fugacity yields the virial coefficients a_{ℓ} . In the first order we have $b_1 = b_1 a_1$ and $a_1 = 1$. The second order gives $b_2 = 2b_2 a_1 + b_1^2 a_2$ and $a_2 = -b_2$, etc.

C. Interacting quantum systems

The expansion of the quantum system can easily be reduced to the classical case. The canonical partition function,

$$Z_N = \text{Tr} e^{-\beta H} \quad (164)$$

can be rewritten by using the resolutions of one

$$\begin{aligned} \mathbb{1} &= \sum_n |n\rangle \langle n|, \\ &= \frac{1}{N!} \int d^{3N} x |x_1, \dots, x_N\rangle \langle x_1, \dots, x_N|, \end{aligned} \quad (165)$$

where $H|n\rangle = E_n|n\rangle$ as

$$\begin{aligned} Z_N &= \frac{1}{N!} \int d^{3N} x \sum_{\alpha} \int d^{3N} \langle x_1, \dots, x_N | e^{-\beta H} | x_1, \dots, x_N \rangle \\ &= \frac{1}{N! \lambda_T^{3N}} \int d^{3N} x W_N(x_1, \dots, x_N), \end{aligned} \quad (166)$$

where

$$\begin{aligned} W_N(x_1, \dots, x_N) &= \lambda_T^{3N} \sum_{\alpha} \langle x_1, \dots, x_N | e^{-\beta H} | x_1, \dots, x_N \rangle \\ &= \lambda_T^{3N} \sum_n \langle x_1, \dots, x_N | n \rangle e^{-\beta E_n} \langle n | x_1, \dots, x_N \rangle \\ &= \lambda_T^{3N} \sum_n |\langle x_1, \dots, x_N | n \rangle|^2 e^{-\beta E_n}. \end{aligned} \quad (167)$$

Note that

$$\begin{aligned} W_1(x) &= \frac{\lambda_T^3}{V} \sum_{\mathbf{p}} e^{-\frac{i}{\hbar} \mathbf{p} \mathbf{x}} \langle \mathbf{p} | e^{-\frac{\beta \hbar}{2m} \Delta} | \mathbf{p} \rangle e^{\frac{i}{\hbar} \mathbf{p} \mathbf{x}} \\ &= \lambda_T^3 \int \frac{d^3 p}{(2\pi)^3 \hbar^3} e^{-\frac{\beta}{2m} \mathbf{p}^2} = 1 \end{aligned} \quad (168)$$

and the functions $W_N(x_1, \dots, x_N)$, the unnormalized probability distributions are symmetric with respect to the permutations of the coordinates.

The connected components of the correlation functions W_N are identified by means of their clusterisation,

$$W_{M+N}(x_1, \dots, x_M, x_{M+1}, \dots, x_{N+M}) \rightarrow W_M(x_1, \dots, x_M)W_N(x_{M+1}, \dots, x_{N+M}) \quad (169)$$

as $|\mathbf{x}_j - \mathbf{x}_k| \rightarrow \infty$ for $1 \leq j \leq M$ and $M+1 \leq k \leq M+N$. This property allows us to introduce the "connected part" C_N of any correlation function W_N in the following, iterative manner. The first step is obvious, $C_1(x) = W_1(x) = 1$. The connected two-point correlation function is defined by

$$W_2(x_1, x_2) = C_1(x_1)C_1(x_2) + C_2(x_1, x_2). \quad (170)$$

The connected three-point function is introduced by

$$W_3(x_1, x_2, x_3) = C_1(x_1)C_1(x_2)C_1(x_3) + C_2(x_1, x_2)C_1(x_3) + C_2(x_1, x_3)C_1(x_2) + C_2(x_2, x_3)C_1(x_1) + C_3(x_1, x_2, x_3). \quad (171)$$

The higher order connected functions are defined in a similar manner,

$$W_N(x_1, \dots, x_N) = \sum'_{\{m_\ell\}} \sum_{\pi} \underbrace{C_1 \cdots C_1}_{m_1} \underbrace{C_2 \cdots C_2}_{m_2} \underbrace{C_3 \cdots C_3}_{m_3} \cdots \quad (172)$$

where the summation is varied out over such permutation $\pi \in S_N$ which correspond to different distribution of the particles among the argument of the connected correlation functions. (No need of permuting the variables of a given C_ℓ because it is already (anti)symmetric). As usual, the prime denotes that the summation is over partitions satisfying $\sum_\ell \ell m_\ell = N$. It is a deep dynamical postulate, that the connected parts, defined in this manner are vanishing, $C_N(x_1, \dots, x_N) \rightarrow 0$ if any of the variables is separated from the rest. One expects that this clusterization is valid due to the assumed absence of genuine long range correlations in a system which has convergent thermodynamical limit. This assumption can be verified by means of the perturbation expansion or by numerical simulation.

The ℓ -cluster integral is defined by

$$b_\ell = \frac{1}{\ell! \lambda_T^{3\ell-3} V} \int d^{3\ell} x C_\ell(x_1, \dots, x_\ell) \quad (173)$$

which yields

$$\begin{aligned} Z_N &= \frac{1}{N! \lambda_T^{3N}} \int d^{3N} x W_N(1, \dots, N) \\ &= \frac{1}{N! \lambda_T^{3N}} \sum'_{\{m_\ell\}} \frac{N!}{\prod_\ell (\ell!)^{m_\ell} m_\ell!} \int d^{3N} x \underbrace{C_1 \cdots C_1}_{m_1} \underbrace{C_2 \cdots C_2}_{m_2} \underbrace{C_3 \cdots C_3}_{m_3} \cdots \\ &= \frac{1}{\lambda_T^{3N}} \sum'_{\{m_\ell\}} \prod_\ell \frac{1}{m_\ell!} \left[\frac{1}{\ell!} \int d^{3\ell} x C_\ell(x_1, \dots, x_\ell) \right]^{m_\ell} \\ &= \frac{1}{\lambda_T^{3N}} \sum'_{\{m_\ell\}} \prod_\ell \frac{(V \lambda^{3\ell-3} b_\ell)^{m_\ell}}{m_\ell!} \\ &= \sum'_{\{m_\ell\}} \prod_\ell \frac{1}{m_\ell!} \left(\frac{V}{\lambda^3} b_\ell \right)^{m_\ell} \end{aligned} \quad (174)$$

and

$$Z = \sum_N z^N Z_N = e^{\frac{V}{\lambda^3} \sum_\ell z^\ell b_\ell}. \quad (175)$$

The calculation followed here aims at the thermodynamic potentials. In a similar manner one can calculate averages of other quantities, as well.

III. PHASE TRANSITIONS

Thermodynamics was developed by remarkable intuitions and lead to the phenomenological description of large systems in a time when no direct indications were known about the existence of the underlying microscopic structure

of matter. This phenomenology was developed for stable matter but can easily be extended to the description of phase transitions. The possibility of such an extension is even more remarkable because the phase transitions bring new universal behavior compared to the stable state and depends more heavily on the microscopic details.

Phase transitions, eg. the freezing or evaporation of water, refer to a non-analytical dependence of the thermodynamical potential for certain values of the phenomenological parameters. The main problem in this phenomenon is the understanding of the origin of singularity in simple quantities as temperature, pressure, density, etc. when these quantities appear in an analytic manner in our microscopic expressions. The key observation is that this analytic dependence of the microscopic laws on the parameters in question guarantees analyticity of the observables for finite system only. Phase transitions arise in the thermodynamical limit only where the diverging particle number generates singularities for certain equilibrium states.

The construction of the microscopic, dynamical picture is a real challenge because one can not rely on kinetic theory to describe a highly non-equilibrium process. What is left in classical physics is the detailed solution of the equations of motion for a large but finite closed system and the extrapolation to the thermodynamic limit with care. A large closed system follows a rather complicated path in its classical phase space. After some time it usually arrives at a certain basin, a coordinate space area surrounded by potential barriers where it reaches an equilibrium state and develops an analytical dependence of the long time averages on the control parameters, appearing analytically in the Hamiltonian. But the motion takes place on a complicated potential landscape and there might be narrow valleys leading to different other basins where the system could display different equilibrium dynamics. For a large but finite system the cross section of the valley is finite, the total energy is sufficient to traverse the valley and the system always explores a number of different basins in its equilibrium and there is no phase transition. But the valley cross section might become a singular function of the energy in the thermodynamical limit. How can this happen?

The best is to imagine an effective theory for the collective coordinate parameterizing the path along the valley. Most of the degrees of freedom are fast changing compared to this coordinate and provide a background noise only. The effective theory, obtained by solving the equations of motion numerically for all other coordinates, has a Langevin-like equation for our collective coordinate which contains an effective potential. This effective potential depends on the total energy of the system and opens the passage in the valley only if the system energy/temperature reaches a certain threshold. The fluctuations which are strong for finite systems round off this transition as a function of the energy/temperature but the opening of the valley becomes sudden in the thermodynamic limit when the fluctuations in forming the effective potential become weak.

How such a mysterious valley effects can show in quantum mechanics? The detailed response is rather involved, it involves functional analysis and C^* algebraic methods in quantum field theory. But the qualitative picture is simple. The quantum description is based on the representation of the basic canonical variables and observables in Hilbert spaces. Neumann's theorem states that this representation is unique for finite systems. This implies that the expectation in a given eigenstate of the Hamiltonian are analytic functions of control parameters as long as these parameters appear in the Hamiltonian in an analytic manner. But the escape of this triviality is offered by the thermodynamical limit. For infinite systems there might be several non-equivalent representations. Each of them provides analytical dependence of the expectation values on the control parameters but the physical system belongs to the representation which maximizes the entropy. Phase transition occurs when the system changes representation. The representations correspond to the equilibrium basins of the classical description and the entropy maximization mechanism stands for the valley.

A compromise between the simple phenomenology of thermodynamics and the heavy mathematical formalism of infinite systems is offered by the renormalization group where the singular features of the phase transitions are established by simple but convincing arguments for large, finite systems as the thermodynamical limit is sought.

The common element of the quantum and classical origin of phase transitions is the inherent ambiguity in the determination of the domain of certain integrals, the path integrals for quantum physics and the partition function in the classical case. The expected relations, such as the equation of motions equation of state, etc., can be derived from these integrals as long as the integration is carried out on a topological trivial, connected domain. But whenever the accessible phase space becomes the union of disconnected pieces further information is needed to reconstruct the desired physics. Phase transitions can be observed at this point.

A phase transition, the singular dependence of the partition function on the parameters may have two qualitatively different origins. The thermodynamical phase transitions stand for the singularities of the partition function in the thermodynamical variables. The partition function depends on the microscopic parameters of the dynamics, too. The average over quantum fluctuations may generate singular dependence on these parameters independently of the thermal environment. These are the quantum phase transition.

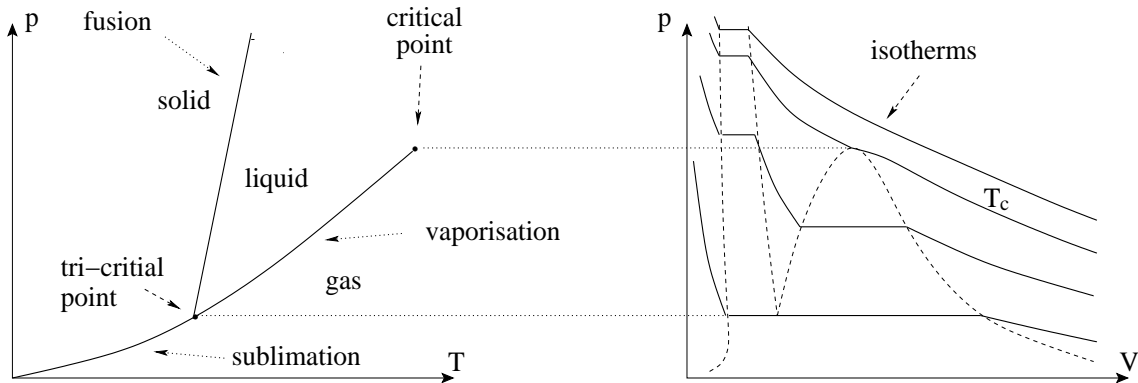


FIG. 8: A typical phase diagram.

A. Thermodynamics

What is singular at the phase transition? Our influence of the material is a local effect, as any other interactions. A small modification of our control parameters induces qualitatively different responses at the two sides of the phase boundary. How does this appear in thermodynamical quantities? Recall that the Euler relation,

$$E = TS - pV + \sum_j \lambda_j F_j \quad (176)$$

where (λ_j, F_j) stands for a pair of intensive and extensive pairs of variables, results from the extensive properties of the variables E , S and F_j alone and is valid in any phase. It is the first law of thermodynamics,

$$dE = TdS - pdV + \sum_j \lambda_j dF_j \quad (177)$$

which expresses the response of the system for small changes of the extensive parameters and contains the equation of state which may change at the phase boundary. Another appearance of the phase difference is in the Gibbs-Duheim relation,

$$SdT = Vdp - \sum_j d\lambda_j F_j \quad (178)$$

which is the difference of the first law and an infinitesimal change of the Euler relation,

$$dE = dTS + TdS - dpV - pdV + \sum_j d\lambda_j F_j + \sum_j \lambda_j dF_j. \quad (179)$$

Each phase is characterized its own equation of state or Gibbs-Duheim relation. A system with n conserved quantities beyond energy has $n+2$ thermodynamical parameters, say the temperature, the pressure and one extensive or intensive parameter per conservation law. The system with p coexisting phases must satisfy p constraints, the Gibbs-Duheim relation for each phase and has $2+n-p$ free parameters. This is Gibb's phase rule, stating for example that a simple system without conserved quantity other than the energy and the particle number the possible phase boundaries form one-dimensional lines. Such a typical phase diagram is shown on Fig. 8.

Let us denote the $n+2$ pairs of thermodynamical variables by (X_j, Y_j) , $j = 1, \dots, n+2$ and suppose that the interaction channels of our system with its environment allows the exchange of quantities $A_j \in \{X_j, Y_j\}$. Then the other partner of the pairs, $B_j \in \{X_j, Y_j\}$, where $\{A_j, B_j\} = \{X_j, Y_j\}$ are the natural variables of the thermodynamical potential of this problem. For a simple gas with no conserved quantity other than the energy and the total particle number the usually the energy and the volume exchange is possible leaving us the Gibbs potential $\mu = \mu(T, p)$, the function of the temperature and pressure to describe the phase structure.

The internal points of a phase represent stable systems. According to the maximal entropy principle the natural variables of the entropy, the extensive thermodynamical variables, are chosen in an equilibrium by maximization. This

amounts to the minimization of the total energy as the function of the extensive variables. The thermodynamical potential $\Phi(B)$ corresponding to the given interaction channels is obtained from the entropy by Legendre transformation and its variables are determined in each phase by minimizing or maximizing the thermodynamical potential. Therefore, the second partial derivative matrix of the thermodynamical potential $S_{jk}(B) = \partial^2 \Phi / \partial B_j \partial B_k$ is positive or negative definite and the thermodynamical potential itself is a convex or concave function for stable systems.

At the phase boundary the second derivative matrix acquires a zero eigenvalue but the first derivatives $\partial \Phi / \partial B_j$, the response of the system for a slight change of the control parameters may differ in the neighboring phases. A phase transition is called discontinuous or first order if the some of these first derivatives differ on the two sides. The discontinuity of the first derivatives, eg. the latent heat $\Delta(\partial F_G(T, p) / \partial T)$, indicates first order phase transitions. In the continuous phase transitions the higher order derivatives differ only. Note that the thermodynamical potential itself, $\Phi(B)$, is always continuous.

What determines the shape of the phase boundaries? The simplest is to answer this question in the case when the phase boundary is a one dimensional curve what we shall take in the (p, T) plane for the sake of simplicity. The corresponding thermodynamical potential is chosen to be the Gibbs free energy which of our simple one component system is $G = N\mu(p, T)$ and the phase transition line is the solution of the equation

$$\mu_1(p, T) = \mu_2(p, T). \quad (180)$$

We seek the slope of the phase boundary and for this end we calculate the derivative of this equation along the phase boundary using the temperature as a parameter of the boundary curve,

$$\frac{\partial \mu_1}{\partial T} \Big|_P + \frac{\partial \mu_1}{\partial P} \Big|_T \frac{dp}{dT} = \frac{\partial \mu_2}{\partial T} \Big|_P + \frac{\partial \mu_2}{\partial P} \Big|_T \frac{dp}{dT}. \quad (181)$$

This equation gives the Clausius-Clapeyron equation,

$$\begin{aligned} \frac{dp}{dT} &= \frac{\frac{\partial \mu_1}{\partial T} \Big|_P - \frac{\partial \mu_2}{\partial T} \Big|_P}{\frac{\partial \mu_2}{\partial P} \Big|_T - \frac{\partial \mu_1}{\partial P} \Big|_T} \\ &= \frac{s_1 - s_2}{v_1 - v_2} = \frac{1}{T} \frac{\Delta h}{\Delta v}, \end{aligned} \quad (182)$$

the slope of the transition line in terms of the specific latent heat h and the change of the specific volume $\Delta v = v_2 - v_1$ where the relations

$$\frac{\partial \mu_1}{\partial T} \Big|_P = -\frac{S}{N} = -s, \quad \frac{\partial \mu_1}{\partial P} \Big|_T = \frac{V}{N} = v \quad (183)$$

and

$$\Delta h = \frac{T \Delta S}{N} \quad (184)$$

have been used in the last equation.

The more detailed analysis of the continuous and discontinuous phase transitions will be embarked later, in the framework of the mean-field approximation.

B. Spontaneous symmetry breaking and order parameter

Phase transitions are characterized by a finite or singular response of the system to some infinitesimal, external perturbations and the phase boundary separates regions where the thermodynamical potentials are analytic functions. In some of cases the symmetry properties of the system differ on the two sides of a phase transition. An example is ferromagnetism which can be identified as a finite response of magnetization, $\langle \mathbf{M} \rangle \neq 0$, to an infinitesimally weak external magnetic field, \mathbf{h} , below the Curie point. The Hamiltonian of the ferromagnet is symmetric with respect to spatial rotations and this symmetry prevents the appearance of non-vanishing magnetization because the latter chooses a preferred direction. This kind of symmetry breaking is to be contrasted with the explicit breaking of the symmetry by an external magnetic field which generates magnetization, as well. The difference between the two kinds of magnetisation can be revealed by introducing an external magnetic field and letting its strength to vanish gradually. The magnetization vanishes with the external magnetic field the rotational symmetry is normally recovered in the absence of external field above the Curie point. The magnetisation survives the removal of the external magnetic



FIG. 9: (a): A flexible ruler is shown in its normal state as a horizontal straight line. (b): A certain force F is applied to push the ruler along its direction while its other end is fixed.

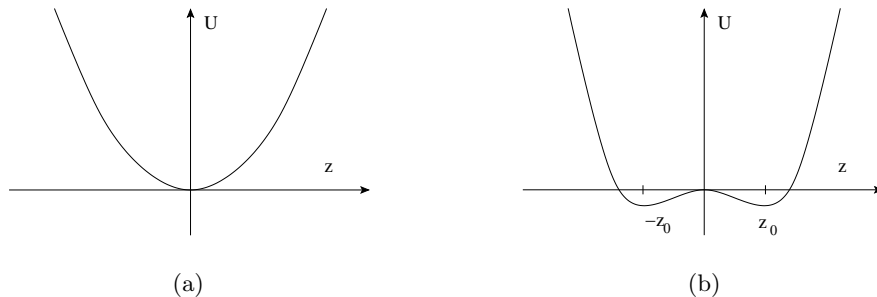


FIG. 10: The internal energy of the ruler (a): in relaxed and (b): stretched state.

field in the ferromagnetic phase. The system is extremely sensitive for the presence of any external breakdown of the rotational symmetry in this phase because an infinitesimal amount of symmetry breaking leaves behind a finite average of a vector.

Let us suppose that the Hamiltonian remains invariant under certain symmetry group. Do all observables reflect this symmetry? It is easy to see what happens in classical mechanics, the planetary orbits around the Sun are not necessarily circular though the Newtonian gravitational field is spherically symmetric. In a similar manner, the eigenstates of the electrons in the Hydrogen atom are not spherically symmetric for non-vanishing angular momentum. But what happens in the "most important" state, in the ground state? When it reflects all symmetries of the Hamiltonian then the symmetries are somehow more completely preserved. Spontaneous symmetry breaking is the phenomenon when the ground state displays a smaller symmetry group than the Hamiltonian. At finite temperature the expectation values of the ground state are replaced by thermal averages. The rotational symmetry is therefore broken in a spontaneous manner by the thermal fluctuations in a ferromagnet below the Curie point. As soon as an infinitesimal amount of fluctuations induces a preferred spatial direction the singular sensitivity of the system, witnessed by the sensitive response to an external field, generates spontaneously a preferred direction develops magnetization along it.

It is usually easy to find a simple diagnostic device for spontaneous symmetry breaking. In fact, it is enough to consider a local quantity, call order parameter, whose non-vanishing values transform in a non-trivial manner under the would be broken symmetry. This is the magnetization in the case of ferromagnetism. The order parameter must have vanishing average in the symmetric phase. The non-vanishing average of the order parameter signals the spontaneous breakdown of the symmetry in question.

A simple demonstration of symmetry breaking can be given by a flexible, plastic ruler. Let us consider a straight ruler as shown in Fig. 9(a). Its dynamics is supposed to be invariant under the reflection $z \rightarrow -z$, hence its internal energy, $U(z)$ is a symmetric function with minimum at $z = 0$ as shown in Fig. 10(a). When a force is applied and the ruler is gently pushed as shown in Fig. 9(b) then the ruler bends. The corresponding energy, shown in Fig. 10(b) has two symmetrical minima at non-vanishing z . How is the minimum of the internal energy is chosen among the two symmetrical position $\pm z_0$? Let us apply the force very carefully, by keeping the ruler at the symmetrical but by now unstable position, $z = 0$. As the force increases the microscopic fluctuations may destabilize this minimum easier. The fluctuations are symmetric, as well but in average only. When a fluctuation happens to be large enough then it pushes the ruler into the valleys, corresponding to its sign. Therefore the choice of the sign of the stable minimum position, $\pm z_0$ is made spontaneously, by random, microscopic fluctuations. The condition of spontaneous symmetry breaking is having symmetrical but non-degenerate minima in the internal energy.

The simplest way to identify a spontaneous symmetry breaking is based on static observations in equilibrium. One usually starts with the static case in equilibrium where the breakdown of the symmetry induced by an explicitly non-symmetrical term with a coefficient g by hand in the Hamiltonian, $H \rightarrow H_{sym} + gH_{asym}$. The dynamics is obviously not symmetrical for $g \neq 0$. If the symmetry is recovered in the limit $g \rightarrow 0$ then the original system, described by $g = 0$ is manifestly symmetrical. When the symmetry is not recovered as $g \rightarrow 0$ then the original system breaks the symmetry spontaneously. This strategy always leads to manifest symmetry when realized in a finite system because

such dynamical systems do not support phase transitions. Therefore, we have to carry out the thermodynamical limit, $V \rightarrow \infty$, too. But the two limits, the restoration of the formal symmetry $g \rightarrow 0$ and the infinitely large system $V \rightarrow \infty$ do not commute. In fact, $\lim_{V \rightarrow \infty} \lim_{g \rightarrow 0}$ produces a symmetric system. To give a chance the dynamics to signal the eventual dynamically driven breakdown of the symmetry we have to perform the thermodynamical limit first and search for possible phase transitions. When the point $g = 0$ falls on a phase boundary then the symmetry is spontaneously broken.

There is another, dynamical way of finding spontaneous symmetry breaking which offers a more detailed picture. Such a signature of symmetry breaking is the slowing down of a collective mode in the thermodynamical limit. The averaging over the phase space of this mode restores the symmetry but the slowing down renders the approximation where this mode is fixed acceptable for any measurement carried out in a finite length of time. Such a subtle dynamical process is coded in the equilibrium ensemble description as a violation of ergodicity. Ergodicity is introduced in Statistical Physics as an assumption which identifies the long time and ensemble averages. Symmetry breaking means the under certain conditions the order parameter which is bounded to be canceled by the summation in the partition function becomes non-vanishing. This corresponds to a restriction of the domain of integration or summation in the partition function. For instance, in the case of ferromagnetism the summation over order local magnetization configurations $\mathbf{M}(\mathbf{x})$ is restricted into the functional space

$$\int d^3x \mathbf{n} \mathbf{M}(\mathbf{x}) > 0 \quad (185)$$

where \mathbf{n} is arbitrarily chosen unit vector.

There is an important feature of system where a continuous symmetry is broken spontaneously by a non-vanishing expectation value for a local order parameter $\phi(\mathbf{x})$ which is supposed to be a local parameter of the symmetry transformation in question, called Goldstone mode. Consider a gas of molecules with trajectories $\xi(t, \mathbf{x}_0)$ where \mathbf{x}_0 is the position of the molecule at $t = 0$. A possible order parameter, monitoring translation invariance in direction \mathbf{n} is $\phi(t, \mathbf{x}) = \mathbf{n} \xi(t, \mathbf{x})$. In general, the local order parameter of a continuous symmetry group is the value of a symmetry transformation, translations in this case, performed locally. The important point is that for the homogeneous, \mathbf{x} -independent transformations belong to symmetry and preserve the energy of the system.

Let us now find the energy of infinitesimal fluctuations of the parameter. Due to translation invariance the normal modes are the Fourier transform of $\phi(\mathbf{x})$, $\tilde{\phi}(\mathbf{k})$, \mathbf{k} being the wave vector and the energy of the Goldstone modes is a regular function, $E(\mathbf{k})$ which should respect the space-time symmetries of the system. We know that homogeneous fluctuations with $\mathbf{k} = 0$ cost no energy, $E(0) = 0$, hence

$$E(\mathbf{k}) = c_2 \mathbf{k}^2 + \mathcal{O}(\mathbf{k}^4), \quad (186)$$

due to rotational invariance. Thus the excitation spectrum of the Goldstone modes starts without gap, infinitesimal energy is enough to excite a large number of modes. According Special Relativity the energy of a particle of momentum \mathbf{p} is $E = c\sqrt{(mc)^2 + \mathbf{p}^2}$. Therefore the energy spectrum without gap must be

$$E(\mathbf{k}) = c|\mathbf{k}| + \mathcal{O}(\mathbf{k}^2), \quad (187)$$

because \mathbf{p} and \mathbf{k} should be proportional due to rotational invariance and we can associate the Goldstone modes with particles. This is a simplified and special case of Goldstone theorem stating that there is a massless particle mode for each spontaneous broken continuous symmetry. Phonons are gapless due the spontaneous breakdown of the continuous translation symmetry by the crystal. One can show that photons are Goldstone particles, as well, they signal the spontaneous breakdown of a four-dimensional subgroup of the gauge symmetry of electrodynamics.

C. Singularities of the partition function

Let us consider a system of hard sphere particles interacting with an attractive, finite range potential and denote its canonical partition function by $Z_N(V)$. The number of particles is clearly bounded by $N < M = V/V_0$ where V_0 is the volume of a particle. We may introduce the grand canonical partition function,

$$Z(z, V) = \sum_{N=1}^M z^N Z_N(V). \quad (188)$$

The first theorem proven by Lee and Yang for the hard sphere model is that the partition function converges in the thermodynamical limit for each value of the fugacity z ,

$$\lim_{V \rightarrow \infty} \frac{1}{V} \ln Z(z, V) = F(z) \quad (189)$$

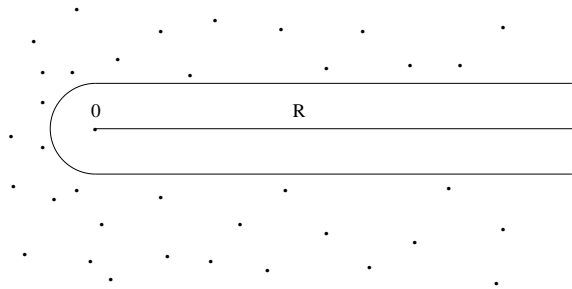


FIG. 11: A region R on the complex fugacity plane where the partition function is analytic. The dots indicate the zeros of the partition function.

to a non-decreasing function. Furthermore, this limit is independent of the shape of the volume as long as its surface is not increasing faster than $V^{2/3}$.

This first theorem assures the existence of the thermodynamical potential, F , for the infinite system and leaves open the issue of phase transitions. In fact, let us follow carefully how the situation changes as the thermodynamic limit is reached. For a fixed, finite volume the parametric form of the equation of state is

$$\frac{p}{T} = \frac{1}{V} \ln Z(z, V), \quad n = \frac{1}{V} z \frac{\partial}{\partial z} \ln Z(z, V). \quad (190)$$

Being a finite system, the partition function is an analytic function of its parameters, the volume in our case and no phase transition can occur. For the infinite system we have

$$\frac{p}{T} = \lim_{V \rightarrow \infty} \frac{1}{V} \ln Z(z, V), \quad n = \lim_{V \rightarrow \infty} \frac{1}{V} z \frac{\partial}{\partial z} \ln Z(z, V). \quad (191)$$

If the analytic property of the right hand sides is preserved in the limit then no phase transition can occur. What is the mathematical condition to preserve the analyticity during a limit which exists point by point? The uniform limit of analytical function is analytic and the derivative converge as well if the convergence is uniform. The difference between point-wise and uniform convergence is that the size of the interval in which the value of the function must be found for large enough volume for the convergence is dependent or independent of the point at which the convergence is tested, respectively. For example, the function $f_n(x) = x^n$ converges point-wise in the interval $0 \leq x \leq 1$ but not uniformly as $n \rightarrow \infty$. Therefore, as long as the thermodynamic limit is uniform then both the pressure and the density remain analytic function and phase transition is excluded.

The second Lee-Yang theorem states that the partition function converges uniformly in any region of the complex fugacity plane which contains no zeros of the partition function. Note that the partition function is strictly positive for physically acceptable, ie. real and positive values of the fugacity thus the zeros can not be found on this semi-axis. Consider now a region including a part of the positive fugacity axis, as shown in Fig. 11. The phase transitions are excluded in the region R according to the second theorem. But in the case shown on Fig. 12 the zeros approaching z_0 cut the positive semi-axis of the fugacity into two parts and there are two different analytic functions, one in R_1 and the other one in R_2 .

Another result interesting result of Lee and Yang concerns the lattice gas model where particles can be found on an infinite spatial lattice and their interaction potential is the sum of pair potentials. For each pair the potential is infinite if the two particles are on the same site and negative otherwise. The zeros of the grand canonical partition function lie on the unit sphere of the complex fugacity plane,

$$Z = \frac{\prod_n (z - e^{-i\theta_n(T)})}{\prod_n (-e^{-i\theta_n(T)})}. \quad (192)$$

Let us introduce the distribution function of the zeros, $\rho(\theta)$, by

$$\frac{1}{V} \sum_n f(\theta_n) = \int_0^{2\pi} d\theta \rho(\theta) f(\theta). \quad (193)$$

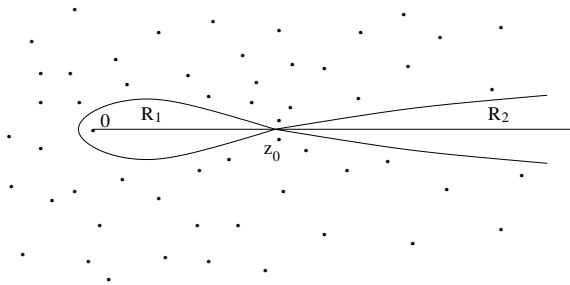


FIG. 12: The partition function realizes two different analytic functions in regions R_1 and R_2 which are joined continuously at $z = z_0$.

The physical partition function is real, therefore $\rho(-\theta) = \rho(\theta)$. and write the logarithm of the partition function as

$$\begin{aligned} \frac{p}{T} &= \int_0^\pi d\theta \rho(\theta) \ln(z - e^{-i\theta})(z - e^{i\theta}) \\ &= \int_0^\pi d\theta \rho(\theta) \ln(1 - 2z \cos \theta + z^2) \end{aligned} \quad (194)$$

and

$$\begin{aligned} n &= 2z \int_0^\pi d\theta \rho(\theta) \frac{z - \cos \theta}{1 - 2z \cos \theta + z^2} \\ &= 2z \int_0^\pi d\theta \rho(\theta) \frac{z - \cos \theta}{(1 - z)^2 + 2(1 - z \cos \theta)}. \end{aligned} \quad (195)$$

The only singularity can occur at $z = 1$ and there is no phase transition when $\rho(0) = 0$.

IV. SPIN MODELS ON LATTICE

We have contradictory goals in physics. On the one hand, we want to understand the basic rules of physical phenomena and this is possible if we can identify few simple enough basic laws. On the other hand, the bewildering complexity of the world around us oblige us to use the simple laws in more and more complex situations and to describe complexity in terms of simple concepts. A pragmatic compromise, developed in the last decades, is the strategy of effective theories. We give up, at the time being, the hunt for the ultimate laws in physics and look for limited theories only, which are supposed to be valid in a given range of (length, time or mass) scale. The degrees of freedom are certainly not elementary but neither very rough, their structure reflects our need, the scale regime where we intend to use them. The central assumption in this enterprise is the hope that once the appropriate (effective) degrees of freedom are found then the dynamics should have "islands" of simplicity, there ought to have family of phenomena governed by universal and simple rules.

A. Effective theories

Let us take a piece of ferromagnet as an example. It consists of a large number of atoms and electrons coupled into a solid. At a very fine resolution we may see the nuclei within the atoms and its more microscopic constituents and the dynamics is based on the Standard Model of High Energy Physics. But from at the energy scale which characterizes solid state physics these degrees of freedom can be considered frozen. What is excited at the scales of solid state physics are mainly the ions, few outer electrons of the atoms and phonons. The effective theory of the solid can be based on certain local excitations of the ion core, on the electrons in conducting band and phonons, say as far as magnetism is concerned. These degrees of freedom are "dressed" by the more elementary interactions and their dynamics can be quite complicated. The transition of the ions among different conformations or the polarization due to an electron can be rather complex issues. But there are important phenomena, mainly second order phase transitions, which show a remarkable simplicity and universality in these complex systems. These offer the hope

of finding simple enough rules for well chosen degrees of freedom and a wide range of phenomena, an assumption which has already been tested in a detailed manner by the renormalization group method. We shall follow now a the construction of a simple effective theory in the context of ferromagnetism.

The excitations of a solid can be elementary, such as the motion of a single particle or collective where a large number of particles contribute to the excitation in a coherent manner. Naturally these are the end points of a spectrum of possibilities, even the elementary excitations have some collective components due to the polarization effects. The low energy collective excitations of a crystal which determine the long range correlations and the phase structure of the system can be approximated by keeping the particles fixed at lattice sites and retaining the short range, mainly exchange interactions between the particles only. One can construct quantum or classical spin models on the lattice in this manner.

B. Spin models

The first and simplest spin model was constructed by Ising for the ferromagnetic transition. One assumes spin 1/2 particles sitting on cubic lattice and approximates the total energy by the sum of exchange interactions for nearest neighbors. The classical energy in the presence if an external magnetic field coupled to the spins is

$$\beta H = - \sum_{\langle i,j \rangle} J_{i,j} s_i s_j - \sum_i h_i s_i \quad (196)$$

where $s_i = \pm 1$ is called the spin variable at the lattice site i . The Helmholtz free-energy, $A(T)$ is given by the partition function

$$e^{-\beta A} = \sum_{\{s_i\}} e^{-\beta H}. \quad (197)$$

What is clear without any calculation is that the positive or negative values of J encourage parallel or anti-parallel ordering of the spins.

In a realistic solid with some disorder these parameters are inhomogeneous in an unknown and uncontrollable manner and the calculation of the free-energy is specially difficult. But it is a natural simplification to ignore the inhomogeneities and the interaction among far separated spins which amounts to the use of the Hamiltonian

$$\beta H = -J \sum_{\langle i,j \rangle} s_i s_j - h \sum_i s_i \quad (198)$$

where the summation in the first term is over the nearest neighbor sites.

It is instructive to consider few different physical realization of the Ising model. The simplest is the lattice gas model where hard sphere particles can occupy the lattice sites. Their hard core allows at most one particle per site and their short range interactions is characterized by the homogeneous parameter J . The grand canonical partition function is

$$\begin{aligned} Z &= \sum_{\{s_i\}} e^{J \sum_{\langle i,j \rangle} \frac{1+s_i}{2} \frac{1+s_j}{2} + \mu \sum_i \frac{1+s_i}{2}} \\ &= \text{const} \cdot \sum_{\{s_i\}} e^{\frac{J}{4} \sum_{\langle i,j \rangle} s_i s_j + \frac{Jd+\mu}{2} \sum_i s_i} \end{aligned} \quad (199)$$

in dimension d . Another realization is the binary alloy where the elementary cell has two different low energy state and the two values of s_i labels these two states at the site i . Finally, the most natural application is for the description of the magnetic properties of local spin-1/2 spin variables distributed on the lattice. In this case the coefficients J and h represent the energy scale of the exchange interaction and the local magnetization, respectively.

The simplest generalization of the Ising model from spin 1/2 to vector spin S variables is based on the Hamiltonian

$$\beta H = -J \sum_{\langle i,j \rangle} \vec{s}_i \vec{s}_j - \vec{h} \sum_i \vec{s}_i \quad (200)$$

where the vectors are of dimension $2S + 1$ and \vec{s} is of unit length, $\vec{s}_i^2 = 1$. The partition function is

$$Z = \prod_i \int d^{2S+1} s_j \delta(\vec{s}_i^2 - 1) e^{-\beta H}. \quad (201)$$

The case of $S = 1$ is called Heisenberg model and is used to describe the magnetic properties of spin one magnetic moments. The vector spin model which is formally $S = 1/2$ is called $X - Y$ model and the parametrization $\vec{s} = (\cos \theta, \sin \theta)$ its partition function is

$$Z = \left(\prod_k \int d\theta_k \right) e^{J \sum_{\langle i,j \rangle} \cos(\theta_i - \theta_j) + h \sum_i \cos \theta_i}. \quad (202)$$

This model is particularly useful to describe superfluids or Bose condensates.

Another class of generalization of the Ising model is the family of Potts models. The q -state Potts model has basic variable s_i which can take q different values, say $s_j \in \{1, \dots, q\}$ and the Hamiltonian is

$$\beta H = -J \sum_{\langle i,j \rangle} \delta_{s_i, s_j}. \quad (203)$$

Finally one should mention the quantum spin models, too. They have a quantum spin variable, $[s_j, s_k] = i\epsilon_{jkl}s_l$ attached at each lattice site and the Hamiltonian is

$$\frac{H}{T} = -J \sum_{\langle i,j \rangle} \vec{s}_i \vec{s}_j - \vec{h} \sum_i \vec{s}_i. \quad (204)$$

The partition function is

$$Z = \text{Tr} e^{-\beta H}. \quad (205)$$

The Hamiltonian preserves the spin S of the state at each site therefore one can talk about spin S quantum spin models where the site has state with a given spin. Notice that for high spin, $S \rightarrow \infty$ the expectation value of the right hand side of the canonical commutator is $\mathcal{O}(S)$ and is negligible compared to the product of two spin variable which yields $\mathcal{O}(S^2)$ numbers. Thus the spin dynamics becomes classical and the classical vector spin models are applicable.

C. Ising model in one dimension

It is easy to calculate the partition function for the one dimensional Ising model, where the spins are placed at the sites $i \in \{1, \dots, N\}$ with periodic boundary conditions, $s_{N+1} = s_1$,

$$\begin{aligned} Z &= \sum_{\{s_i\}} e^{J \sum_{i=1}^N s_{i+1} s_i + h \sum_{i=1}^N s_i} \\ &= \sum_{\{s_i\}} e^{J \sum_{i=1}^N s_{i+1} s_i + \frac{h}{2} \sum_{i=1}^N (s_{i+1} + s_i)}. \end{aligned} \quad (206)$$

The spin variables at the end points have $h/2$ as external magnetic field, a modification of the original Ising partition function which can be neglected in the thermodynamic limit. We introduce the transfer matrix T , a 2×2 matrix

$$\langle s|T|s' \rangle = e^{J s s' + \frac{h}{2}(s+s')}, \quad (207)$$

that is

$$T = \begin{pmatrix} e^{J+h} & e^{-J} \\ e^{-J} & e^{J-h} \end{pmatrix}. \quad (208)$$

It allows us to write the partition function as

$$Z = \text{tr} T^N. \quad (209)$$

The power of the transfer matrix formalism is the easy calculation of the trace in the basis where it is diagonal. Its eigenvectors, λ_{\pm} satisfy the characteristic equation

$$\begin{aligned} \det \begin{pmatrix} e^{J+h} - \lambda & e^{-J} \\ e^{-J} & e^{J-h} - \lambda \end{pmatrix} &= (e^{J+h} - \lambda)(e^{J-h} - \lambda) - e^{-2J} \\ &= \lambda^2 - \lambda(e^{J-h} + e^{J+h}) + e^{2J} - e^{-2J} \\ &= 0, \end{aligned} \quad (210)$$

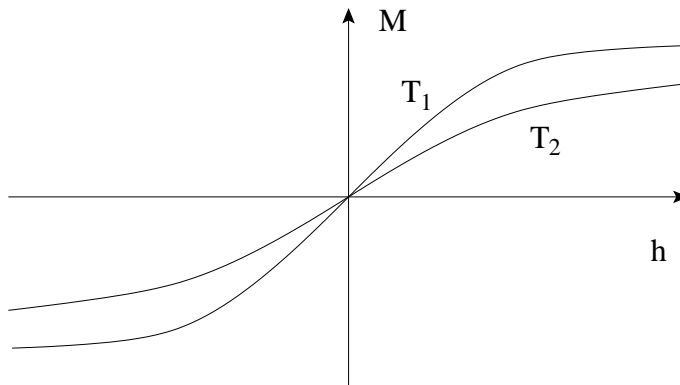


FIG. 13: Magnetization of the one dimensional Ising model for $T_1 < T_2$.

therefore,

$$\begin{aligned}\lambda_{\pm} &= e^J (\cosh h \pm \sqrt{\cosh^2 h - 1 + e^{-4J}}) \\ &= e^J (\cosh h \pm \sqrt{\sinh^2 h + e^{-4J}}),\end{aligned}\quad (211)$$

and we have

$$\begin{aligned}Z &= \lambda_+^N + \lambda_-^N \\ &\approx \langle f|+\rangle \langle +|i\rangle \lambda_+^{N-1}\end{aligned}\quad (212)$$

in the thermodynamical limit because $\lambda_+ > \lambda_-$. The Helmholtz free energy

$$\lim_{N \rightarrow \infty} \frac{\beta A}{N} = - \lim_{N \rightarrow \infty} \frac{\ln Z}{N} = - \ln \lambda_+ = -J - \ln(\cosh h + \sqrt{\sinh^2 h + e^{-4J}})\quad (213)$$

gives the magnetization per spin

$$\begin{aligned}M &= -\frac{1}{N} \frac{\partial \beta A}{\partial h} \\ &= \frac{\sinh h + \frac{\cosh h \sinh h}{\sqrt{\sinh^2 h + e^{-4J}}}}{\cosh h + \sqrt{\sinh^2 h + e^{-4J}}} \\ &= \frac{\sinh h}{\sqrt{\sinh^2 h + e^{-4J}}},\end{aligned}\quad (214)$$

shown qualitatively in Fig. 13. Note the absence of singularity or phase transition.

The phase transition, the appearance of spontaneous magnetization would show up as a singularity at $h = 0$ where the magnetization curve would acquire infinitely large slope. In other words, we would have $M_0 = \lim_{h \rightarrow 0^+} M(h) = -\lim_{h \rightarrow 0^-} M(h) \neq 0$ in the absence of external magnetic field h . The formal symmetry of the Hamiltonian, corresponding to the change of sign of the magnetic field, $s_i \rightarrow -s_i$ and $h \rightarrow -h$ would be broken in this case.

It is easy to understand the absence of spontaneous magnetization or spontaneous symmetry breaking in the one dimensional Ising model. Let us imagine a spin configuration, $\{s_i\}$ of the model. We shall call the regions with the same spin orientation domains. The two neighboring domains are separated by a pair of spins with opposite directions. If we fix one spin in the lattice the remaining spins can be reconstructed if we know the location of the domain walls. Thus we can imagine the summation over the spin configuration as a summation over the location of domain walls. The energy of a domain wall is $2\epsilon = 2J/\beta$ and its entropy is $k_B \ln(N-1)$. Thus its free energy,

$$A_{\text{dw}} = E - TS = 2\epsilon - k_B T \ln(N-1),\quad (215)$$

calculated by ignoring the presence of other domain walls, tends to $-\infty$ in the thermodynamical limit. Hence the domain walls dominate the system for non-vanishing temperature and prevent the emergence of an ordered phase.

D. High temperature expansion for the Ising model

It is easy to establish a high temperature expansion in arbitrary dimensions. Let us start by calculating the partition function

$$Z = \sum_{\{s\}} e^{J \sum_{\langle i,j \rangle} s_i s_j} \quad (216)$$

for small J by expanding the exponential functions,

$$Z = \sum_{n=1}^{\infty} \frac{J^n}{n!} \sum_{\{s\}} \left(\sum_{\langle i,j \rangle} s_i s_j \right)^n. \quad (217)$$

Due to the identity $\sum_{s=\pm 1} s^{2k+1} = 0$ the non-vanishing $\mathcal{O}(J^\ell)$ contributions come from ℓ pairs of spins placed on even number par site on closed loops. The $\mathcal{O}(J^2)$ leading order comes from $(s_i s_j)^2$, a term belonging to a link on the lattice. The site i can be chosen anywhere on the lattice therefore the number of such contributions is $\mathcal{O}(N)$. The $\mathcal{O}(J^4)$ contributions contain $\mathcal{O}(N)$ and $\mathcal{O}(N^2)$ terms. The latter comes two links, both contributing by a factor $(s_i s_j)^2$. They can be chosen independently of each other except when the two links touch each other or are separated by one lattice spacing only,

$$\begin{aligned} Z &= 2^N \left[1 + \frac{J^2}{2!} dN + \frac{J^4}{4!} \frac{4!}{2^2} (dN)^2 \left(1 + \mathcal{O}\left(\frac{1}{N}\right) \right) + \mathcal{O}(J^6) \right] \\ &= e^{N[\ln 2 + \frac{1}{2} dJ^2 + \mathcal{O}(\frac{1}{N}) + \mathcal{O}(J^4)]} \end{aligned} \quad (218)$$

in d -dimensions. The linked cluster theorem assures that the logarithm of the partition function remains extensive and all contributions proportional to the higher powers of the volume cancels.

One can calculate in this scheme more illuminating averages, for example the correlation function

$$\langle s_x s_y \rangle = \frac{\sum_{\{s\}} e^{J \sum_{\langle i,j \rangle} s_i s_j} s_x s_y}{\sum_{\{s\}} e^{J \sum_{\langle i,j \rangle} s_i s_j}}. \quad (219)$$

This function displays the way a pair of spins becomes less correlated when their separation is increased. In fact, $s_x s_y = 1$ for completely correlated spins, $s_x = s_y$, and one expects $\langle s_x s_y \rangle \approx 1$ for $x \approx y$. For two, statistically independent spin we have $\langle s_x s_y \rangle = 0$. Clusterisation requires the asymptotics

$$\langle s_x s_y \rangle \rightarrow \langle s_x \rangle \langle s_y \rangle = \langle s \rangle^2 \quad (220)$$

as $|x - y| \rightarrow \infty$.

The expansion of the numerator involves spins placed along a line connecting the points x and y and on closed loops. These latter contributions produce a multiplicative factor which cancels against the denominator. (The overlapping open and closed line cases can be ignored in the thermodynamical limit.) We find

$$\langle s_x s_y \rangle = 2(2J)^{|x-y|} (1 + \mathcal{O}(J^2)). \quad (221)$$

This result, together with clusterisation (220) implies $\langle s \rangle = 0$, the absence of ordered phase. The free energy and the correlation functions are analytic in the temperature when the high temperature expansion is truncated at any finite order because they involve loops with bounded perimeter which test correlations up to finite distances only. One can show that the high temperature expansion has a finite radius of convergence in J . This result proves that the Ising model is in the disordered phase for sufficiently small J in any dimensions. We shown next that in two dimensions where one can find exact results easier there is an ordered, ferromagnetic phase at sufficiently large J .

E. Ordered phase in the Ising model in two dimension dimensions

The phase transition is detected by the increased sensitivity of the magnetization on the boundary conditions. In order to test this sensitivity we set the spin to $+$ on the boundary. This boundary condition brakes the spin up-spin down symmetry and the model has a symmetry broken phase if the average magnetization is non-vanishing in the

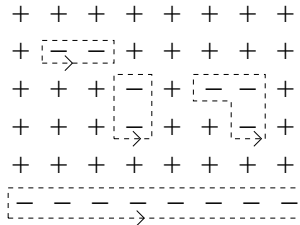


FIG. 14: Domain walls in the two dimensional Ising model.

thermodynamic limit. To show that the magnetization is non-vanishing for sufficiently low temperature we give an upper bound for the ratio of the average number of spin $\langle N_- \rangle$ with value -1 over the total number of spin variables N which is less than $1/2$, implying $\langle s \rangle = \langle N_+ - N_- \rangle / N = \langle N - 2N_- \rangle / N = 1 - 2\langle N_- \rangle / N > 0$.

Following the intuitive picture of the one-dimensional Ising model where the domain walls were useful to clarify the fate of the ferromagnetic phase we shall use domain structure here, as well, to identify the spin configurations. Let us define the domain walls as rectangles traversing the middle of the bonds with opposite spins, as shown in Fig. 14. Due to the periodic boundary conditions the domain walls are closed curves, their orientation is defined by having the $-$ spin at the left side. In case of ambiguities the domain wall line turns to left. The domain walls do not cross. Since the spins are all $+1$ on the boundary the domain walls identify all spins within the lattice. Let us consider domains with a given perimeter ℓ . There are finite number of such domains on our finite lattice, they will be distinguished from each other by means of an index $j = 1, \dots, m(\ell)$.

We establish now several inequalities, the last being a lower bound for $\langle s \rangle$.

1. The maximal area of a rectangular for a given length is realized by the square. Thus the area of the domain (ℓ, j) is not bigger than $\ell^2/16$.
2. An upper bound for $m(\ell)$, the number of self avoiding closed loops on the lattice with length ℓ , can be found by counting the number of paths of length ℓ . There are N possibility to place the initial point of the path. Then we have 4 possibility to choose its first link. Each further new link can be placed on three different manner at the end of a path by avoiding to step back along the same path. Therefore the number of lines of length ℓ is $N \cdot 4 \cdot 3^{\ell-1}$, yielding the inequality

$$m(\ell) \leq N \cdot 4 \cdot 3^{\ell-1}. \quad (222)$$

3. Let us introduce the characteristic function of the domain (ℓ, j) ,

$$\chi_{\{s\}}(\ell, j) = \begin{cases} 1 & \text{the domain } (\ell, j) \text{ occurs in } \{s\} \\ 0 & \text{otherwise} \end{cases} \quad (223)$$

on the spin configuration space. Since the spin is $+$ on the boundary every $-$ spin is in a domain, therefore N_- satisfies the inequality

$$N_- \leq \sum_{\ell} \frac{\ell^2}{16} \sum_{j=1}^{m(\ell)} \chi_{\{s\}}(\ell, j). \quad (224)$$

4. Let us find an upper bound for the average

$$\langle \chi_{\{s\}}(\ell, j) \rangle = \frac{\sum'_{\{s\}} e^{-\beta H[\{s\}]} e^{-\beta H[\{s\}_{(\ell, j)}]}}{\sum_{\{s\}} e^{-\beta H[\{s\}]}} \quad (225)$$

where the prime indicates the that the sum is carried over the spin configuration where the domain (ℓ, j) occurs. We introduce the spin configuration $\{s\}_{(\ell, j)}$ which is obtained from $\{s\}$ by flipping each spin inside the domain (ℓ, j) . If the domain occurs in $\{s\}$ then it is absent in $\{s\}_{(\ell, j)}$. The energy increase due to a link at the domain wall is $2J$, thus we have

$$\beta H[\{s\}] = \beta H[\{s\}_{(\ell, j)}] + 2J\ell \quad (226)$$

for configuration containing the domain (ℓ, j) . An upper bound for $\langle \chi_{\{s\}}(\ell, j) \rangle$ can be found by restricting the sum in the denominator for the flipped version of configurations entering in the numerator,

$$\langle \chi_{\{s\}}(\ell, j) \rangle \leq \frac{\sum'_{\{s\}} e^{-\beta H[\{s\}]}}{\sum'_{\{s\}} e^{-\beta H[\{s\}(\ell, j)]}} = e^{-2J\ell}. \quad (227)$$

In fact, the partition function in the denominator is the sum of positive terms which becomes smaller when some of the contributions are omitted.

5. The bound for the magnetization arises finally as

$$\begin{aligned} \frac{\langle N_- \rangle}{N} &\leq \sum_{\ell} \frac{\ell^2}{16N} \sum_{j=1}^{m(\ell)} \langle \chi_{\{s\}}(\ell, j) \rangle \\ &\leq \frac{1}{12} \sum_{\ell=2}^{\infty} (2\ell)^2 3^{2\ell} e^{-4J\ell} \\ &= \frac{z^2}{3(1-z)} \left(1 - \frac{3}{4}z + \frac{1}{4}z^2 \right), \end{aligned} \quad (228)$$

with $z = 9e^{-2J}$ and it is less than $1/2$ for sufficiently large J .

The high temperature expansion which has finite convergence radius predicts a phase which respects the symmetry $s_i \rightarrow -s_i$ and produces $\langle s_i \rangle = 0$ and $\langle N_- \rangle / N = 1/2$. The inequality obtained above proves that the magnetization is non-vanishing for sufficiently low temperature, $\langle s_i \rangle \neq 0$, and the spin-flip symmetry is broken. A symmetry can not break gradually and there must be a well defined critical temperature where it happens. The value of the critical temperature is known exactly for $d = 2$ and can be determined by numerical simulations in higher dimensions.

V. CRITICAL PHENOMENA

The partition function always remains a continuous function of the thermodynamical variables and the microscopic parameters if the dynamics but its derivatives develop singularities at phase transitions. A phase transition is of first order or discontinuous when some first derivatives of the thermodynamic potential and certain thermal averages develop a jump. In higher order, or continuous phase transition higher order derivative become singular. The distinguishing feature of these phase transitions, called critical points, is that the system supports large amplitude fluctuations with strong correlations at well separated points in space. The existence of correlations at large separation indicates that the correlation length reaches arbitrarily large values in the vicinity of a critical point. The amplitude of the long range fluctuations are large because the energy of a fluctuation mode with a given amplitude tends to become smaller with its wave vector.

Let us consider a ferromagnet with Helmholtz free energy $A(T, h)$, described by the Ising model,

$$e^{-\beta A(T, h)} = \sum_{\{s\}} e^{-\beta(H[s] + h \sum_x s_x)}. \quad (229)$$

First let us show that the amount of correlation in the energy is measured by the specific heat, c , defined by

$$Vc = T^2 \frac{\partial^2 G(T, 0)}{\partial T^2} = 2\beta \frac{\partial G(T, 0)}{\partial \beta} + \beta^2 \frac{\partial^2 G(T, 0)}{\partial \beta^2}. \quad (230)$$

The last term,

$$\begin{aligned} \frac{\partial^2 \ln Z}{\partial \beta^2} &= \frac{\partial}{\partial \beta} \frac{1}{Z} \frac{\partial Z}{\partial \beta} \\ &= -\frac{\partial}{\partial \beta} \frac{\sum_{\{s\}} H[s] e^{-\beta H[s]}}{\sum_{\{s\}} e^{-\beta H[s]}} \\ &= \frac{\sum_{\{s\}} H^2[s] e^{-\beta H[s]}}{\sum_{\{s\}} e^{-\beta H[s]}} - \left(\frac{\sum_{\{s\}} H[s] e^{-\beta H[s]}}{\sum_{\{s\}} e^{-\beta H[s]}} \right)^2 \\ &= \langle H^2 \rangle - \langle H \rangle^2 = \langle (H - \langle H \rangle)^2 \rangle, \end{aligned} \quad (231)$$

calculated at $h = 0$ gives the fluctuation of the energy and becomes singular at the critical point. Since the contribution of a spin to the energy is bounded, large fluctuations imply correlations among a large number of spin.

The critical phenomena display the following surprising properties:

1. **Critical exponents:** It was found that the singularities, characterising critical phenomas are of power singularity. Let us consider the approach of the critical point, eg. the Curie temperature in terms of the dimensionless reduced temperature, $t = (T - T_c)/T_c$. The divergence which develops at the critical point is usually a power singularity of the reduced temperature. The power of the singularity, called critical exponent, characterizes the phase transition. Few critical exponents, identified experimentally already in the early stage of developments in critical phenomena are coming from the diverging heat capacity,

$$c \approx |t|^{-\alpha}, \quad (232)$$

the singularity of the order parameter,

$$M = -\frac{\partial G(T, 0)}{\partial h} \approx |t|^\beta, \quad (t < 0), \quad (233)$$

and the diverging susceptibility,

$$\chi = \frac{1}{V} \frac{\partial M}{\partial h} \approx |t|^{-\gamma}, \quad (t < 0). \quad (234)$$

Other singularities can be observed, too, such as the equation of state just at the critical point,

$$M \approx \text{sign}(h)|h|^{1/\delta}, \quad (t = 0). \quad (235)$$

The approximation in these equations consists of ignoring less singular functions, such as polynomials or power singularities with lower powers.

2. **Universality:** The critical exponents are universal, ie. are independent of most of the microscopic details of the system. The universality class, systems with identical critical exponents are characterised by some generat features, like the space dimensions, the number of order parameters, the symmetry becoming broken spontaneously.
3. **Hyperscaling relations:** The critical exponents satisfy certain simple relations.

A. Correlation length

Some of these remarkable features, namely the scaling relations can be understood in simple terms. Let us start with the definition of the correlation length by considering the correlation function,

$$C(\mathbf{x} - \mathbf{y}) = \langle \Phi(\mathbf{x})\Phi(\mathbf{y}) \rangle - \langle \Phi(\mathbf{x}) \rangle \langle \Phi(\mathbf{y}) \rangle \quad (236)$$

of a local order parameter $\Phi(\mathbf{x})$ in a homogeneous system. The disconnected part, the second term is subtracted and the clusterization property of a stable phase imposes the limit $\lim_{|\mathbf{x}-\mathbf{y}| \rightarrow \infty} C(\mathbf{x} - \mathbf{y}) = 0$. It is advantageous to consider the Fourier transform of the correlation function,

$$\tilde{C}(\mathbf{k}) = \int d^3x e^{-i\mathbf{k}\mathbf{x}} C(\mathbf{x}), \quad (237)$$

which is a regular function at $\mathbf{k} = 0$ for non-critical system. Rotational and spatial inversion symmetry yield the form

$$\tilde{C}(\mathbf{k}) = a + b\mathbf{k}^2 + \mathcal{O}(\mathbf{k}^4). \quad (238)$$

We have to improve this form in the vicinity of a critical point. The reason is that the susceptibility

$$\begin{aligned} V\chi &= \frac{\partial^2 \ln Z}{\partial h^2} = \frac{\sum_{\{s\}} (\sum_x s_x)^2 e^{-\beta(H[s] + h \sum_x s_x)}}{\sum_{\{s\}} e^{-\beta(H[s] + h \sum_x s_x)}} - \left(\frac{\sum_{\{s\}} \sum_x s_x e^{-\beta(H[s] + h \sum_x s_x)}}{\sum_{\{s\}} e^{-\beta(H[s] + h \sum_x s_x)}} \right)^2 \\ &= \langle (\sum_x s_x)^2 \rangle - \langle \sum_x s_x \rangle^2 = \langle (\sum_x s_x - \langle \sum_x s_x \rangle)^2 \rangle, \end{aligned} \quad (239)$$

of a homogeneous system,

$$\begin{aligned}
\chi &= \frac{1}{V} \left[\left\langle \left(\int d^3x \Phi(\mathbf{x}) \right)^2 \right\rangle - \left(\left\langle \int d^3x \Phi(\mathbf{x}) \right\rangle \right)^2 \right] \\
&= \frac{1}{V} \left[\int d^3x d^3y (\langle \Phi(\mathbf{x}) \Phi(\mathbf{y}) \rangle - \langle \Phi(\mathbf{x}) \rangle \langle \Phi(\mathbf{y}) \rangle) \right] \\
&= \frac{1}{V} \left[\int d^3x d^3y (\langle \Phi(\mathbf{x} + \mathbf{y}) \Phi(\mathbf{x}) \rangle - \langle \Phi(\mathbf{x} + \mathbf{y}) \rangle \langle \Phi(\mathbf{x}) \rangle) \right] \\
&= \int d^3y C(\mathbf{y}) \\
&= \tilde{C}(\mathbf{0}),
\end{aligned} \tag{240}$$

is diverging in that region. Such kinds of singularities originate from the thermodynamical rather than \mathbf{k} which is our diagnostic parameter only. Thus we use the Ornstein-Zernike form,

$$\tilde{C}(\mathbf{k}) = \frac{1}{r + z\mathbf{k}^2 + \mathcal{O}(\mathbf{k}^4)} \tag{241}$$

which has the advantage that it diverges at $\mathbf{k} = 0$ when $r \rightarrow 0$. This form will be supported by the Landau-Ginzburg effective theory for the critical point, introduced below. The Fourier transform is supposed to reach its peak at vanishing wave vector in a monotonous manner, hence $\text{sign}(r) = \text{sign}(a)$. The susceptibility, the second moment of a probability distribution function is always non-negative therefore we have $r, a \geq 0$. The correlation function of the Ornstein-Zernike form is

$$\begin{aligned}
C(\mathbf{x}) &= \int \frac{d^3k}{(2\pi)^3} \frac{e^{i\mathbf{k}\mathbf{x}}}{r + z\mathbf{k}^2} \\
&= \frac{1}{(2\pi)^2} \int_0^\infty dk k^2 \int_{-1}^1 d(\cos\theta) \frac{e^{ik|\mathbf{x}|\cos\theta}}{r + zk^2} \\
&= \frac{1}{(2\pi)^2 i|\mathbf{x}|} \int_0^\infty dk k \frac{e^{ik|\mathbf{x}|} - e^{-ik|\mathbf{x}|}}{r + zk^2} \\
&= \frac{1}{(2\pi)^2 iz|\mathbf{x}|} \int_{-\infty}^\infty dk k \frac{e^{ik|\mathbf{x}|}}{(k + i\xi^{-1})(k - i\xi^{-1})},
\end{aligned} \tag{242}$$

where $\xi = \sqrt{z/r}$. The integral can be calculated by means of the residuum theorem when the contour of integration is closed along the half sphere of the upper half plane, yielding

$$C(\mathbf{x}) = \frac{e^{-\frac{|\mathbf{x}|}{\xi}}}{4\pi z|\mathbf{x}|} \tag{243}$$

The correlation length ξ is the parameter of dimension of length which must appear in the correlation function $C(\mathbf{x})$ due to dimensional reason, to remove the length dimension of \mathbf{x} . The correlations tend to decrease with separation and the correlation length characterizes the distance where they become negligible.

B. Scaling laws

As emphasised before, the specific feature of critical phenomena is the divergence of the correlation length diverges as the critical point is approached. This is a power divergence, as well,

$$\xi \approx |t|^{-\nu}, \tag{244}$$

with critical exponent ν . In other words, one finds long range correlations among degrees of freedom in the vicinity of a critical point. The diverging correlation length can even be considered as the definition of critical phenomena or second order phase transitions.

The system may have a number of characteristic lengths, such as lattice spacing, size of molecules, etc. beside the correlation length. What is special in critical points is that the correlation length becomes the largest length

scale of the system. The dynamics of the order parameter is not important at distances much shorter or longer than the correlation length. In fact, the order parameter can approximately be considered to be completely correlated or uncorrelated at these distances, respectively. It seems therefore reasonable to assume that the other length scales, being too small, decouple from the dynamics of the order parameter around the critical point. In other words, the only length scale characterizing the dynamics around the critical point is ξ . This length scale is infinite exactly at the critical point t_c , ie. disappears from the physical system. Thus one expects that critical systems display scale invariance, the independence of the physical constants of the critical system from the choice of the unit length, as long as the other, finite length scales can be ignored. This observation brings dimensional arguments into the discussion of critical phenomena.

The dimensional analysis is based on the trivially sounding observation that every physical quantity has well defined dimension. The number of independent dimensions is a convention, based on the numerical values of “physical constants”. For instance, we might as well measure time in length unit and set the speed of light to unity, $c = 1$, as usually done in special relativity. But whatever conventions one uses, a measuring process can produce quantities with well defined dimensions only. Let us now consider a quantity A of length dimension $[A]$, constructed by means of the length scale $\ell = |\mathbf{x}|$ and constants p_1, \dots, p_n , $A = A(\ell, c_1, \dots, c_n)$. There are two ways to describe the effect of the rescaling $cm \rightarrow s \cdot cm$ of the unit in which the length is expressed in A . On the one hand, the dimension of A can be used to find the response $A \rightarrow s^{-[A]}A$. On the other hand, the change of A can be found by rescaling its dimensional constants, $\ell \rightarrow s^{-1}\ell$, $c_j \rightarrow s^{-[c_j]}c_j$, as well. The equivalence of these two responses amounts to the equation

$$A(s^{-1}\ell, s^{-[c_1]}c_1, \dots, s^{-[c_n]}c_n) = s^{-[A]}A(\ell, c_1, \dots, c_n), \quad (245)$$

which can be used to eliminate one variable from A . In fact, by choosing $s = \ell$ one can eliminate one independent variable,

$$A(\ell, c_1, \dots, c_n) = \ell^{[A]}A(1, \ell^{-[c_1]}c_1, \dots, \ell^{-[c_n]}c_n). \quad (246)$$

The function on the right hand side not only has one less variable, one sees, as well, that the dimension of A is provided by ℓ and the remaining dependence in ℓ comes through the other parameters only.

Let us apply this argument to the correlation function (241) where the form $z = 1$ is achieved by the rescaling $\Phi \rightarrow \sqrt{z}\Phi$ of the order parameter, $[\tilde{C}]$. The length dimension of the Fourier integral, $-d$, yields $[C] = 2 - d$ in d -dimensional space. Therefore we have

$$C(\ell, r) = s^{2-d}C(s^{-1}\ell, s^2r). \quad (247)$$

If one ignores r in the vicinity of the critical point where its numerical value is small then the unique solution, $C(\mathbf{x}) \approx c|\mathbf{x}|^{2-d}$, follows in a trivial manner. In the presence of r we set $s = \ell$ as mentioned above and write

$$C(\ell, r) = \ell^{2-d}C(1, \ell^2r). \quad (248)$$

Do we really recover scale invariance as the critical point is approached? The power-like dependence, predicted by the naive dimensional analysis in the approximation $r = 0$ is an encouraging sign but the actual value of the power is a simple length dimension which does not agree with the critical exponents observed. The almost critical correlation function at large distances, shown for at large ℓ and small r by (247) follows mainly the naive scaling law, given by the dimension of the correlation function, $2 - d$. But for $\ell > 1/\sqrt{r}$ the form (241) leads to a faster decrease as the distance is further increased. One can incorporate this feature without renouncing the power-like structure by assuming that the presence of the small dimensional constants in the correlation function amounts to a simple modification of the exponent in the scaling law, the introduction of an anomalous dimension η ,

$$C(s^{-1}\mathbf{x}, r) = s^{d-2+\eta}C(\mathbf{x}, r) + C'(\mathbf{x}, r), \quad (249)$$

where $s^{d-2+\eta}C'(\mathbf{x}, r) \rightarrow 0$ in the limit $s \rightarrow 0$, $r = \mathcal{O}(s^2)$. The anomalous dimension, η , defined in this manner for the correlation function characterizes the critical point.

The approximation $r = 0$ in the vicinity of the critical point is based on the intuitive idea that effects, taking place at highly different length scales, at r and \mathbf{x} are not related to each other. The renormalization group, a procedure to follow the scale dependence in physical laws, actually has identified the violation of this assumption and it is called anomaly. It reflects the fact that the remaining length scales of the system do play some role in the dynamics which does not diminish with the separation of the correlation length from the other scales, as the critical point is approached. As an example one may mention the decay of a neutral π -meson into two photons is possible due to the existence of a short distance scale under which no electromagnetic interactions take place. The actual value of this

minial length scale is not known but its existence can safely be inferred from the observed pion decay. One reaches at this point a rather disquieting conclusion which may invalidate the very basic assumption of our scientific thinking, namely a whole system can be more than the sum of its constituents.

But let us now return to critical phenomena where one can easily calculate the length dimensions needed for the critical exponents β and γ ,

$$\begin{aligned} \left[\frac{M}{V} \right]_{\ell} &= \frac{1}{2} [C]_{\ell} = \frac{2-d-\eta}{2} \\ M_{\ell} &= \frac{2+d-\eta}{2} \\ [\chi]_{\ell} &= [\tilde{C}]_{\ell} = [C]_{\ell} + d = 2 - \eta \end{aligned} \quad (250)$$

As of the exponent α is concerned which is defined by taking derivatives with respect to the temperature one needs more care because these derivations amplify the dependence of the correlation function on r . Hence one applies the dimensional argument before taking the derivatives. The logarithm of the partition function is dimensionless, $[\beta G]_{\ell} = 0$ and $[\beta G]_{\ell} = -d$.

$$\left[\frac{\beta G}{V} \right]_{\ell} = -d. \quad (251)$$

The scaling hypothesis consists of the following assumptions:

1. The only length scale of the near critical system is the correlation length. The other, much shorter length scale decouple from the dynamics, leaving anomalous dimensions behind only.
2. The singularities at the critical point are generated by the diverging correlation length alone and physical quantities, expressed in length units of the correlation length show no singularity anymore at the critical point.

The second point implies that the only anomalous dimension which enters in the scaling relations is that of the correlation function.

The scaling hypothesis assures that the expressions of the diverging quantities remain regular as the critical point is approached if the length is expressed in units of the correlation length, $A \rightarrow A\xi^{-[A]_{\ell}}$. According to the dimensional argument presented above this leads to the relations

$$\begin{aligned} M &\approx \xi^{\frac{\eta-2-d}{2}} \approx |t|^{\beta} \approx \xi^{-\frac{\beta}{\nu}}, \\ \chi &\approx \xi^{\eta-2} \approx |t|^{-\gamma} \approx \xi^{\frac{\gamma}{\nu}}, \end{aligned} \quad (252)$$

due to $\xi \approx |t|^{-\nu}$. To find the expression for α we start with

$$\frac{\beta G}{V} \approx \xi^{-d} \approx t^{d\nu}, \quad (253)$$

and write

$$c \approx \frac{\partial^2}{\partial t^2} \frac{\beta G}{V} \approx |t|^{d\nu-2} \approx |t|^{-\alpha}. \quad (254)$$

We arrive in this manner at scaling relations

$$\begin{aligned} \alpha &= 2 - d\nu \\ \beta &= \frac{\nu}{2}(d + 2 - \eta) \\ \gamma &= \nu(2 - \eta) \end{aligned} \quad (255)$$

C. Scaling laws from the correlation function

It is instructive to make explicit the dependence of the correlation function $C(\mathbf{x}, h)$ on the temperature and the external field by means of the scaling hypothesis. In the absence of external magnetic field one expects

$$C(\mathbf{x}, 0) \approx |\mathbf{x}|^{2-d-\eta} f_{\pm} \left(\frac{|\mathbf{x}|}{\xi}, 0 \right) \quad (256)$$

for $t \rightarrow 0^\pm$ with a regular function f . When the external magnetic field is turned on it tends to align the local magnetic moments within a distance within a distance ℓ_{align} . It is clear that $\ell_{\text{align}} \rightarrow \infty$ as the critical point is approached therefore one expects an anomalous dimension κ to ℓ_{align} giving $\ell_{\text{align}} \rightarrow \xi^{1+\kappa}$ and an amplification factor $|t|^{-d\nu(1+\kappa)}$ to h in the correlation function,

$$C(\mathbf{x}, h) \approx |\mathbf{x}|^{2-d-\eta} f_{\pm}(|\mathbf{x}||t|^\nu, h|t|^{-\Delta}), \quad (257)$$

where $\Delta = d\nu(1 + \kappa)$. We can now express the susceptibility first in the absence of magnetic field as

$$\begin{aligned} \chi &\approx \int d^d x |\mathbf{x}|^{2-d-\eta} f_{\pm}(|\mathbf{x}||t|^\nu, 0) \\ &= |t|^{\nu(\eta-2)} \int d^d x' |\mathbf{x}'|^{2-d-\eta} f_{\pm}(|\mathbf{x}'|, 0), \end{aligned} \quad (258)$$

and find again $\nu(2 - \eta) = \gamma$ because the integral in the last line is temperature independent.

In the presence of the magnetic field one has in a similar manner

$$\begin{aligned} \chi &\approx \int d^d x |\mathbf{x}|^{2-d-\eta} f_{\pm}(|\mathbf{x}||t|^\nu, h|t|^{-\Delta}) \\ &= |t|^{-\gamma} f_{1\pm}(H|t|^{-\Delta}), \end{aligned} \quad (259)$$

whose integral with respect to h gives

$$\begin{aligned} M &= \text{const.} + V \int dh \chi(h) \\ &= \text{const.} + V |t|^{-\gamma} \int dh f_{1\pm}(h|t|^{-\Delta}) \\ &\approx |t|^{\Delta-\gamma} f_{2\pm}(h|t|^{-\Delta}). \end{aligned} \quad (260)$$

We set first $h = 0$ and look for the temperature dependence,

$$M \approx |t|^{\Delta-\gamma} \quad (261)$$

giving $\Delta = \beta + \gamma$. A further integration yields

$$\begin{aligned} G(T, h) &= \text{const.} - \int dh M(h) \\ &\approx |t|^{\Delta-\gamma} \int dh f_{2\pm}(h|t|^{-\Delta}) \\ &\approx |t|^{2\Delta-\gamma} f_{3\pm}(h|t|^{-\Delta}). \end{aligned} \quad (262)$$

Evaluating it at $h = 0$ we find $G \approx |t|^{2\Delta-\gamma}$ which in turn gives

$$C = T^2 \frac{\partial^2 G(T, 0)}{\partial T^2} \approx |t|^{\Delta-\gamma-2} = |t|^{2\beta+\gamma-2} \quad (263)$$

and

$$\alpha + 2\beta + \gamma = 2. \quad (264)$$

We now look into the h -dependence. The order parameter is non-vanishing for $h \neq 0$ at any temperature, thus

$$f_{2\pm}(h|t|^{-\Delta}) \approx |t|^{\gamma-\Delta} = |t|^{-\beta} \quad (265)$$

giving

$$f_{2\pm}(s) \approx s^{\beta/\Delta}, \quad (266)$$

and

$$M \approx |t|^\beta (h|t|^{-\Delta})^{\beta/\Delta} = h^{\beta/\Delta} \quad (267)$$

which amount to the relation $\delta = \Delta/\beta$ or $\gamma = \beta(\delta - 1)$ between the critical exponents.

Finally we mention the hyperscaling assumption, stating that the thermal energy stored in a region of size ξ is in the order of magnitude of $k_B T$ in the absence of other length scale. This gives

$$G \approx k_B T \frac{V}{\xi^d} \approx |t|^{\nu d} \quad (268)$$

yielding

$$\nu d = 2\Delta - \gamma = 2 - \alpha. \quad (269)$$

The origin of the critical exponents and their universal feature, together with the relations satisfied by them can systematically be clarified in the framework of the renormalization group.

D. Landau-Ginzburg double expansion

The strategy of constructing an effective theory is particularly promising for almost critical systems because a small parameter helps to organize the dynamics in order of importance. The typical fluctuations take place at the order of magnitude of the correlation length. Therefore, the fluctuations tend to stretch over long distances as the critical point is approached. Our small parameter will be the wavelength of the fluctuations which can formally be identified with the partial derivative with respect to space coordinates.

One may rely on another small parameter, the magnitude of the fluctuations. This is rather dangerous assumption because of the scale invariant feature of critical systems. In fact, the order parameter has usually nontrivial dimensions and the scale invariance, recovered at the critical point makes its distribution widely spread. Thus we assumed to be close to but not exactly on the critical point and should be ready to give up this small parameter in a sufficiently close vicinity of criticality.

We assume for the sake of simplicity we are given local, single component field $\Phi(\mathbf{x})$ as order parameter for a spontaneous symmetry breaking. The partition function of the system,

$$Z = \sum_n e^{-\beta E_n} \quad (270)$$

can be written as

$$Z = \sum_n e^{-\beta E_n} \prod_{\mathbf{x}} \int d\Phi(\mathbf{x}) \delta(\Phi(\mathbf{x}) - \langle n | \Phi(\mathbf{x}) | n \rangle). \quad (271)$$

We exchange the order of summation and integration and write

$$Z = \int D[\Phi] e^{-\beta F[\Phi]} \quad (272)$$

where the integral measure

$$D[\Phi] = \prod_{\mathbf{x}} d\Phi(\mathbf{x}) \quad (273)$$

has been introduced and the effective free energy $F[\Phi]$ of the order parameter is defined by

$$e^{-\beta F[\Phi]} = \sum_n \prod_{\mathbf{x}} \delta(\Phi(\mathbf{x}) - \langle n | \Phi(\mathbf{x}) | n \rangle) e^{-\beta E_n}. \quad (274)$$

The next step is the determination of the effective free energy. Instead of the frontal attack on the formula let us follow a simpler phenomenological argument, based on (i) locality, (ii) existence of small parameters and (iii) symmetry. All fundamental laws of physics are supposed to be local in space-time. The physical quantities may involve derivatives with respect time and space but all functions are evaluated at the same space-time points in a fundamental equation. What we are set to construct is not a fundamental theory but it is still reasonable to expect that non-local effects would remain unimportant to understand the impact of a diverging correlation length. Therefore, the free energy of the order parameter is assumed to take the form of an integral of a local free energy density in space. The structure of this density is determined by means of two small parameters in the vicinity of a critical point,

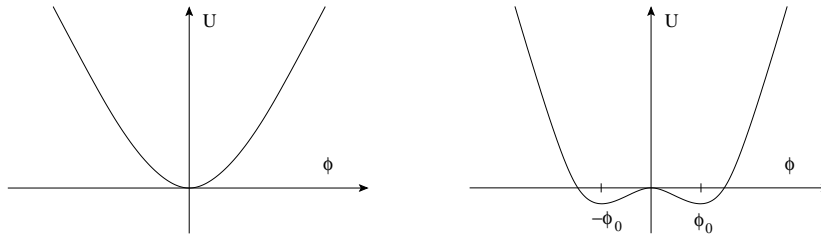


FIG. 15: The local potential of the Landau-Ginzburg free energy functional with $j = 0$ for $r > 0$ and for $r < 0$.

the magnitude and the inverse wave length of the fluctuations. Let us consider first the gradient expansion. The zeroth order term is an arbitrary function of the local order parameter, $U(\Phi(\mathbf{x}))$. The first order term in the gradient must be a vector which is excluded by rotational symmetry, to be assumed for the free energy. Hence the gradient appears in the second order as $(\nabla\Phi(\mathbf{x}))^2$, being the only invariant under rotation, up to partial integration,

$$\beta F[\Phi] = \int d^3x \left[\frac{1}{2} Z(\Phi(\mathbf{x})) (\nabla\Phi(\mathbf{x}))^2 + U(\Phi(\mathbf{x})) + \mathcal{O}(\nabla^4) \right]. \quad (275)$$

Note that invariance under spatial rotations limit the order of the gradient to even. We consider now the universality class of the ferromagnetic transition whose simplest characterization is that the symmetry $\Phi(\mathbf{x}) \rightarrow -\Phi(\mathbf{x})$ is broken spontaneously. Thus this symmetry is kept intact on the level of the free energy and appears broken by the integration over the order parameter configurations in the partition function only. Therefore, the relations $U(\Phi) = U(-\Phi)$, $Z(\Phi) = Z(-\Phi)$ follow. We use finally the amplitude of the order parameter, Φ , as small parameter to simplify the functions in the free energy density,

$$\begin{aligned} U(\Phi) &= j\Phi + \frac{r}{2}\Phi^2 + \frac{g}{4!}\Phi^4 + \frac{s}{6!}\Phi^6 + \mathcal{O}(\Phi^8) \\ Z(\Phi) &= 1 + \mathcal{O}(\Phi^2) \end{aligned} \quad (276)$$

where the $\mathcal{O}(\Phi)$ term represents an external symmetry breaking field, coupled linearly to the order parameter for diagnostic purposes and $\mathcal{O}(\Phi^0)$ value of Z is set by the appropriate rescaling of the order parameter. Rather involved arguments, based on the renormalization group show that the ignored terms are not influencing the universal properties of critical points in three spatial dimensions.

E. Mean field solution

Since we are interested in an almost critical system where the correlation length is large and the fluctuations are long range the most natural approximation is assuming the absence of any fluctuation, namely approximating the integration over all field configurations $\Phi(\mathbf{x})$ in the partition function by the contribution of the most important single configuration $\Phi_0(\mathbf{x})$ which minimizes the free energy. Since the spatial inhomogeneities contribute to a positive semidefinite term the minimum corresponds to homogeneous configuration, $\Phi(\mathbf{x}) = \Phi_0$ and Φ_0 minimizes the local potential $U(\Phi)$ and $\beta F[\Phi_0] = VU(\Phi_0)$.

We set first $j = 0$ and note that the local potential, shown in Fig. 15, is a symmetric function, $U(\Phi) = U(-\Phi)$, and has a single minimum at $\Phi_0 = 0$ which is symmetric with respect to the discrete symmetry transformation. The most important configuration displays the same symmetry as the free energy, therefore the symmetry is intact for $r > 0$. Below the critical temperature, $T < T_c$ and $r < 0$, the potential has two degenerate minima related by the symmetry transformation $\Phi \rightarrow -\Phi$, indicating the spontaneous breakdown of the symmetry in this phase. A phase transition is taking place at $r = 0$ because the order parameter,

$$|\langle\Phi(x)\rangle| \approx \Phi_0 = \Phi_{0,j=0}(r) = \begin{cases} 0 & r > 0, \\ \sqrt{\frac{-6r}{g}} & r < 0, \end{cases} \quad (j = s = 0) \quad (277)$$

changes in a singular manner at $r = 0$. This behavior suggests the identification $r \approx t = (T - T_c)/T_c$ in the vicinity of the phase transition in order to recover the typical behavior of the magnetization around the Curie temperature

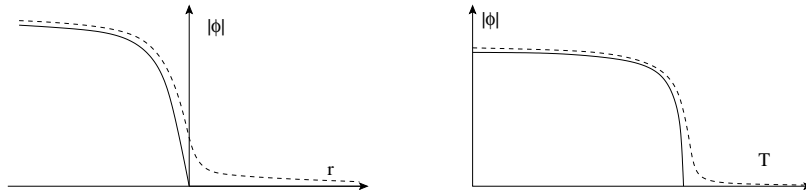


FIG. 16: The first figure displays the absolute magnitude of the order parameter as the function of r . The second one shows qualitatively the magnetization around the Curie temperature. The dashed lines correspond to $j < 0$.

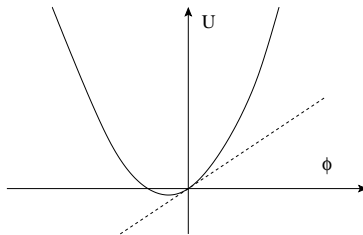


FIG. 17: The potential with $j > 0$ and $r > 0$. The dashed line indicates the symmetry breaking part, $j\Phi$.

as shown in Fig. 16. We find the mean field value $\beta = 1/2$ for the critical exponent of the order parameter. The low temperature phase is called ordered because the spontaneous symmetry breaking aligns the order parameter. This transition seems to be of second order because the order parameter is continuous but non-differentiable at that point. This expectation will be confirmed by the calculation of the correlation length for $r \approx 0$.

The condition $j = 0$ rendered the free energy explicitly symmetric with respect to inversion, $\Phi(\mathbf{x}) \rightarrow -\Phi(\mathbf{x})$ and it was the spontaneous symmetry breaking mechanism which generated non-vanishing order parameter. What is the phase structure on the parameter planes (r, j) when explicit symmetry breaking occurs, too? The symmetry is broken explicitly by the external field which generates a stable, non-vanishing order parameter value for arbitrary values of r or the temperature. We keep the identification $r = c(T - T_c)/T_c$ for $j \neq 0$ and the potential is asymmetric and has a stable minimum at $\Phi_0 \neq \Phi_{0,j=0}(r) = 0$ for $r > 0$ and $j \neq 0$, cf. Fig. 17.

The situation is more complicated below the critical temperature. The order parameter is aligned by two different symmetry breaking mechanisms, the spontaneous and the explicit one. The two possible values of the order parameter, preferred by the spontaneous symmetry breaking are not equivalent with respect to the explicit symmetry breaking mechanism. If the order parameter value chosen spontaneously agrees with the alignment preferred by the external symmetry breaking field then the two symmetry breaking mechanisms work parallel and the order parameter settles at a larger value in an absolute minimum of the potential as shown in Fig. 18 and indicated by the dashed lines in Figs. 16. The order parameter of the absolute minimum as the function of the external symmetry breaking term,

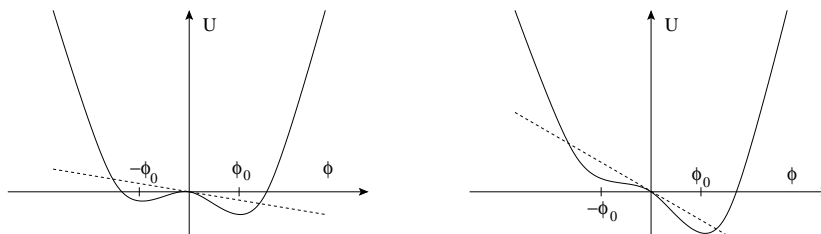


FIG. 18: The potential with $j < 0$ and $r < 0$.

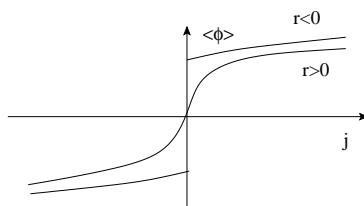


FIG. 19: The order parameter as the function of the strength of the explicit symmetry breaking

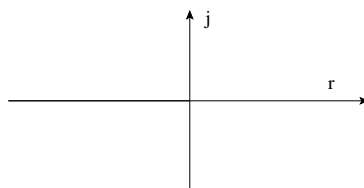


FIG. 20: The phase structure on the planes (r, j) and $(\langle\Phi\rangle, r)$. The ordered phase with spontaneous symmetry breaking is the solid line $j = 0, r < 0$.

shown in Fig. 19, displays a first order phase transition in function of j in the ordered phase, $r < 0$. The resulting phase structure is depicted in Fig. 20. The transition is of second order in r for $j = \langle\Phi\rangle = 0$. We shall argue below that it is of first order in j for fixed $r < 0$. The order parameter becomes a regular function of r and the second order phase transition at $r = 0$ is washed away for $j \neq 0$. The equation

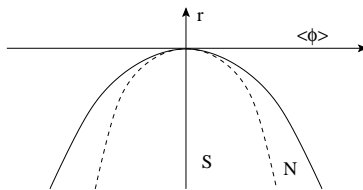
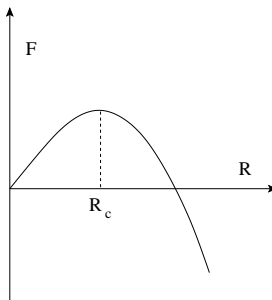
$$U'(\Phi_0) = 0 \quad (278)$$

gives the mean field critical exponent $\delta = 3$ for $r = j = 0$.

The simplicity of Fig. 20 is deceptive, there are differences in the dynamics of the system which are not easy to identify by following a homogeneous mean field order parameter only. Inhomogeneities should be considered when the order parameter happens to be around the minimum of the symmetric potential which is not preferred by the external field. Then the two symmetry breaking mechanisms compete and the order parameter reduces its magnitude. For weak enough external field the local minimum is the convex part of the potential $U(\Phi)$, $\sqrt{-2r/g} < |\Phi_0| < \sqrt{-6r/g}$. This is indicated in the first graph of Figs. 18 and this region is denoted by N in Fig. 21. The order parameter is now in a local minimum which is unstable with respect to fluctuations of finite, large enough amplitude.

As the strength of the explicit symmetry breaking is increases then the position of the local minimum reaches the concave part of the potential, $|\Phi_0| < \sqrt{-2r/g}$. This is shown in second graph of Figs. 18 and the corresponding region is denoted by S in Fig. 21. Here the order parameter becomes unstable even with respect to infinitesimal fluctuations.

We come to the point mentioned above, that the transition is of first order in j for fixed $r < 0$ in Fig. 20. The difference between the weak and strong explicit symmetry breaking regimes, denoted by N and S in Fig. 21 can be understood by considering qualitatively the kind of inhomogeneities which arise around the homogeneous mean field. The competition between the two almost degenerate minima in the weak explicit symmetry breaking region N creates domains with $\langle\Phi(\mathbf{x})\rangle \approx \pm\Phi_{0,j=0}(r)$. Let us apply the simple model for the domains where they have a free energy density $f_0 \pm f_1$ with $f_1 > 0$ and the domain wall contributes to the free energy by a finite amount of free energy $f_s > 0$ per unit surface, independently of the shape of the domain. Imagine that the whole system is driven adiabatically into the unstable minimum of the free energy and a domain in a sphere of radius R with order parameter at the absolute minimum of the free energy is created by a fluctuation. The free energy of this domain, embedded in the unstable

FIG. 21: The phase structure on the plane $(\langle\Phi\rangle, r)$.FIG. 22: The free energy of a stable, spherical domain embedded into the unstable order parameter state. R_c is the critical bubble size beyond which the bubble grows without limit.

order parameter state,

$$F(R) = -\frac{8\pi}{3}f_1R^3 + 4\pi f_s R, \quad (279)$$

is depicted in Fig. 22. Thus the creation of small domains with the preferred alignment of the order parameter cost free energy and are suppressed. The "wrongly" aligned system is stable against these inhomogeneous fluctuations. But once a domain with sufficiently large volume is created, $R > R_c = \sqrt{f_s/2f_1}$ in the case of a spherical bubble, the free energy is lowered because the gain in the bulk free energy is more important than the loss at the surface. This is a nucleation phase where the system may be in the "wrong" domain as long as the thermal fluctuations are sufficiently weak and the system is kept away from large amplitude disturbances. The overheated or under-cold fluids are to be found in this state.

As the external symmetry breaking is strengthened the free energy gain in the volume is increased in the "right" domains and the critical domain size is decreased until the thermal fluctuations smear out the domain walls and cancel f_s , what happens at $|\Phi_0| = \sqrt{-2r/g}$ in the mean field solution. We enter here the spinodal instability regime where no domains with finite size are observed and the system is in a mixed state of two competing, homogeneous order parameter states. This is the mixed phase of a first order phase transition, developed as the function of j .

How does this picture change when a higher order, ϕ^6 term is added to the free energy? Such term influences the spontaneous symmetry breaking by developing tree minima for $r < 0$ as shown in Fig. 23. When the region $g < 0$ is explored for $j = 0$ and $r, s > 0$, what is possible because the highest power of Φ has positive coefficient, the symmetry breaking minima shift the homogeneous mean field value of the order parameter in a discontinuous manner, as shown in Fig. 24, and the second order phase transition at $r = 0$ of the potential $s = 0$ changes into a first order transition.

We return finally to the Ising model in d -dimensions which produces a second order phase transition at $J = J_c$ according to the numerical simulations. The analogous mean field solution, employed around the critical point, is based on the introduction of a homogeneous magnetization μ . The dependence of the Hamiltonian on a given spin s is approximated by replacing the neighboring spin variables by this average magnetization,

$$\frac{H(s)}{T} = -Js \sum_j s_j - hs \rightarrow -2dJ\mu s - hs \quad (280)$$

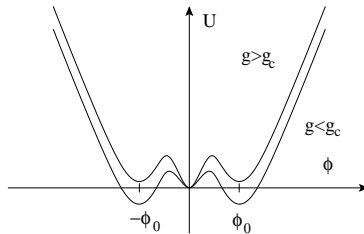


FIG. 23: The symmetric potential free energy for $r, s > 0$ and $g < 0$.

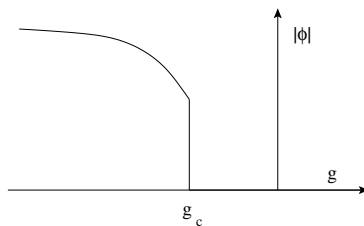


FIG. 24: The order parameter as the function of the coupling constant g for a sixth order potential.

and the partition function for our single active spin variable is

$$Z = e^{2dJ\mu+h} + e^{-2dJ\mu-h}. \quad (281)$$

The magnetization induced by this variable,

$$\langle s \rangle = \frac{1}{Z} \frac{\partial Z}{\partial h} = \tanh(2dJ\mu + h). \quad (282)$$

The self consistency condition.

$$\mu = \langle s \rangle \quad (283)$$

can be solved graphically as shown in Fig. 25 for $h = 0$ and the resulting magnetization as the function of J is similar to the second graph of Figs. 16 with $T_c = 1/2d$.

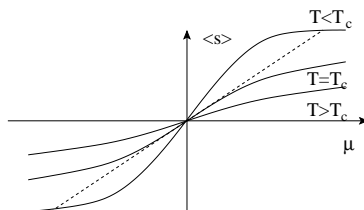


FIG. 25: The average spin as the function of free mean field magnetization μ .

F. Fluctuations and the critical point

As the next, less trivial use of the phenomenological Landau-Ginzburg free energy for the order parameter we calculate the correlation function. For this end we write the order parameter as the sum of a mean field and fluctuations,

$$\Phi(\mathbf{x}) = \Phi_0 + \phi(\mathbf{x}). \quad (284)$$

The leading order, $\mathcal{O}(\phi^2)$, approximation of the free energy for $j = 0$ is

$$\beta F^{(2)}[\phi] = \int d^3x \left[\frac{z}{2} (\nabla \phi(\mathbf{x}))^2 + \frac{r}{2} \phi^2(\mathbf{x}) \right], \quad (285)$$

where $r = U''(\Phi_0)$ and the constant $U(\Phi_0)$ has been ignored. This expression can be diagonalized by using the normal modes of the fluctuations which are plane waves in the case of a homogeneous mean field,

$$\tilde{\phi}(\mathbf{k}) = \int d^3x e^{-i\mathbf{k}\mathbf{x}} \phi(\mathbf{x}) \quad (286)$$

where the real order parameter requires $\tilde{\phi}^*(\mathbf{k}) = \tilde{\phi}(-\mathbf{k})$. The free energy turns out to be

$$\begin{aligned} \beta F^{(2)}[\phi] &= \frac{1}{2} \int d^3x \frac{d^3k}{(2\pi)^3} \frac{d^3q}{(2\pi)^3} e^{i(\mathbf{k}+\mathbf{q})\mathbf{x}} \tilde{\phi}(\mathbf{k}) \tilde{\phi}(\mathbf{q}) (r - z\mathbf{k}\mathbf{q}) \\ &= \frac{1}{2} \int \frac{d^3k}{(2\pi)^3} |\tilde{\phi}(\mathbf{q})|^2 (z\mathbf{k}^2 + r) \end{aligned} \quad (287)$$

in terms of the normal modes.

The correlation function,

$$\begin{aligned} C(\mathbf{x} - \mathbf{y}) &= \langle \Phi(\mathbf{x}) \Phi(\mathbf{y}) \rangle - \langle \Phi(\mathbf{x}) \rangle \langle \Phi(\mathbf{y}) \rangle \\ &= \frac{\int D[\Phi] e^{-\beta F[\Phi]} \Phi(\mathbf{x}) \Phi(\mathbf{y})}{\int D[\Phi] e^{-\beta F[\Phi]}} - \frac{\int D[\Phi] e^{-\beta F[\Phi]} \Phi(\mathbf{x})}{\int D[\Phi] e^{-\beta F[\Phi]}} \frac{\int D[\Phi] e^{-\beta F[\Phi]} \Phi(\mathbf{y})}{\int D[\Phi] e^{-\beta F[\Phi]}} \end{aligned} \quad (288)$$

approximated by means of the quadratic free energy is written as

$$\begin{aligned} C(\mathbf{x}) &\approx \frac{\int D[\phi] e^{-\beta F^{(2)}[\phi]} (\Phi_0 + \phi(\mathbf{x})) (\Phi_0 + \phi(\mathbf{0}))}{\int D[\Phi] e^{-\beta F[\Phi]}} \\ &\quad - \frac{\int D[\phi] e^{-\beta F^{(2)}[\phi]} (\Phi_0 + \phi(\mathbf{x}))}{\int D[\phi] e^{-\beta F^{(2)}[\Phi]}} \frac{\int D[\phi] e^{-\beta F^{(2)}[\phi]} (\Phi_0 + \phi(\mathbf{0}))}{\int D[\phi] e^{-\beta F^{(2)}[\Phi]}} \\ &= \frac{\int D[\phi] e^{-\beta F^{(2)}[\phi]} \phi(\mathbf{x}) \phi(\mathbf{0})}{\int D[\phi] e^{-\beta F^{(2)}[\Phi]}} \end{aligned} \quad (289)$$

because the discrete symmetry $F^{(2)}[-\phi] = F^{(2)}[\phi]$ cancels the averages of odd powers of the fluctuations,

$$\int D[\phi] e^{-\beta F^{(2)}[\phi]} \phi^{2n+1}(\mathbf{x}) = 0. \quad (290)$$

The functional integral will be calculated by the help of the normal mode amplitudes as integral variables. Since $\tilde{\phi}^*(\mathbf{k}) = \tilde{\phi}(-\mathbf{k})$ it is enough to consider half of the complex variables $\tilde{\phi}(-\mathbf{k})$ in the integration. A possible choice is to keep $\Re \tilde{\phi}(\mathbf{k})$ and $\Im \tilde{\phi}(\mathbf{k})$ for $k_z > 0$. We do not commit ourself to any specific choice, instead we shall make integration over all components keeping it mind that we visit each degree of freedom in this process.

$$\begin{aligned} Z &\approx \int D[\phi] e^{-\beta F^{(2)}[\phi]} \\ &= C \int D[\tilde{\phi}] e^{-\frac{1}{2} \int \frac{d^3k}{(2\pi)^3} |\tilde{\phi}(\mathbf{k})|^2 (z\mathbf{k}^2 + r) + \int d^3x U(\Phi_0)}, \end{aligned} \quad (291)$$

where C denotes the Jacobian corresponding to the change of integral variables $\phi(\mathbf{x}) \rightarrow \tilde{\phi}(\mathbf{k})$ and the integral measure is

$$D[\tilde{\phi}] = \prod_{\mathbf{k}} \int d\tilde{\phi}(\mathbf{k}). \quad (292)$$

The relation $\Delta k = 2\pi/L$ and the Gauss integral

$$I(a) = \int_{-\infty}^{\infty} dx e^{-\frac{a}{2}x^2} = \sqrt{\frac{2\pi}{a}}. \quad (293)$$

allows us to write

$$\begin{aligned} Z &= C \prod_{\mathbf{k}} \int d\tilde{\phi}(\mathbf{k}) e^{-\frac{1}{2V}|\tilde{\phi}(\mathbf{k})|^2(z\mathbf{k}^2+r)} \\ &= C \sqrt{\prod_{\mathbf{k}} \frac{2\pi V}{z\mathbf{k}^2+r}} \end{aligned} \quad (294)$$

with $V = L^3$ and the square root is to take into account the double counting of the degrees of freedom in integrating over all Fourier modes of a real field.

Using $I(a)$ as generating function we have

$$\int_{-\infty}^{\infty} dx e^{-\frac{a}{2}x^2} x^2 = -2 \frac{dI(a)}{da} = \frac{1}{a} \int_{-\infty}^{\infty} dx e^{-\frac{a}{2}x^2} \quad (295)$$

and we find

$$\begin{aligned} \int D[\phi] e^{-\beta F^{(2)}[\phi]} \phi(\mathbf{x}) \phi(\mathbf{y}) &= C \sum_{\mathbf{q}, \mathbf{q}'} e^{i\mathbf{q}\mathbf{x} - i\mathbf{q}'\mathbf{y}} \prod_{\mathbf{k}} \int d\tilde{\phi}(\mathbf{k}) e^{-\frac{1}{2V}|\tilde{\phi}(\mathbf{k})|^2(z\mathbf{k}^2+r)} \phi(\mathbf{q}) \phi^*(\mathbf{q}') \\ &= CV \sum_{\mathbf{q}} \frac{e^{i\mathbf{q}(\mathbf{x}-\mathbf{y})}}{z\mathbf{q}^2+r} \prod_{\mathbf{k}} \frac{2\pi}{z\mathbf{k}^2+r} \\ &= \int \frac{d^3q}{(2\pi)^3} \frac{e^{i\mathbf{q}(\mathbf{x}-\mathbf{y})}}{r+z\mathbf{q}^2} \int D[\phi] e^{-\beta F^{(2)}[\phi]}, \end{aligned} \quad (296)$$

and the Ornstein-Zernike form of the correlation function is recovered. It supports the identification $r = 0$ as the critical point and the critical exponents $\nu = 1/2$, $\eta = 0$ and $\gamma = 1$ are found.

The mean field solution together with the quadratic approximation for the fluctuation is reliable if the fluctuations are weak. As the critical point is approached $r \rightarrow 0$ and the "restoring force" acting on the fluctuations decreases. Thus one expects that the approximation breaks down in a sufficiently small vicinity of the critical point. This is the Ginzburg condition. When the space dimensionality is changed one expects stronger fluctuation at lower dimension because the integral measure q^{d-1} in the integration over the wave numbers in polar coordinates allows the singularity $1/q^2$ to be more dominant. Thus there should be critical dimension above which this approximation is applicable. This critical dimension turns out to be $d = 4$. Despite these limitations the approximations followed above give a good guideline to identify the interesting and problematic aspects of critical phenomena.

VI. BOSE SYSTEMS

The particle exchange statistics has a fundamental impact on the properties of a many-particle state. The Fermi-Dirac statistics renders the multi-fermion systems weakly interacting in the absence of attractive forces and the Bose-Einstein statistics may produce macroscopically occupied states or symmetry breaking.

A. Noninteracting bosons

The grand canonical partition function for a gas of free, spineless, indistinguishable particles,

$$\begin{aligned} Z = e^{-\beta F} &= \prod_{\mathbf{p}} \sum_{n_{\mathbf{p}}} e^{-\beta(\epsilon_{\mathbf{p}} - \mu)n_{\mathbf{p}}} \\ &= \prod_{\mathbf{p}} \frac{1}{1 - e^{-\beta(\epsilon_{\mathbf{p}} - \mu)}} \end{aligned} \quad (297)$$

gives the grand canonical free energy

$$F(T, \mu) = \frac{1}{\beta} \sum_{\mathbf{p}} \ln(1 - e^{-\beta(\epsilon_{\mathbf{p}} - \mu)}) \quad (298)$$

which becomes

$$F = \frac{V}{\beta} \int \frac{d^3 p}{(2\pi)^3 \hbar^3} \ln(1 - e^{-\beta(\epsilon_{\mathbf{p}} - \mu)}) \quad (299)$$

in the thermodynamical limit. The density

$$\begin{aligned} n &= \frac{\langle N \rangle}{V} \\ &= -\frac{1}{V} \frac{\partial F}{\partial \mu} \\ &= \int \frac{d^3 p}{(2\pi)^3 \hbar^3} \frac{z e^{-\beta \epsilon_{\mathbf{p}}}}{1 - z e^{-\beta \epsilon_{\mathbf{p}}}} \end{aligned} \quad (300)$$

with $z = e^{\beta \mu}$ is a monotonically increasing function of z or μ for $z < 1$, $\mu < 0$,

$$\begin{aligned} n &= \int \frac{d^3 p}{(2\pi)^3 \hbar^3} \frac{z e^{-\frac{\beta p^2}{2m}}}{1 - z e^{-\frac{\beta p^2}{2m}}} \\ &= \frac{1}{2\pi^2 \hbar^3} \int_0^\infty dp p^2 \frac{z e^{-\frac{\beta p^2}{2m}}}{1 - z e^{-\frac{\beta p^2}{2m}}} \\ &= \frac{(2mk_B T)^{3/2}}{2\pi^2 \hbar^3} \int_0^\infty dx x^2 \frac{z e^{-x^2}}{1 - z e^{-x^2}} \\ &= \frac{(2mk_B T)^{3/2}}{4\pi^2 \hbar^3} \int_{-\infty}^\infty dx x^2 \sum_{n=1}^\infty z^n e^{-nx^2} \\ &= -\frac{(2mk_B T)^{3/2}}{4\pi^2 \hbar^3} \sum_{\ell=1}^\infty z^\ell \frac{d}{d\ell} \underbrace{\int_{-\infty}^\infty dx e^{-\ell x^2}}_{\sqrt{\pi/\ell}} \\ &= \underbrace{\frac{(2mk_B T)^{3/2}}{8\pi^{3/2} \hbar^3}}_{\lambda_T^{-3}} \sum_{\ell=1}^\infty \frac{z^\ell}{\ell^{3/2}}, \end{aligned} \quad (301)$$

and the series in the last equation is convergent for $|z| < 1$.

The key point is that the density remains finite at $z = 1$, at the singularity. Therefore the phase transition on the (T, n) plane is at a line $z = 1$ or $\mu = 0$,

$$\begin{aligned} n_c &= \left(\frac{mk_B T}{2\pi \hbar^2} \right)^{3/2} \sum_{\ell=1}^\infty \frac{1}{\ell^{3/2}} \approx \frac{2.612}{\lambda_{T_c}^3}, \\ k_B T_c &= \frac{2\pi \hbar^2}{m} \left(\frac{n}{\sum_{\ell=1}^\infty \frac{1}{\ell^{3/2}}} \right)^{2/3} \approx \frac{2\pi \hbar^2}{m} \left(\frac{n}{2.612} \right)^{2/3}, \end{aligned} \quad (302)$$

shown qualitatively on Fig. 26. This line shows the maximal capacity of accommodating particles with microscopic occupation numbers. All momentum integrals are well defined and finite under this curve. When the system is pushed on the other side of the critical curve then the naive idea of occupying each energy level by a microscopic manner, ie. by having a continuous occupation number

$$n_{\mathbf{p}} = \frac{1}{e^{\beta(\epsilon_{\mathbf{p}} - \mu)} - 1} \quad (303)$$

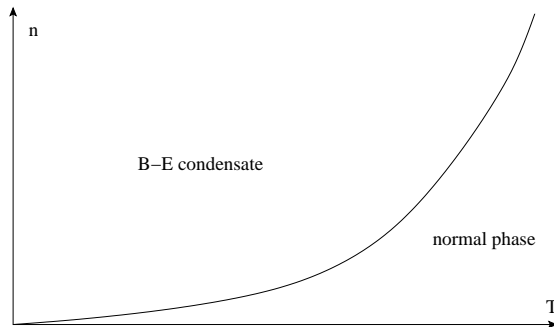


FIG. 26: The phase structure of an ideal Bose-Einstein gas on the (n, T) plane.

turns out to be wrong because the integrals containing the occupation number are divergent. To understand the origin of the unexpected complication we have to return to the case of the discrete spectrum and consider a simple sum over momenta,

$$\begin{aligned} N &= \sum_{\mathbf{p}} \frac{e^{-\beta(\epsilon_{\mathbf{p}} - \mu)}}{1 - e^{-\beta(\epsilon_{\mathbf{p}} - \mu)}} \\ &= \sum_{\mathbf{p}} \frac{1}{e^{\beta(\epsilon_{\mathbf{p}} - \mu)} - 1}. \end{aligned} \quad (304)$$

This shows that the approximation of the sum by an integral is problematic when $z \geq 1$ due to the vanishing denominator. The maximal number of particles the system can accommodate with continuous and integrable occupation number distribution $n_{\mathbf{p}}$ in thermodynamical limit corresponds to the density $2.612(mk_B T / 2\pi\hbar^2)^{3/2}$, the critical line of Fig. 26. The further decrease of the temperature for fixed particle number or increase of the particle number with fixed temperature is possible only by occupying some energy levels in a discontinuous manner. It is obvious that these extra particles should be placed in the minimal energy single particle state, $\mathbf{p} = 0$. Therefore above the critical curve the homogeneous, zero energy state will contain particles with density

$$n_{\text{cond}}(n, T) = \max\left(0, n - \frac{2.612}{\lambda_T^3}\right). \quad (305)$$

Such a Bose-Einstein condensate produces genuine macroscopic quantum effects because particles in the condensate remain coherent over macroscopic distances. The hard core due to the Pauli exclusion principle prevents condensation for fermions.

It is not difficult to construct an order parameter signaling the onset of the condensation,

$$\eta = \frac{n_{\text{cond}}(n, T)}{n} = \max\left(0, 1 - \frac{2.612}{\lambda_T^3 n}\right) = \max\left(0, 1 - \left(\frac{T}{T_c(n)}\right)^3\right). \quad (306)$$

One can upgrade this order parameter to a local field by considering the wave function of the particles in the condensate,

$$\psi_{\text{cond}}(\mathbf{x}) = \sqrt{N_{\text{cond}}}\psi_0(\mathbf{x}), \quad (307)$$

where N_{cond} is the number of particles in condensate, eg. $N_{\text{cond}} = V n_{\text{cond}}(n, T)$ and $\psi_0(\mathbf{x}) = 1/\sqrt{V}$ for homogeneous condensates. This function represents the coherent quantum effects of the condensate and becomes a nontrivial function of the coordinate \mathbf{x} in the presence of inhomogeneous external perturbations.

B. Phases of Helium

Many fermion system systems usually arrive at a solid phase at low temperature where the attractive van der Waals forces become stronger than forces arising from thermal collisions and a periodic ground state is formed. An exception

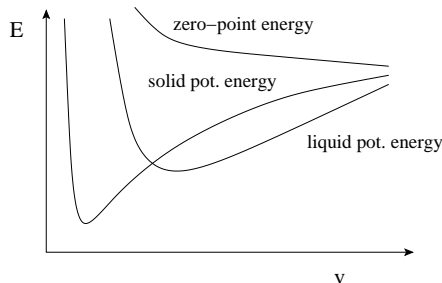


FIG. 27: The localization (zero-point) energy together with the solid or liquid potential energy as the functions of the molar volume $v = V/N$.

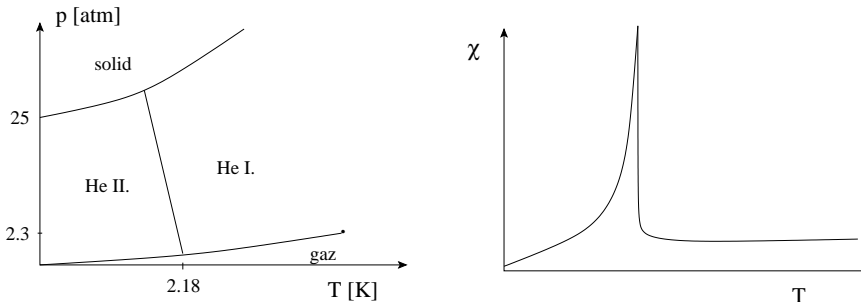


FIG. 28: The phase structure of ${}^4\text{He}$ and the specific heat in the fluid phase.

to this rule is the Helium which retains the fluid phase down to $T = 0$ for sufficiently low pressure. Being a noble gas, the van der Waals forces are weak. But other noble gas atoms can be solidified, the additional unique feature of the Helium is its low mass. The localization of a particle into a box of size L requires the energy $d\hbar/2mL^2$ in d -dimensions, and the lighter the particle we intend to localize the more energy will be stored in the localized state. For light enough particles, such as the ${}^3\text{He}$ or ${}^4\text{He}$ atoms, the gain in energy from letting the particles extend over large region dominates the gain from forming a coherent solid around the minimum of the potential energy in the solid as shown in Fig. 27. On the contrary, the zero-point energy drops slow enough around the minimum of the potential energy in the liquid phase, $r_{\min} \approx 3A$ to stabilize the low temperature liquid at $r_0 \approx 4.6A$ with $v_0 \approx 46A^3$. As a result, the zero temperature He atoms form liquid at low enough pressure.

When the pressure is increased the atoms starts to overlap and to experience the Pauli exclusion principle for their fermionic constituents which is represented by the hard repulsive core of the potential energy of Fig. 27. When the atoms are squeezed against this repulsive core their potential energy raises rendering the dynamics semiclassical. This classical dynamics leads to the formation of a periodic crystal, the solid phase.

The overlap between fermion states of different He atoms is weak below nuclear densities and the exchange statistics of the atoms is determined by the exchange of the whole bound state. Therefore, the ${}^4\text{He}$ and ${}^3\text{He}$ atoms behave as bosons or fermions at low densities, where the separation of the atoms is much larger than their size. Thus one expects the appearance of Bose-Einstein condensate in ${}^4\text{He}$.

At even lower pression the density drops below the threshold for Bose-Einstein condensate and the normal ${}^4\text{He}$ gas is recovered.

A similar phenomenon, observed in ${}^3\text{He}$, can be understood by the formation of loosely bound pairs of two ${}^3\text{He}$ atoms into a bosonic quasi-particles which condense. Due to this complication we discuss the case of ${}^4\text{He}$ only.

The phase structure and the specific heat of ${}^4\text{He}$ are shown in Figs. 28. The peak in the specific heat, seen at low pressure when we cross the division line between the He I and He II phases suggests a second order phase transition, He II supporting Bose-Einstein condensate.

C. He II

The most natural, approximate description of the He II phase is Tisza's two-fluid model where we assume that the fluid is made up by two fluids, one containing the condensed atoms and the other the atoms corresponding to

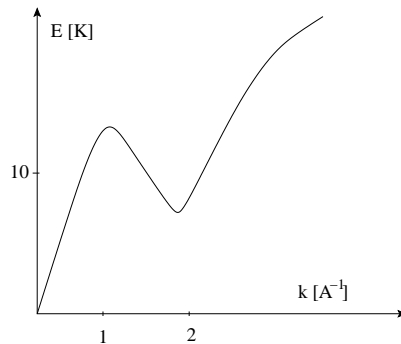


FIG. 29: The dispersion relation for the elementary excitations of He II.

microscopic occupation number. The density and the velocity of the fluid is supposed to be

$$\begin{aligned}\rho &= \rho_n + \rho_s, \\ \rho \mathbf{v} &= \rho_n \mathbf{v}_n + \rho_s \mathbf{v}_s.\end{aligned}\tag{308}$$

The He consists of identical He atoms and their separation into two different fluid is formal method, based on the different correlations the atoms experience in a macroscopically or microscopically populated state.

The distinguishing features of the super-fluid component is its vanishing entropy and viscosity. These give rise to the mechanocaloric and the fountain effects. Let us consider two containers A and B of He II, connected by a very narrow tube. This tube acts as a filter for the super-fluid component because the viscosity makes the hole impenetrable for the normal fluid. If the entropy-less super-fluid flows from A to B then the entropy per particle is increased in A and decreased in B. As a result, A warms up and B cools down, the super-fluid carries "cold". In the inverse experiment two open vessel (same pressure) are connected by a narrow tube and the temperature difference is increased. This is followed by the flow of the super-fluid which was so strong in an early experiment that the He II fluid was thrown up in a jet in the colder vessel.

Another unique phenomenon related to the super-fluid component is the second sound. Many particle systems usually support sound waves, propagating disturbances of the particle density. The normal sound waves which have linear dispersion relation for long wavelength excitations, $E(k) = \hbar\omega(k) = \mathcal{O}(k)$, are called first sound. A generalization of the ordinary sound wave, the zero sound, occurs in Fermi liquids, the weakly interacting fermion systems. In fact, the rearrangement of the particle density at long distances requires the cooperation of a number of particles due to the conserved particle number. This diffusive cooperative phenomenon slows down the processes and makes it low energetic. We have a second sound in He II where the two components may establish an oscillatory motion with opposite phase (the same phase motion is a kind of first sound). The lowest energy realization of this oscillations keeps the density time independent and entropy is propagating along the wave. Low energy neutron scattering experiments provide the dispersion relation, the energy as the function of the momentum, for elementary excitations. In fact, the slow neutrons interact with the He atoms by creating thermal excitations only. The result supported Landau's assumption, the presence of new type of excitations at non-vanishing momenta. The qualitative dispersion relation, shown in Fig. 29, can be approximated as

$$E(k) = \begin{cases} \hbar ck & k \approx 0 \\ E_0 + \frac{\hbar^2(k-k_0)^2}{2m_0} & k \approx k_0, \end{cases}\tag{309}$$

with $c = 240\text{m/s}$, $E_0 = 8.65\text{K}$, $k_0 = 1.92\text{\AA}^{-1}$, $m_0/m = 0.16$. The density of state,

$$n(E) = \frac{k^2}{2\pi^2 \frac{dE}{dk}},\tag{310}$$

is large for the roton excitations with $k \approx k_0$ thus these two regions cover the important parts of the dispersion relation from the point of view of low temperature excitations.

D. Energy damping in super-fluid

The vanishing entropy of the super-fluid can easily be understood by noting that the condensate is represented by a single pure state. The nontrivial features of the super-fluid is its vanishing viscosity. The key to understand it is the

absence of gap in the elementary excitation spectrum, the fact that long wavelength excitations have linear dispersion relation. Feynman had a qualitative argument about the absence of other than phonon excitations in He II liquid. A more systematic way of understanding of the gapless spectrum comes from Goldstone theorem. This theorem assures in a trivial manner that the phonons have gapless, linear dispersion relation in solids. But for which symmetry is supposed to be broken by the super-fluid component? The order parameter of the Bose-Einstein condensate, $\psi(\mathbf{x})$, is the wave function of the lowest lying state weighted by the square root of the number of particles in the condensate. This quantity corresponds to macroscopic number of particles and as such can be obtained as an expectation value. The detailed manner this expectation value is calculated is rather involved and requires the formalism of Quantum Field Theory. It is enough to assume now that this local order parameter is given as an expectation value which breaks the continuous phase symmetry,

$$\psi(\mathbf{x}) \rightarrow e^{i\alpha}\psi(\mathbf{x}) \quad (311)$$

of Quantum Mechanics. The corresponding Goldstone gapless modes are the phonons of He II.

Once the linear dispersion relation is accepted then the vanishing viscosity of the super-fluid can easily be understood by following Landau's arguments. He assumes that the excited states of He II with occupation number $n_{\mathbf{k}}$ have the spectrum

$$E_{\{n\}} = E_{\text{cond}} + \sum_{\mathbf{k}} \hbar\omega_{\mathbf{k}}n_{\mathbf{k}}, \quad (312)$$

where E_0 denotes the energy of the condensate and

$$\langle n_{\mathbf{k}} \rangle = \frac{1}{e^{\beta\hbar\omega_{\mathbf{k}}} - 1}. \quad (313)$$

Let us now consider He II flowing through of a straight pipe line at sufficiently low temperature where the normal excitations have negligible weight. we regard the motion in the rest frame of the He II where we see the wall moving with velocity \mathbf{V} and momentum $\mathbf{P} = M\mathbf{V}$. Let us suppose that the moving wall creates phonons with occupation number $n_{\mathbf{p}}$. Then the energy and momentum loss of the tube are

$$\Delta E = \sum_{\mathbf{p}} c|\mathbf{p}|n_{\mathbf{p}}, \quad \Delta \mathbf{P} = \sum_{\mathbf{p}} \mathbf{p}n_{\mathbf{p}}, \quad (314)$$

satisfying the inequality

$$|\Delta \mathbf{P}| \leq \sum_{\mathbf{p}} |\mathbf{p}|n_{\mathbf{p}} = \frac{\Delta E}{c} = \frac{\mathbf{V}\Delta \mathbf{P}}{c}. \quad (315)$$

Thus the energy loss due to creation of gapless phonons is impossible for

$$|\mathbf{V}| < c. \quad (316)$$

The low momentum phonons give the upper bound $|\mathbf{V}| \leq 240\text{m/s}$ and rotons require $|\mathbf{V}| \leq 60\text{m/s}$. This argument valid for low enough temperatures where the phonon gas is dilute and the phonon-phonon interactions are negligible. But experiments show that superfluidity is already lost for much slower motion, for velocities few times m/s. Such a radical decrease of the maximal velocity is related to the dynamics of the vortex lines, to be considered next.

E. Vortices

The current represented by a particle of mass m and wave function $\psi(\mathbf{x})$ is given by the probability flux vector,

$$\mathbf{j}(\mathbf{x}) = \frac{\hbar}{2im}[\psi^*(\mathbf{x})\nabla\psi(\mathbf{x}) - \nabla\psi^*(\mathbf{x})\psi(\mathbf{x})] \quad (317)$$

and the local velocity can be defined by $\mathbf{v}(\mathbf{x}) = \mathbf{j}(\mathbf{x})/\psi^*(\mathbf{x})\psi(\mathbf{x})$. One can introduce the velocity of the condensate in a similar manner, by identifying $\psi(\mathbf{x})$ in the expression above with the order parameter of the condensate which is written as

$$\psi_{\text{cond}}(\mathbf{x}) = \sqrt{\rho_{\text{cond}}(\mathbf{x})}e^{i\phi(\mathbf{x})}. \quad (318)$$

A further simplification is made by assuming that $\rho_{\text{cond}}(\mathbf{x})$ is slowly varying compared to the phase $\phi(\mathbf{x})$,

$$\mathbf{v}_s(\mathbf{x}) = \frac{\hbar}{m} \nabla \phi(\mathbf{x}). \quad (319)$$

This velocity flow is irrotational,

$$\nabla \times \mathbf{v}_s = 0. \quad (320)$$

What happens if we place a He II in a cylinder which adiabatically brought into slow rotation with angular velocity ω ? Due to the finite temperature there are phonons in the system which contribute to the normal fluid and they interact. These interactions will slowly accelerate the super-fluid component, too. It has been demonstrated experimentally that we can bring the whole system into rotational motion in this manner. But the velocity profile in this case would be

$$\mathbf{v}_s(\mathbf{x}) = \mathbf{e}_\phi \omega r \quad (321)$$

and the circulation, defined by

$$\kappa = \oint_\gamma d\mathbf{x} \mathbf{v}_s \quad (322)$$

for a closed path γ would be non-vanishing. This is an apparent contradiction with the irrotational nature of the super-fluid because of the integral theorem

$$\oint_{\partial\Sigma} d\mathbf{x} \mathbf{v}_s = \int_\Sigma d\mathbf{n} \nabla \times \mathbf{v}_s, \quad (323)$$

where the boundary of the surface Σ is denoted by $\partial\Sigma$. The way out for this problem is to recall that the integral theorem is proven by breaking Σ into infinitesimal squares and summing up their circulation. This strategy, the cancellation of the line integral on the internal edges requires that the region σ be simply connected, ie. any closed loop in σ can be contracted into a point without leaving Σ . As soon as Σ is multiply connected and some points are missing in it the integral theorem is violated. Therefore, a natural way of saving the irrotational nature of the super-fluid is to assume that the density of the condensate is vanishing along some curves, called vortex lines. The circulation can be non-vanishing for any surface which is traversed by vortex line.

An important property of the super-fluid vortices is their quantized strength. This is due to the well defined nature of the phase $\phi(\mathbf{x})$ profile, requiring

$$\kappa = \frac{\hbar}{m} \oint_{\partial\Sigma} d\mathbf{x} \nabla \phi(\mathbf{x}) = 2\pi n \frac{\hbar}{m}. \quad (324)$$

The low energy, long distance excitations of the super-fluid are described by an irrotational, approximately incompressible fluid with quantized vorticity. It is worth recalling that the circulation in an ideal, isentropic fluid is conserved. Therefore, the vortex lines are such collective degrees of freedom of the super-fluid which acquire time dependence through the interaction with the normal component only.

VII. NONEQUILLIBRIUM PROCESSES

A. Stochastic processes

Definition: A family of random variables $X_t \in \mathbb{R}$, $t \in \mathbb{R}$ is called stochastic processes. It is characterized by the joint probability distributions

$$p_\ell(x_\ell, t_\ell, \dots, x_1, t_1) = P(X_{t_\ell} = x_\ell, \dots, X_{t_1} = x_1) \quad (325)$$

for $t_\ell > t_{\ell-1} \dots > t_1$ satisfying the following conditions

1. $p_\ell \geq 0$,
2. $\int dx_\ell p_\ell(x_\ell, t_\ell, \dots, x_1, t_1) = p_{\ell-1}(x_{\ell-1}, t_{\ell-1}, \dots, x_1, t_1)$, ($\ell \geq 2$),

$$3. \int dx p_1(x, t) = 1.$$

Furthermore, one introduces the correlation functions

$$\langle X_{t_1} \cdots X_{t_k} \rangle = \int d^\ell x p_\ell(x_\ell, t_\ell, \cdots, x_1, t_1) x_1 \cdots x_\ell \quad (326)$$

and the conditional probabilities

$$p_{k|\ell}(x_{\ell+k}, t_{\ell+k}, \cdots, x_{\ell+1}, t_{\ell+1} | x_\ell, t_\ell, \cdots, x_1, t_1) = \frac{p_{k+\ell}(x_{\ell+\ell}, t_{\ell+\ell}, \cdots, x_1, t_1)}{p_\ell(x_\ell, t_\ell, \cdots, x_1, t_1)}. \quad (327)$$

The stochastic process is called stationary if

$$\langle X_{t_1} \cdots X_{t_k} \rangle = \langle X_{t_1+\tau} \cdots X_{t_k+\tau} \rangle. \quad (328)$$

If the fundamental laws are invariant under time translation then the dynamics reaches equilibrium after some time and the corresponding stochastic process becomes stationary.

Example: Our system is a small, classical particle of coordinate $x(t)$ in a classical gas.

B. Markov process

Definition: A stochastic process is called Markov process if

$$p_{k|\ell}(x_{\ell+k}, t_{\ell+k}, \cdots, x_{\ell+1}, t_{\ell+1} | x_\ell, t_\ell, \cdots, x_1, t_1) = p_{k|1}(x_{\ell+k}, t_{\ell+k}, \cdots, x_{\ell+1}, t_{\ell+1} | x_\ell, t_\ell) \quad (329)$$

for $t_m \geq t_n$, $m > n$. This condition corresponds to first order differential equation as deterministic equation of motion. In fact, it is enough to specify one data for each degree of freedom to follow its dynamics.

Examples:

1. Disintegration process: Let X_t the number of radioactive nuclei at time t , $w(t) = e^{-\gamma t}$ denotes the probability that a radioactive nucleon survives time t and N stands for the total number of nuclei:

$$\begin{aligned} p_1^{(N)}(n, t) &= p^{(N)}(n) = \binom{N}{n} e^{-n\gamma t} (1 - e^{-\gamma t})^{N-n} \\ p_{1|1}(n, t | n', t') &= p(n, t | n', t') = p^{(n')}(n, t - t') = \binom{n'}{n} e^{-n\gamma(t-t')} (1 - e^{-\gamma(t-t')})^{n'-n}. \end{aligned} \quad (330)$$

2. Ehrenfest urn: One distributes the balls $1, \dots, N$ in two urns. In each minutes one generates a uniformly distributed random number $n_t \in \{1, \dots, N\}$ and puts the ball n in the other urn. The transition probability is

$$p(n, t + 1 | n', t) = \frac{n'}{N} \delta_{n, n'-1} + \left(1 - \frac{n'}{N}\right) \delta_{n, n'+1}. \quad (331)$$

3. Wiener process: A Markov process is specified by the initial probability distribution, $p(x, 0)$ and the transition probability, $p_{1|1}(n, t | n', t') = p(n, t | n', t')$. The Wiener process is defined by

$$p(x, t | x', t') = \frac{e^{-\frac{(x-x')^2}{4D(t-t')}}}{[4\pi D(t-t')]^{d/2}}, \quad (t > t'). \quad (332)$$

The physical relevance of this process is assured by the fact that the transition probability satisfies the heat equation,

$$\partial_t p(x, t | x', t') = D \Delta p(x, t | x', t'). \quad (333)$$

Theorem: The conditional probability $p(x_2, t_2 | x_1, t_1) = p_{1|1}(x_2, t_2 | x_1, t_1)$ of a Markov process for a numerical variable $X_t \in \mathbb{R}^n$ satisfies that Chapman-Kolmogorov equation,

$$p(x_2, t_2 | x_1, t_1) = \int dz p(x_2, t_2 | z, t) p(z, t | x_1, t_1) \quad (334)$$

where $t_1 \leq t \leq t_2$. This equation can be proven by comparing the first and last line in

$$\begin{aligned}
p(x_3, t_3) &= \int dx_1 p(x_3, t_3 | x_1, t_1) p(x_1, t_1) \\
&= \int dx_2 p(x_3, t_3 | x_2, t_2) p(x_2, t_2) \\
&= \int dx_2 p(x_3, t_3 | x_2, t_2) \underbrace{\int dx_1 p(x_2, t_2 | x_1, t_1) p(x_1, t_1)}_{p(x_2, t_2)}.
\end{aligned} \tag{335}$$

Example: Ornstein-Uhlenbeck process,

$$p_t(x, y) = \frac{e^{-\frac{(x-y)e^{-t}}{2(1-e^{-2t})}}}{\sqrt{2\pi(1-e^{-2t})}} \tag{336}$$

is a non-trivial realization of the Chapman-Kolmogorov equation.

Theorem: (Doob) The Ornstein-Uhlenbeck process is the only Markov stationary and Gaussian process.

Definition: A Markov process is homogeneous if $p(x, t | x', t') = p_{t-t'}(x, x')$, and stationary if it is homogeneous and $p(x, t) = p(x)$ (equilibrium).

C. Markov chain

We can not carry out measurement with arbitrary precision and must be satisfied by reproducing the observed phenomena in terms of discrete variables. The Markov chain is a simplified Markov process which is based on discrete rather than continuous variables.

Definition: The Markov process X_t is a Markov chain if $X_t \in N$ and $t = n\Delta t$. The transfer matrix of the Markov chain is $T_{\ell, m}(n\Delta t) = P(\ell, (n+1)\Delta t | m, n\Delta t)$.

Remark: For a homogeneous Markov chain with transfer matrix $T(n\Delta t) = T$ we have

$$P(\ell, n\Delta t | m, 0) = (T^n)_{\ell, m} \tag{337}$$

Definition: The matrix M is called stochastic if $M_{j, k} \geq 0$ and $\sum_j M_{j, k} = 1$.

Remark: T is a stochastic matrix.

Examples:

1. Two-state system:

$$T = \begin{pmatrix} 1-p & p \\ q & 1-q \end{pmatrix}. \tag{338}$$

2. Random walk:

$$p_2(n, t + \Delta t | n, t) = p, \quad p_2(n \pm 1, t + \Delta t | n, t) = q = \frac{1-p}{2} \tag{339}$$

$$T_{\text{abs. bound.}} = \begin{pmatrix} 1 & q & 0 & \cdots & 0 & 0 & 0 \\ 0 & p & q & \cdots & 0 & 0 & 0 \\ 0 & q & p & \cdots & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & \cdots & p & q & 0 \\ 0 & 0 & 0 & \cdots & q & p & 0 \\ 0 & 0 & 0 & \cdots & 0 & q & 1 \end{pmatrix}, \quad T_{\text{refl. bound.}} = \begin{pmatrix} p+q & q & 0 & \cdots & 0 & 0 & 0 \\ q & p & q & \cdots & 0 & 0 & 0 \\ 0 & q & p & \cdots & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & \cdots & p & q & 0 \\ 0 & 0 & 0 & \cdots & q & p & q \\ 0 & 0 & 0 & \cdots & 0 & q & p+q \end{pmatrix} \tag{340}$$

3. Ehrenfest urn:

$$T = \begin{pmatrix} 0 & \frac{1}{N} & 0 & \cdots & 0 & 0 & 0 \\ 1 & 0 & \frac{2}{N} & \cdots & 0 & 0 & 0 \\ 0 & \frac{N-1}{N} & 0 & \cdots & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & \cdots & 0 & \frac{1-N}{N} & 0 \\ 0 & 0 & 0 & \cdots & \frac{2}{N} & 0 & 1 \\ 0 & 0 & 0 & \cdots & 0 & \frac{1}{N} & 0 \end{pmatrix} \quad (341)$$

D. Master equation

The the Chapman-Kolmogorov equation describes the evolution of the transition probability during a finite time. The simplification when the evolution over infinitesimal time is considered is that the system can not make a finite jump and the integral equation reduces a differential equation, the master equation.

Theorem: Denote $p_t(x, y)$ the transition probability of a homogeneous Markov process which can be written in the limit $t \rightarrow 0$ as

$$p_t(x, y) = [1 - a(y)t]\delta(x - y) + tW(x, y) + \mathcal{O}(t^2), \quad (342)$$

where $W \geq 0$ and $a(y) = \int dx W(x, y)$. The Chapman-Kolmogorov equation

$$\begin{aligned} p_{t+t'}(x, y) &= \int p_{t'}(x, z)p_t(z, y)dz \\ &= [1 - a(x)t']p_t(x, y) + t' \int W(x, z)p_t(z, y) + \mathcal{O}(t'^2) \end{aligned} \quad (343)$$

gives

$$\partial_t p_t(x, y) = \int [W(x, z)p_t(z, y) - W(z, x)p_t(x, y)]dz \quad (344)$$

for $t' \rightarrow 0$.

Remarks:

1. The master equation reads for the probability distribution $p(x, t) = \int p_t(x, y)p(y, 0)dy$ as

$$\partial_t p(x, t) = \int [W(x, z)p(z, t) - W(z, x)p(x, t)]dz. \quad (345)$$

2. The Master equation for a Markov chain is

$$\partial_t p_n(t) = \sum_m [W_{n,m}p_m(t) - W_{m,n}p_n(t)] = \sum_{m \neq n} [W_{n,m}p_m(t) - W_{m,n}p_n(t)] \quad (346)$$

Example: The disintegration process is defined by the transition probability

$$p_{\Delta t}(m, n) = \begin{cases} 0 & \text{if } m > n, \\ n\gamma\Delta t & \text{if } m = n - 1, \\ \mathcal{O}(\Delta^2 t) & \text{if } m < n - 1, \end{cases} \quad (347)$$

yielding

$$W_{m,n} = \gamma n \delta_{m,n-1} \quad (m \neq n). \quad (348)$$

The Master equation,

$$\begin{aligned}\dot{p}_n(t) &= \sum_m [W_{n,m}p_m(t) - W_{m,n}p_n(t)] \\ &= \gamma(n+1)p_{n+1}(t) - \gamma np_n(t)\end{aligned}\tag{349}$$

yields the differential equation

$$\begin{aligned}\partial_t \langle n(t) \rangle &= \sum_{n=0}^{\infty} n \dot{p}_n \\ &= \gamma \sum_{n=0}^{\infty} n(n+1)p_{n+1}(t) - \gamma \sum_{n=0}^{\infty} n^2 p_n(t) \\ &= \gamma \sum_{n=0}^{\infty} (n-1)np_n(t) - \gamma \sum_{n=0}^{\infty} n^2 p_n(t) \\ &= -\gamma \sum_{n=0}^{\infty} np_n(t) \\ &= -\gamma \langle n(t) \rangle\end{aligned}\tag{350}$$

whose solution is

$$s \langle n(t) \rangle = n_0 e^{-\gamma t}.\tag{351}$$

E. Equilibrium

It is of central importance to establish the condition of stationary, i.e. equilibrium of stochastic processes. Two theorems are mentioned here without proof.

Theorem: All finite dimensional stochastic matrix generate equilibrium except some special cases (Perron-Frobenius).

If p_n^s is a stationary probability distribution then

$$\sum_m W_{n,m}p_m^s = \left(\sum_m W_{m,n}\right)p_n^s,\tag{352}$$

the gain and loss balance each other. A stronger conditions, the detailed balance is

$$W_{n,m}p_m^s = W_{m,n}p_n^s.\tag{353}$$

Theorem: The detailed balance is a sufficient condition that the distribution p_n^s be stationary.

This theorem is the basis of the Monte-Carlo simulation method.

VIII. BROWNIAN MOTION

The simplest physical realization of a stochastic process is the Brownian motion, the dynamics of a dust particle in the air.

A. Diffusion equation

The probabilistic dynamics of a classical particle is based on the probability density $n(\mathbf{x}, t)$ and the probability current $\mathbf{j}(\mathbf{x}, t)$, satisfying the continuity equation $\partial_t n = -\nabla \cdot \mathbf{j}$. Fick equation relates the current to the inhomogeneity of the probability density and a drift, caused by the external force \mathbf{F} ,

$$\mathbf{j} = -D \nabla n + \frac{1}{f} n \mathbf{F},\tag{354}$$

where D and f denote the diffusion and the friction constants, respectively. Together with the continuity equation we have the diffusion equation

$$\partial_t n = D\Delta n - \frac{1}{f}\nabla(n\mathbf{F}) = D\Delta n - \frac{1}{f}\mathbf{F}\nabla n - \frac{1}{f}\nabla\mathbf{F}n. \quad (355)$$

Remark: Observe that the diffusion equation can formally be obtained from the Schrödinger equation,

$$\begin{aligned} i\hbar\partial_t\psi &= \frac{1}{2m}\underbrace{\left(\frac{\hbar}{i}\nabla - \frac{e}{c}\mathbf{A}\right)}_{\hat{p}}^2\psi + U\psi \\ &= -\frac{\hbar^2}{2m}\Delta\psi + \frac{ie\hbar}{2mc}(\nabla\mathbf{A} + \mathbf{A}\nabla)\psi + \frac{e^2}{2mc^2}\mathbf{A}^2\psi + U\psi \\ &= -\underbrace{\frac{\hbar^2}{2m}\Delta\psi}_D + \underbrace{\frac{ie\hbar}{mc}\mathbf{A}\nabla\psi}_{\mathbf{F}/f} + \underbrace{\left[\frac{e}{2mc}\left(i\hbar\nabla\mathbf{A} + \frac{e}{c}\mathbf{A}^2\right) + U\right]}_{\nabla\mathbf{F}/f}\psi \end{aligned} \quad (356)$$

by the Wick rotation, ie. the analytic continuation to complex time, $t \rightarrow -i\hbar\tau$. This relation between Quantum Mechanics and classical Statistical Physics, one can be obtained by a Wick rotation from the other, is not restricted to this case and can be traced down to the choice of the density matrix of the canonical ensemble.

The unusual term with the first derivative can easily be eliminated by the gauge transformation

$$\begin{aligned} \psi(\mathbf{x}, t) &\rightarrow e^{i\frac{e}{\hbar c}\theta(\mathbf{x})}\psi(\mathbf{x}, t) \\ \mathbf{A}(\mathbf{x}, t) &\rightarrow \mathbf{A}(\mathbf{x}, t) + \nabla\theta \end{aligned} \quad (357)$$

for which $\hat{p}\psi \rightarrow e^{i\frac{e}{\hbar c}\theta}\hat{p}\psi$. By writing $\mathbf{A} = \nabla\phi$, $\psi = e^{-i\frac{e}{\hbar c}\phi}\chi$ we find

$$i\hbar\partial_t\chi = -\frac{\hbar^2}{2m}\Delta\chi. \quad (358)$$

In an analogous manner one looks for the solution of the diffusion equation in the form $n = pe^{\kappa u}$. The relations

$$\begin{aligned} \nabla n &= (\nabla p + \kappa p\nabla u)e^{\kappa u} \\ \Delta n &= [\Delta p + 2\kappa\nabla p\nabla u + \kappa p\Delta u + \kappa^2 p(\nabla u)^2]e^{\kappa u} \end{aligned} \quad (359)$$

give

$$\begin{aligned} \partial_t p &= D\Delta p + 2D\kappa\nabla p\nabla u + D\kappa p\Delta u + D\kappa^2 p(\nabla u)^2 + \frac{1}{f}\nabla u\nabla p + \frac{1}{f}p\kappa(\nabla u)^2 + \frac{1}{f}p\Delta u \\ &= D\Delta p + \underbrace{\left(2D\kappa + \frac{1}{f}\right)}_0\nabla p\nabla u + \underbrace{\left(D\kappa\Delta u + D\kappa^2(\nabla u)^2 + \frac{1}{f}\kappa(\nabla u)^2 + \frac{1}{f}\Delta u\right)}_U p. \end{aligned} \quad (360)$$

where the choice $f^{-1} = -2D\kappa$ was made.

The solution of the diffusion equation is particularly simple for free particles, $\mathbf{F} = 0$, when $\partial_t p = D\Delta p$. The solution which corresponds to the initial condition $p(\mathbf{x}, t_0) = p_0(\mathbf{x})$ is written as

$$p(\mathbf{x}, t) = \int d^3y \underbrace{G(\mathbf{x}, t, \mathbf{y}; t_0)}_{propagator} p_0(\mathbf{y}) \quad (361)$$

where the master equation gives

$$\partial_t G(\mathbf{x}, t, \mathbf{y}; t_0) = D\Delta_x G(\mathbf{x}, t, \mathbf{y}; t_0). \quad (362)$$

The initial condition $G(\mathbf{x}, t, \mathbf{y}; t) = \delta(\mathbf{x} - \mathbf{y})$ leads to the solution

$$G(\mathbf{x}, t, \mathbf{y}; t_0) = \frac{1}{[4\pi D(t - t_0)]^{3/2}} e^{-\frac{(\mathbf{x} - \mathbf{y})^2}{4D(t - t_0)}} \quad (363)$$

which satisfies the Chapman-Kolmogorov equation.

$$G(\mathbf{x}, t, \mathbf{y}; t_0) = \int d^3z G(\mathbf{x}, t, \mathbf{z}; t_1) G(\mathbf{z}, t_1, \mathbf{y}; t_0) \quad (364)$$

with $t_0 \leq t_1 \leq t$.

B. Fokker-Planck equation

The master equation, an integro-differential equation, can systematically be truncated and a differential equation can be recovered for certain Markov processes. This scheme goes under the name Kramers-Moyal (gradient) expansion. The probability distribution $p(x, t)$ of a Markov process satisfies the master equation

$$\begin{aligned}\partial_t p(x, t) &= \int W(x, z)p(z, t)dz - p(x, t) \int W(z, x)dz \\ &= \int w(z, x - z)p(x - z, t)dz - p(x, t) \int w(-z, x)dz,\end{aligned}\quad (365)$$

where $w(x - y, y) = W(x, y)$. Let us assume that

1. the jump is sufficiently small, ie. $W(x, z) \approx 0$ for large $|x - z|$ and
2. the probability distribution $p(x, t)$ and the conditional probability $w(y, x)$ vary sufficiently slowly in x .

The Taylor expansion

$$p(z, t) \approx p(x, t) + (z - x)p'(z, t) + \frac{1}{2}(z - x)^2 p''(z, t) + \dots \quad (366)$$

yields the form

$$\partial_t p(x, t) = \int dz \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} z^n \partial_x^n [w(z, x)p(x, t)] - p(x, t) \int dz w(-z, x) \quad (367)$$

for the master equation. One introduces the moments of the jump,

$$M_n(x) = \int dz z^n w(z, x) \quad (368)$$

and finds

$$\partial_t p(x, t) = \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \partial_x^n [M_n(x)p(x, t)]. \quad (369)$$

Conditions 2. and 1. above assure the availability of the expansion in the jump in the arguments $x - z$ of the master equation and the finiteness of the moments M_n , respectively.

The following theorem covers an important class of Markov process, the Brownian motion.

Theorem: The Markov process X whose moments are

$$M_n(x) = \int dz z^n \frac{1}{\Delta t} p(x + z, t + \Delta t | x, t) = \begin{cases} \mathcal{O}((\Delta t)^0) & n = 1 \\ \mathcal{O}((\Delta t)^{n/2-1}) & n \geq 2 \end{cases} \quad (370)$$

the master equation can be truncated at $n = 2$ and the probability distribution $p(X(t) = t) = p(x, t)$ satisfies the Fokker-Planck equation

$$\partial_t p(x, t) = - \underbrace{\partial_x [M_1(x)p(x, t)]}_{\text{transport, drift}} + \frac{1}{2} \underbrace{\partial_x^2 [M_2(x)p(x, t)]}_{\text{fluctuation, diffusion}}. \quad (371)$$

Exemples:

1. The transition probability of a d -dimensional homogeneous motion, the Brownian motion is given by

$$p(\mathbf{x}, t + \Delta t | \mathbf{y}, t) = \frac{1}{(4\pi D \Delta t)^{d/2}} e^{-\frac{(\mathbf{x}-\mathbf{y})^2}{4D\Delta t}}, \quad (372)$$

where Δt is a time scale longer than the microscopic collision time and the relaxation time of the velocity, $\tau_{\text{coll}}, \tau_{\text{rel}} \ll \Delta t$. The moments of the jump in time Δt are

$$\begin{aligned}
M_{2n} &= \frac{1}{\Delta t (4\pi D \Delta t)^{1/2}} \int dy y^{2n} e^{-\frac{y^2}{4D\Delta t}} \\
&= \frac{(4D\Delta t)^{n+\frac{1}{2}}}{\Delta t (4\pi D \Delta t)^{1/2}} \int dz^{2n} e^{-z^2} \\
&= \frac{(4D\Delta t)^{n+\frac{1}{2}}}{\Delta t (4\pi D \Delta t)^{1/2}} (-1)^n \partial_c^n \underbrace{\int dz e^{-cz^2}}_{(\pi/c)^{1/2}} \Big|_{c=1} \\
&= \frac{1 \cdot 3 \cdots 2n-1}{2^n} (4D)^n \Delta t^{n-1} = \mathcal{O}\left(\frac{|\Delta x|^{2n}}{\Delta t}\right)
\end{aligned} \tag{373}$$

In particular,

$$\frac{|\Delta x|}{\Delta t} = \mathcal{O}\left(\Delta t^{-1/2}\right) \tag{374}$$

and the trajectory is nowhere differentiable, the velocity is diverging. This is naturally a mathematical problem only because our simple description of the motion loses validity in the limit $\Delta t \rightarrow 0$. The scaling law $\langle (\Delta x)^2 \rangle = 2D\Delta t$ is called diffusive.

2. One dimensional inhomogeneous motion: The probability density p and vector J satisfy the continuity equation, $\partial_t p = -\partial_x J$, therefore the Fokker-Planck equation can be integrated yielding

$$J = M_1(x, t)p(x, t) - \frac{1}{2}\partial_x[M_2(x, t)p(x, t)]. \tag{375}$$

- The stationary solution for $J_x = J = 0$ satisfies the equation

$$0 = \frac{M_1(x)}{M_2(x)} \underbrace{M_2(x)p(x)}_{y(x)} - \frac{1}{2}\partial_x[M_2(x)p(x)] \tag{376}$$

which can be integrated again,

$$\int^x dx \frac{M_1(x)}{M_2(x)} = \frac{1}{2} \ln y(x) + C. \tag{377}$$

The solution is

$$\begin{aligned}
p(x) &= \frac{N}{M_2(x)} e^{2 \int^x dx \frac{M_1(x)}{M_2(x)}} \\
&= N e^{-\Phi(x)}, \quad \Phi(x) = \ln M_2(x) - 2 \int^x dx \frac{M_1(x)}{M_2(x)}.
\end{aligned} \tag{378}$$

- The stationary state solution $J_x = J \neq 0$ is parametrized as

$$p(x) = J e^{-\Phi(x)} f(x) \tag{379}$$

and the function $f(x)$ satisfies the equation

$$\begin{aligned}
1 &= \frac{M_1(x)}{M_2(x)} e^{-\Phi(x)} M_2(x) f(x) - \frac{1}{2} \partial_x [e^{-\Phi(x)} M_2(x) f(x)] \\
&= \frac{M_1(x)}{M_2(x)} e^{-\Phi(x)} M_2(x) f(x) - \frac{1}{2} M_2(x) f(x) \partial_x e^{-\Phi(x)} - \frac{1}{2} e^{-\Phi(x)} \partial_x (M_2(x) f(x)) \\
&= -\frac{1}{2} e^{-\Phi(x)} \partial_x (M_2(x) f(x))
\end{aligned} \tag{380}$$

which can easily be integrated,

$$f(x) = f(x_0) \frac{M_2(x_0)}{M_2(x)} - \frac{2 \int_{x_0}^x dx' e^{\Phi(x')}}{M_2(x)} \quad (381)$$

where C is an integration constant. Therefore, the solution is

$$\begin{aligned} p(x) &= J \frac{e^{-\Phi(x)}}{M_2(x)} \left(f(x_0) M_2(x_0) - 2 \int_{x_0}^x dx e^{\Phi(x)} \right) \\ &= e^{-\Phi(x)} \left(p(x_0) e^{\Phi(x_0)} \frac{M_2(x_0)}{M_2(x)} - \frac{2J \int_{x_0}^x dx' e^{\Phi(x')}}{M_2(x)} \right). \end{aligned} \quad (382)$$

3. The master equation for a one-dimensional random walk,

$$\dot{p}(an, t) = \alpha[p(a(n+1), t) - p(an, t)] + \beta[p(a(n-1), t) - p(an, t)] \quad (383)$$

becomes a differential equation,

$$\begin{aligned} \dot{p}(x, t) &= \left(\frac{B}{2a^2} - \frac{A}{2a} \right) \left(a \partial_x p(x, t) + \frac{1}{2} a^2 \partial_x^2 p(x, t) + \dots \right) \\ &\quad + \left(\frac{B}{2a^2} + \frac{A}{2a} \right) \left(-a \partial_x p(x, t) + \frac{1}{2} a^2 \partial_x^2 p(x, t) - \dots \right) \\ &= -A \partial_x p(x, t) + \frac{1}{2} B \partial_x^2 p(x, t) + \mathcal{O}(a^2), \end{aligned} \quad (384)$$

in the continuum limit, $a \rightarrow 0$, where

$$\beta - \alpha = \frac{A}{a}, \quad \beta + \alpha = \frac{B}{a^2}. \quad (385)$$

4. Let us consider the one-dimensional motion of a particle under the influence of a homogeneous gravitational force $-gm$ and the friction force $-\gamma m \dot{x}$, when we have

$$\begin{aligned} M_1 &= \frac{\langle \Delta X \rangle}{\Delta t} = -\frac{g}{\gamma}, \\ M_2 &= 2D. \end{aligned} \quad (386)$$

The Fokker-Planck equation,

$$\partial_t p(x, t) = \frac{g}{\gamma} \partial_x p(x, t) + D \partial_x^2 p(x, t), \quad (387)$$

can be integrated by taking into account the continuity equation,

$$J(x, t) = -\frac{g}{\gamma} p(x, t) - D \partial_x p(x, t). \quad (388)$$

The stationary solution for with the boundary condition $J(0, t) = 0$ is

$$p^s(x) = \text{const.} e^{-\frac{g}{\gamma D} x}. \quad (389)$$

The comparison with the barometric formula,

$$p^s(x) = \text{const.} e^{-\frac{gm}{T} x} \quad (390)$$

yields the Einstein relation $D = T/m\gamma$ and

$$\frac{\langle (\Delta X)^2 \rangle}{\Delta t} = \frac{2T}{m\gamma}. \quad (391)$$

5. We now assume an inhomogeneous external force $F(x)$ and the friction force, $-\gamma m\dot{x}$, acting on the particle. If the external force varies slowly within the correlation length of the velocity then we have a Fokker-Planck equation for the probability distribution of the coordinate,

$$\partial_t p(x, t) = -\partial_x \left[\frac{F(x)}{m\gamma} p(x, t) \right] + D \partial_x^2 p(x, t) \quad (392)$$

(Kramer). If $F(x)$ varies faster then we need a bi-dimensional Fokker-Planck equation for the probability distribution $p(x, v, t)$,

$$\begin{aligned} D_{\text{conv}} p(x, v, t) &= \partial_t p(x, v, t) + \underbrace{v}_{\text{"}\dot{x}\text{"}} \partial_x p(x, v, t) + \underbrace{\frac{F(x)}{m}}_{\text{"}\dot{v}\text{"}} \partial_v p(x, v, t) \\ &= \gamma \left(\partial_v [vp(v, t)] + \frac{T}{m} \partial_v^2 p(v, t) \right), \end{aligned} \quad (393)$$

where

$$\begin{aligned} \langle \Delta X \rangle &= V \Delta t \\ \langle \Delta V \rangle &= \left(\frac{F(X)}{m} - \gamma V \right) \Delta t \\ \langle (\Delta X)^2 \rangle &= V^2 (\Delta t)^2 \rightarrow 0 \\ \langle \Delta V \Delta X \rangle &= V \left(\frac{F(X)}{m} - \gamma V \right) (\Delta t)^2 \rightarrow 0 \\ \langle (\Delta V)^2 \rangle &= \gamma \frac{T}{m} \Delta t \end{aligned} \quad (394)$$

6. The Rayleigh particle is subject of a dynamics which is followed by the observational time step Δt with $\tau_{\text{coll}} \ll \Delta t \ll \tau_{v \text{ rel}}$. The latter inequality suggests that the velocity is overdamped, $\langle \dot{V} \rangle = -\gamma \langle V \rangle$, and we have

$$\begin{aligned} M_1(V) &= \frac{\langle \Delta V \rangle}{\Delta t} = -\gamma V \\ M_2(V) &= a_2 + \mathcal{O}(V^2) \approx a_2 > 0 \end{aligned} \quad (395)$$

yielding

$$\partial_t p(v, t) = \gamma \partial_v [vp(v, t)] + \frac{M_2}{2} \partial_v^2 p(v, t). \quad (396)$$

Remarks:

- (a) The stationary solution with $J = 0$ is

$$\begin{aligned} \Phi(v) &= \ln a_2 + \frac{\gamma v^2}{M_2} \\ p(v) &= N' e^{-\frac{\gamma v^2}{a_2}} = N' e^{-\frac{mv^2}{2T}} \end{aligned} \quad (397)$$

and $M_2 = 2\gamma T/m$.

- (b) The solution of the equation

$$\partial_t p(v, t) = \gamma \left(\partial_v [vp(v, t)] + \frac{T}{m} \partial_v^2 p(v, t) \right) \quad (398)$$

which corresponds to the initial condition $p(v, 0) = \delta(v - v_0)$,

$$p(v, t) = \frac{1}{\sqrt{\frac{2\pi T}{m}(1 - e^{-2\gamma t})}} e^{-\frac{m}{2T} \frac{(v - v_0 e^{-\gamma t})^2}{1 - e^{-2\gamma t}}}, \quad (399)$$

is an Ornstein-Uhlenbeck process.

IX. LINEAR RESPONSE

The large, truly non-equilibrium systems are beyond our analytic capabilities. But the weak non-equilibrium, a small subsystem embedded in a reservoir, can be handled in perturbation expansion in the interaction between the system and the reservoir.

A. Response function

Let us suppose that the environment, the external perturbations can be taken into account by the extension $H = H_0 + V$ of the Hamiltonian where

$$V = \sum_j g_j h_j(t), \quad (400)$$

$\{g_j(q, p)\}$ being a set of dynamical quantity. We start with the classical description and write the equation of motion for a dynamical quantities, $f(q, p)$,

$$\dot{f} = \{f, H\} \quad (401)$$

in terms of the Poisson bracket,

$$\{f(q, p), g(q, p)\} = \sum_i \left(\frac{\partial f}{\partial q_i} \frac{\partial g}{\partial p_i} - \frac{\partial f}{\partial p_i} \frac{\partial g}{\partial q_i} \right) \quad (402)$$

and the Hamiltonian H . The formal integral of the equation of motion

$$f(t) = f(t_0) + \sum_j \int_{t_0}^t dt' \{f, H_0 + g_j\} h_j(t'), \quad (403)$$

can easily be linearized in the perturbation. We write $f(t) = f_0(t) + \delta f(t) + \mathcal{O}(h^2)$ and find

$$\delta f(t) = \sum_j \int_{t_0}^t dt' \{f_0, g_{0j}\} h_j(t'), \quad (404)$$

where the 0 subscript indicates that the quantity is considered in the absence of external perturbations. The Poisson bracket in the integrand, called the response function or susceptibility, describes the linear response of $f(t)$ to the perturbation $h(t')$. It can in principle be calculated but it is enough to state now that it is simply a function $\tilde{\chi}_{f, g_i}(t, t')$ appearing in the linear response formula

$$\delta f(t) = \sum_j \int_{-\infty}^{\infty} \tilde{\chi}_{f, g_j}(t, t') h_j(t'). \quad (405)$$

In case of a random environment one finds

$$\langle \delta f(t) \rangle = \sum_j \int_{-\infty}^{\infty} \tilde{\chi}_{f, g_j}(t, t') h_j(t'). \quad (406)$$

with $\tilde{\chi}_{f, g_j}(t, t') = \langle \{f_0, g_{0j}\} \rangle$.

The quantum mechanical description is based on the Schrödinger equation

$$i\hbar \partial_t |\psi(t)\rangle = H |\psi(t)\rangle \quad (407)$$

whose solution can be written as

$$|\psi(t)\rangle = U(t, t_0) |\psi(t_0)\rangle \quad (408)$$

by introducing the time evolution operator $U(t, t_0)$ which is $e^{-\frac{i}{\hbar}(t-t_0)H}$ for a time independent Hamiltonian H . In order to treat the environment as a perturbation we go over the interaction representation and "take out" the time dependence generated by the unperturbed Hamiltonian by performing a time dependent basis transformation,

$$|\psi(t)\rangle \rightarrow |\psi(t)\rangle_i = e^{\frac{i}{\hbar}(t-t_0)H_0} |\psi(t)\rangle. \quad (409)$$

The expectation values should be the same in the new representation than in the original one, therefore the operators acquire a time dependence,

$$A_i(t) = e^{\frac{i}{\hbar}(t-t_0)H_0} A e^{-\frac{i}{\hbar}(t-t_0)H_0} \quad (410)$$

which amounts to the equation of motion

$$i\hbar\partial_t A_i = [A_i, H_0]. \quad (411)$$

The state vector satisfies the Schrödinger equation

$$\begin{aligned} i\hbar\partial_t |\psi(t)\rangle_i &= i\hbar\partial_t [e^{\frac{i}{\hbar}(t-t_0)H_0} |\psi(t)\rangle] \\ &= -H_0 e^{\frac{i}{\hbar}(t-t_0)H_0} |\psi(t)\rangle + e^{\frac{i}{\hbar}(t-t_0)H_0} (H_0 + V) |\psi(t)\rangle \\ &= e^{\frac{i}{\hbar}(t-t_0)H_0} V \underbrace{e^{-\frac{i}{\hbar}(t-t_0)H_0} e^{\frac{i}{\hbar}(t-t_0)H_0}}_{\mathbb{1}} |\psi(t)\rangle \\ &= V_i |\psi(t)\rangle_i \end{aligned} \quad (412)$$

involving the interaction Hamiltonian

$$V_i(t) = \sum_j g_{ji}(t) h_j(t) \quad (413)$$

only. The equation of motion for the density matrix (cf. Appendix B) in the interaction representation is

$$\begin{aligned} i\hbar\partial_t \rho_i &= i\hbar\partial_t \sum_n |n\rangle p_n \langle n| \\ &= V_i \sum_n |n\rangle p_n \langle n| - \sum_n |n\rangle p_n \langle n| V_i \\ &= [V_i, \rho_i] \end{aligned} \quad (414)$$

which can be solved iteratively,

$$\rho_i(t) = \rho(t_0) - \frac{i}{\hbar} \int_{t_0}^t dt' [V_i(t'), \rho(t_0)] + \mathcal{O}(V^2). \quad (415)$$

The average of an observable A is

$$\begin{aligned} \langle A(t) \rangle &= \text{Tr}[A_i(t) \rho_i(t)] \\ &= \text{Tr}[A_i(t) \rho(t_0)] - \frac{i}{\hbar} \int_{t_0}^t dt' \text{Tr}[A_i(t) [V_i(t'), \rho(t_0)]] \\ &= \langle A(t) \rangle_0 - \frac{i}{\hbar} \int_{t_0}^t dt' (\text{Tr}[A_i(t) V_i(t') \rho(t_0)] - \text{Tr}[A_i(t) \rho(t_0) V_i(t')]) \\ &= \langle A(t) \rangle_0 - \frac{i}{\hbar} \int_{t_0}^t dt' (\text{Tr}[\rho(t_0) A_i(t) V_i(t')] - \text{Tr}[\rho(t_0) V_i(t') A_i(t)]) \\ &= \langle A(t) \rangle_0 + \frac{i}{\hbar} \int_{t_0}^t dt' \text{Tr}[\rho(t_0) [V_i(t'), A_i(t)]]. \end{aligned} \quad (416)$$

up to non-linear terms $\mathcal{O}(V^2)$. Note that this result can be recovered from the classical expressions by the formal replacement of the Poisson bracket by $1/i\hbar$ times the commutator and considering the expectation values. The linear response is thus

$$\begin{aligned} \delta\langle A(t) \rangle &= -\frac{i}{\hbar} \int_{t_0}^t dt' \text{Tr}[\rho(t_0) [A_i(t), V_i(t')]] \\ &= \sum_j \int_{t_0}^{\infty} dt' \tilde{\chi}_{A, g_j}(t, t') h_j(t') \end{aligned} \quad (417)$$

where the linear response function

$$\chi_{A, B}(t, t') = G_{A, B}^R(t', t) \quad (418)$$

is defined in terms of the retarded Green function

$$i\hbar G_{A, B}^R(t, t') = \Theta(t - t') \text{Tr}[\rho(t_0) [A(t), B(t')]]. \quad (419)$$

B. Kubo formula for the electric conductivity

Let us apply this formalism for the electric conductivity σ defined as the proportion of a weak external electric field and the current induced by it,

$$j_k = \sigma_{k,\ell} E_\ell. \quad (420)$$

The minimal coupling prescription, $\mathbf{p} \rightarrow \mathbf{p} - e\mathbf{A}$ produces the electric current operator $\hat{\mathbf{j}}_c$ with the matrix elements

$$\begin{aligned} \langle \phi | \hat{\mathbf{j}}_c(\mathbf{x}) | \psi \rangle &= \frac{e\hbar}{2mi} \left[\phi^*(\mathbf{x}) \left(\nabla - \frac{ie}{\hbar} \mathbf{A}(\mathbf{x}) \right) \psi(\mathbf{x}) - \left(\left(\nabla - \frac{ie}{\hbar} \mathbf{A}(\mathbf{x}) \right) \phi(\mathbf{x}) \right)^* \psi(\mathbf{x}) \right] \\ &= \langle \phi | \hat{\mathbf{j}}(\mathbf{x}) | \psi \rangle - \frac{e^2}{m} \mathbf{A}(\mathbf{x}) \phi^*(\mathbf{x}) \psi(\mathbf{x}) \end{aligned} \quad (421)$$

where

$$\langle \phi | \hat{\mathbf{j}}(\mathbf{x}) | \psi \rangle = \frac{e\hbar}{2mi} (\phi^*(\mathbf{x}) \nabla \psi(\mathbf{x}) - \nabla \phi^*(\mathbf{x}) \psi(\mathbf{x})). \quad (422)$$

The Hamiltonian

$$\begin{aligned} H &= \frac{1}{2m} (\mathbf{p} - e\mathbf{A})^2 \\ &= \frac{\mathbf{p}^2}{2m} - \frac{e}{2m} (\mathbf{p}\mathbf{A} + \mathbf{A}\mathbf{p}) + \frac{e}{2m} \mathbf{A}^2, \end{aligned} \quad (423)$$

yields the perturbation

$$V = - \int d^3x \mathbf{j}(\mathbf{x}) \mathbf{A}(\mathbf{x}) + \int d^3x \frac{e}{2m} \mathbf{A}^2. \quad (424)$$

In fact,

$$\langle \phi | V | \psi \rangle = - \int d^3x \frac{e\hbar}{2mi} (\phi^*(\mathbf{x}) \nabla \psi(\mathbf{x}) - \nabla \phi^*(\mathbf{x}) \psi(\mathbf{x})) \mathbf{A}(\mathbf{x}) + \int d^3x \frac{e}{2m} \mathbf{A}^2. \quad (425)$$

In the leading order we can neglect the term $\mathcal{O}(\mathbf{A}^2)$ and arrive at the Kubo formula,

$$\langle \langle j_k(t, \mathbf{x}) \rangle \rangle = - \frac{e^2 n}{m} A_k(t, \mathbf{x}) - \int dt' d^3y G_{j_k, j_\ell}^R((t, \mathbf{x}), (t', \mathbf{y})) A_\ell(t', \mathbf{y}) \quad (426)$$

where $n = n(t, \mathbf{x})$ is the homogeneous, unperturbed density. The Fourier transformation gives

$$\begin{aligned} j_k(\omega, \mathbf{k}) &= \int dt d^3x e^{i\omega t - i\mathbf{x}\mathbf{k}} j_k(t, \mathbf{x}) \\ &= - \frac{e^2 n}{m} \int dt d^3x \frac{d\omega' d^3k'}{(2\pi)^4} e^{i(\omega - \omega')t - i\mathbf{x}(\mathbf{k} - \mathbf{k}')} A_k(\omega', \mathbf{k}') \\ &\quad - \int dt d^3x dt' d^3y \frac{d\omega' d^3k' d\omega'' d^3k''}{(2\pi)^8} e^{i\omega t - i\mathbf{x}\mathbf{k} - i\omega'(t-t') + i\mathbf{k}'(\mathbf{x}-\mathbf{y}) - i\omega''t' + i\mathbf{k}''\mathbf{y}} \\ &\quad \times G_{j_k, j_\ell}^R(\omega', \mathbf{k}') A_\ell(\omega'', \mathbf{k}'') \\ &= - \left[\frac{e^2 n}{m} \delta_{k,\ell} + G_{j_k, j_\ell}^R(\omega, \mathbf{k}) \right] A_\ell(\omega, \mathbf{k}) \end{aligned} \quad (427)$$

identifying the AD conductivity

$$\sigma_{k,\ell}(\omega, \mathbf{k}) = - \frac{e^2 n}{m\omega} \delta_{k,\ell} - \frac{1}{\omega} G_{j_k, j_\ell}^R(\omega, \mathbf{k}) \quad (428)$$

because $\mathbf{E} = -\partial_t \mathbf{A}$.

C. Causality and analytic structure

Causality stands for our daily experience that the integration in the above linear response formula should be carried out between the initial and the observation time only, the effects propagate in a retarded and not an advanced manner. This can formally be achieved by inserting a Heavyside function as a multiplicative factor in the response function

$$\tilde{\chi}_{fg}(t, t') = \tilde{\chi}_{fg}(t - t') = 2i\Theta(t - t')\tilde{\chi}_{fg}^{(2)}(t, t'). \quad (429)$$

Note that the reduced response function $\chi^{(2)}$ is purely imaginary.

We turn now to the study of the consequences of causality in the analytical structure of the response function. For this end we go over frequency space by introducing the Fourier transforms

$$f(t) = \int \frac{d\omega}{2\pi} e^{-i\omega t} f(\omega), \quad f(\omega) = \int dt e^{i\omega t} f(t). \quad (430)$$

We assume now that the original Hamiltonian is time independent. Then the unperturbed equations of motion are invariant under time reversal, $t \rightarrow -t$, then the right hand side of the first order equations of motions changes sign under time reversal,

$$\tilde{\chi}_{xy}^{(2)}(t + \tau, \tau) = \tilde{\chi}_{xy}^{(2)}(t) = \tilde{\chi}_{yx}^{(2)*}(-t) \quad (431)$$

which translates into the property

$$\chi_{xy}^{(2)}(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} \tilde{\chi}_{xy}^{(2)}(t) = \int_{-\infty}^{\infty} dt e^{i\omega t} \tilde{\chi}_{xy}^{(2)*}(-t) = \chi_{yx}^{(2)*}(\omega) \quad (432)$$

of the reduced response function in the frequency space. Our goal is to gain some light on the analytical structure of the Fourier-Laplace transform of the complete response function

$$\chi(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} \tilde{\chi}(t) = 2i \int_0^{\infty} dt e^{i\omega t} \tilde{\chi}^{(2)}(t) \quad (433)$$

which relates the perturbation and the response as

$$\langle \delta f(\omega) \rangle = \sum_j \chi_{fg_j}(\omega) h_j(\omega). \quad (434)$$

We shall find that it is analytic on the upper half of the complex ω frequency plane as a result of causality.

The starting point is the well known relation that the multiplication becomes convolution under a Fourier transformation,

$$\begin{aligned} \tilde{f}(t)\tilde{g}(t) &= \int \frac{d\omega'}{2\pi} \frac{d\omega''}{2\pi} e^{-i(\omega'+\omega'')t} f(\omega')g(\omega'') \\ \int dt \tilde{f}(t)\tilde{g}(t)e^{i\omega t} &= \int \frac{d\omega'}{2\pi} \frac{d\omega''}{2\pi} dt e^{-i(\omega'+\omega''-\omega)t} f(\omega')g(\omega'') \\ &= \int \frac{d\omega'}{2\pi} g(\omega - \omega')f(\omega'). \end{aligned} \quad (435)$$

We use the Fourier representation

$$\Theta(t) = i \int \frac{d\omega}{2\pi} \frac{e^{-i\omega t}}{\omega + i\epsilon} \quad (436)$$

of the Heavyside function and have

$$\chi(\omega) = - \int \frac{d\omega'}{\pi} \frac{\chi^{(2)}(\omega')}{\omega - \omega' + i\epsilon} = \int \frac{d\omega'}{\pi} \frac{\chi^{(2)}(\omega')}{\omega' - \omega - i\epsilon}. \quad (437)$$

The important lesson of this representation is that the response function is analytic on the upper half plane, $\Im\omega > 0$. The main ingredient of the argument is the relation

$$\frac{1}{\omega \pm i\epsilon} = P\frac{1}{\omega} \mp i\pi\delta(\omega) \quad (438)$$

for distributions which yields

$$\chi(\omega) = \chi^{(1)}(\omega) + i\chi^{(2)}(\omega), \quad (439)$$

with the obvious relation between the real and imaginary part of the Fourier transformed response function

$$\chi^{(1)}(\omega) = P \int \frac{d\omega'}{\pi} \frac{\chi^{(2)}(\omega')}{\omega' - \omega}, \quad (440)$$

the Kramers-Krönig relation. It can be inverted by considering an integration over the infinite half-circle on the upper half plane

$$\chi(\omega + i\epsilon) = \oint \frac{dz}{2\pi i} \frac{\chi(z)}{z - \omega - i\epsilon} \quad (441)$$

where the numerator of the integrand is analytic. One can show that $\chi(z) = o(|z^{-1}|)$ and the integral along the half-circle is vanishing, yielding

$$\chi(\omega + i\epsilon) = \int_{-\infty+i\epsilon}^{\infty+i\epsilon} \frac{dz}{2\pi i} \chi(z) \left(P \frac{1}{z - \omega} + i\pi\delta(z - \omega) \right) \quad (442)$$

and

$$\chi(\omega + i\epsilon) = \int_{-\infty+i\epsilon}^{\infty+i\epsilon} \frac{dz}{\pi i} P \frac{\chi(z)}{z - \omega} \quad (443)$$

or

$$\chi^{(2)}(\omega) = - \int_{-\infty+i\epsilon}^{\infty+i\epsilon} \frac{dz}{\pi} P \frac{\chi^{(1)}(z)}{z - \omega}. \quad (444)$$

D. Harmonic oscillator

The simplest and most important application of the formalism introduced above is in the case of a single, damped harmonic oscillator with equation of motion

$$\ddot{x} + \omega_0^2 x + \gamma \dot{x} = \frac{f e^{-i\omega t}}{m} \quad (445)$$

where the right hand side represents a periodic external force. The last term on the left hand side contains the parameter $\gamma = \alpha/m$ given in terms of the friction coefficient α and breaks the time-reversal invariance, $T : t \rightarrow -t$. The solution of the linear equation of motion is written as the sum of the homogeneous and inhomogeneous solutions,

$$x(t) = x_{\text{hom}}(t) + x_{\text{inhom}}(t) = x_n e^{-i\omega_n t} + x_0 e^{-i\omega t}. \quad (446)$$

Let us start with the homogeneous solution for which

$$-\omega_n^2 + \omega_0^2 - i\gamma\omega_n = 0 \quad (447)$$

and

$$\omega_n = -\frac{i\gamma}{2} \pm \sqrt{\omega_0^2 - \frac{\gamma^2}{4}} = \pm\tilde{\omega} - \frac{i\gamma}{2}. \quad (448)$$

It is more realistic to consider an overdamped oscillator with $\gamma > 2\omega_0$ when there are two relaxation time scales,

$$\tau_f^{-1} = \frac{\gamma}{2} \left[1 + \sqrt{1 - \frac{4\omega_0^2}{\gamma^2}} \right], \quad \tau_s^{-1} = \frac{\gamma}{2} \left[1 - \sqrt{1 - \frac{4\omega_0^2}{\gamma^2}} \right]. \quad (449)$$

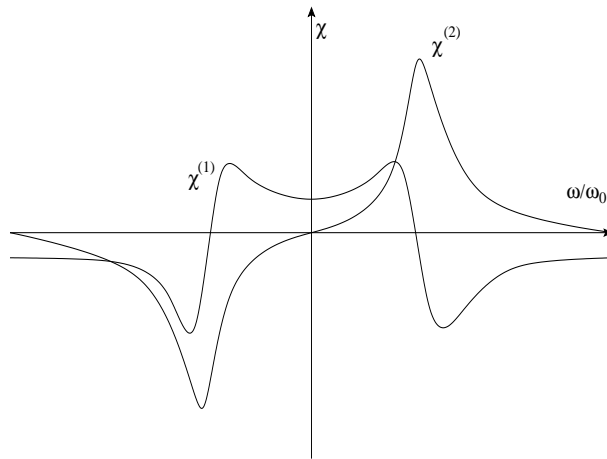


FIG. 30: The response function of a harmonic oscillator.

The mode with τ_f becomes quickly negligible for strongly overdamped oscillator, $\gamma \gg 2\omega$ and the equation of motion can be simplified to a first order one,

$$\ddot{x} + \omega_0^2 x + \gamma \dot{x} \rightarrow \omega_0^2 x + \gamma \dot{x} = \frac{f}{m}. \quad (450)$$

For $t \gg \tau_s$ the homogeneous solution can be ignored therefore we now consider the inhomogeneous solution and introduce the response function

$$\chi(\omega) = \frac{x_0}{f} = \frac{1}{m} \frac{1}{-\omega^2 + \omega_0^2 - i\gamma\omega} = -\frac{1}{m} \frac{1}{(\omega - \tilde{\omega} + \frac{i\gamma}{2})(\omega + \tilde{\omega} + \frac{i\gamma}{2})} \quad (451)$$

for the coordinate which obviously satisfies the Kramers-Krönig relation due to the analyticity on the upper half plane. The response function becomes

$$\chi(\omega) \rightarrow -\frac{1}{m} P \frac{1}{\omega_0^2 - \omega^2} + \text{sign}(\omega) \frac{i\pi}{m} \delta(\omega_0^2 - \omega^2) \quad (452)$$

in the limit $\gamma \rightarrow 0$. The Kramers-Krönig relation shows that the imaginary part of the response function can be interpreted as a distribution of the strength of the normal modes in the frequency. In fact, the integrand on the right hand side of the Kramers-Krönig relation with its linear frequency dependence in the denominator is just the response function of an overdamped oscillator. For weak damping, more precisely for time much longer than the relaxation time the inhomogeneous solution consists mainly damped modes with frequencies close to the resonance.

The real and imaginary parts of the response function are

$$\chi^{(1)}(\omega) = \frac{1}{m} \frac{\omega_0^2 - \omega^2}{(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2} \quad (453)$$

and

$$\chi^{(2)}(\omega) = \frac{1}{m} \frac{\gamma\omega}{(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2}. \quad (454)$$

The amplitude and the phase shift defined by the form $x(t) = f|\chi|e^{-i\omega t + i\phi}$ are

$$\begin{aligned} |\chi| &= \frac{1}{m} \frac{1}{\sqrt{(\omega^2 - \omega_0^2)^2 + \gamma^2 \omega^2}}, \\ \tan \phi &= \frac{\gamma\omega}{\omega_0^2 - \omega^2}. \end{aligned} \quad (455)$$

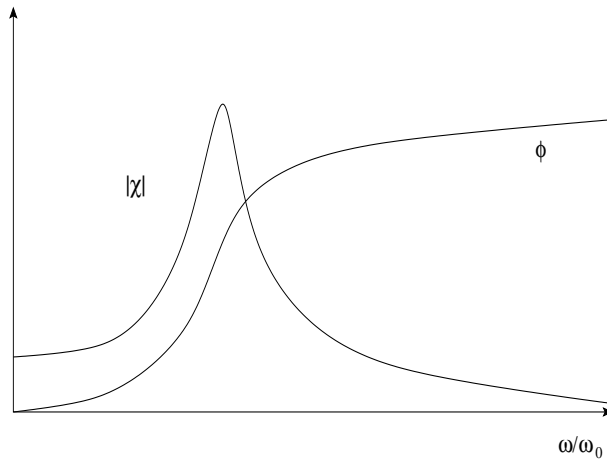


FIG. 31: Amplitude and the phase of the response function of a harmonic oscillator.

There is another important interpretation of the imaginary part of the response function. the dissipation due to a periodic motion,

$$\begin{aligned}
 \frac{dW}{dt} &= \langle f\dot{x} \rangle = \frac{1}{T} \int_0^T dt f(t)\dot{x}(t) \\
 &= \frac{f^2\omega|\chi(\omega)|}{T} \int_0^T dt \cos \omega t \sin(\omega t - \phi) \\
 &= \frac{1}{2} f^2\omega|\chi(\omega)| \sin \phi \\
 &= \frac{1}{2} f^2\omega\chi^{(2)}(\omega),
 \end{aligned} \tag{456}$$

is proportional to the imaginary part. This is the origin of the fluctuation-dissipation theorems, the imaginary part determines both the spectral distribution of the fluctuations and dissipation.

E. Langevin equation

The master or diffusion equation method provides us a description of stochastic dynamics for long time scales. One may need a more detailed level of description which represents a bridge between the deterministic dynamics observed for time scales much shorter than the time span between microscopic collision or interaction processes and the longer time scales. The motion is called ballistic in the former time range, as opposed to the diffusive dynamics for long time. Stochastic differential equations provide us such a description. Let us consider a one-dimensional particle subject of a friction and a stochastic external forces which lead to the Langevin equation

$$m\dot{v}(t) + \alpha v(t) = \xi(t). \tag{457}$$

where the distribution of the white-noise force is

$$p(\xi_1, t_1, \dots, \xi_n, t_n) = \frac{1}{(2\pi\sigma)^{n/2}} e^{-\frac{1}{2\sigma} \sum_j \xi_j^2}, \tag{458}$$

giving

$$\begin{aligned}
 \langle \xi(t) \rangle &= 0, \\
 \langle \xi(t)\xi(t') \rangle &= \sigma\delta(t-t'), \\
 \langle \xi(\omega)\xi(\omega') \rangle &= \int dt dt' e^{i\omega t + i\omega' t'} \sigma\delta(t-t') = 2\pi\sigma\delta(\omega + \omega').
 \end{aligned} \tag{459}$$

The simplest is to consider the homogeneous solution only which is important for $t \ll 1/\gamma = m/\alpha$, when the Fourier transformed velocity is

$$v(\omega) = \frac{\xi(\omega)}{-i\omega m + \alpha} \tag{460}$$

The correlation function $C_{vv}(t) = \langle v(t + \tau)v(\tau) \rangle$ turns out to be

$$\begin{aligned}
C_{vv}(\omega) &= \int dt e^{i\omega t} C(t) \\
&= \int dt \frac{d\omega' d\omega''}{(2\pi)^2} e^{i(\omega - \omega')t} \langle v(\omega')v(\omega'') \rangle \\
&= \int \frac{d\omega''}{2\pi} \langle v(\omega)v(\omega'') \rangle \\
&= \int \frac{d\omega''}{2\pi} \frac{\langle \xi(\omega)\xi(\omega'') \rangle}{(-i\omega m + \alpha)(-i\omega'' m + \alpha'')} \\
&= \frac{\sigma}{m^2(\omega^2 + \gamma^2)}
\end{aligned} \tag{461}$$

in the frequency space. The inverse Fourier transformation gives

$$\begin{aligned}
C_{vv}(t) &= \frac{\sigma}{m^2} \int \frac{d\omega}{2\pi} \frac{e^{-i\omega t}}{(\omega + i\gamma)(\omega - i\gamma)} \\
&= i \frac{\sigma}{m^2} \frac{e^{-i\gamma|t|}}{2i\gamma} \\
&= \frac{\sigma}{2m^2\gamma} e^{-i\gamma|t|}
\end{aligned} \tag{462}$$

Let us assume now that the thermalization between our particle and its environment takes place at shorter time scale than the relaxation time γ^{-1} and we can use the equipartition theorem,

$$T = m\langle v^2 \rangle = m \int \frac{d\omega}{2\pi} C_{vv}(\omega) = \frac{\sigma}{2\alpha}, \tag{463}$$

giving

$$C_{vv}(t) = \frac{T}{m} e^{-i\gamma|t|}. \tag{464}$$

We seek the complete solution of the Langevin equation first for the velocity. The initial condition $v(0) = v_0$ gives

$$\begin{aligned}
v(t) &= v_0 e^{-\gamma t} + \frac{1}{m} \int_0^t dt' e^{-\gamma(t-t')} \xi(t') \\
\langle v(t) \rangle &= v_0 e^{-\gamma t}.
\end{aligned} \tag{465}$$

The correlation function for the velocity is

$$\begin{aligned}
\langle v(t)v(t') \rangle &= \left\langle \left[v_0 e^{-\gamma t} + \frac{1}{m} \int_0^t dt_1 e^{-\gamma(t-t_1)} \xi(t_1) \right] \left[v_0 e^{-\gamma t'} + \frac{1}{m} \int_0^{t'} dt_2 e^{-\gamma(t'-t_2)} \xi(t_2) \right] \right\rangle \\
&= v_0^2 e^{-\gamma(t+t')} + \frac{1}{m^2} \int_0^t dt_1 e^{-\gamma(t-t_1)} \int_0^{t'} dt_2 e^{-\gamma(t'-t_2)} \underbrace{\langle \xi(t_1)\xi(t_2) \rangle}_{\sigma\delta(t_1-t_2)} \\
&= e^{-\gamma(t+t')} \left[v_0^2 + \frac{\sigma}{m^2} \int_0^t dt_1 \int_0^{t'} dt_2 e^{\gamma(t_1+t_2)} \delta(t_1 - t_2) \right] \\
&= e^{-\gamma(t+t')} \left[v_0^2 + \frac{\sigma}{m^2} \int_0^{\min(t,t')} dt_1 e^{2\gamma t_1} \right] \\
&= v_0^2 e^{-\gamma(t+t')} + \frac{\sigma}{2\gamma m^2} e^{-\gamma(t+t') + 2\gamma \min(t,t')} \\
&= v_0^2 e^{-\gamma(t+t')} + \frac{\sigma}{2\gamma m^2} e^{-\gamma|t-t'|}.
\end{aligned} \tag{466}$$

Assuming that the thermal equilibrium reached at time shorter than γ^{-1} we have

$$T = m\langle v^2 \rangle = \frac{\sigma}{2\gamma m} = \frac{\sigma}{2\alpha} \tag{467}$$

which produces the normalization

$$\langle \xi(t)\xi(t') \rangle = 2T\alpha\delta(t-t') = 2Tm\gamma\delta(t-t') \tag{468}$$

of the noise-noise correlation function and leads to

$$\langle v(t)v(t') \rangle = v_0^2 e^{-\gamma(t+t')} + \frac{T}{m} e^{-\gamma|t-t'|}. \quad (469)$$

The coordinate can be found by an integration,

$$\begin{aligned} x(t) &= x_0 + \int_0^t dt' v(t') \\ \langle x(t) \rangle &= x_0 + v_0 \int_0^t dt' e^{-\gamma t'} \\ &= x_0 + \frac{v_0}{\gamma} (1 - e^{-\gamma t}) \end{aligned} \quad (470)$$

and second moment of the average drift is given by

$$\begin{aligned} \langle (x(t) - x(t'))^2 \rangle &= \left\langle \left(\int_{t'}^t dt_1 v(t_1) \right)^2 \right\rangle \\ &= \int_{t'}^t dt_1 dt_2 \left[v_0^2 e^{-\gamma(t_1+t_2)} + \frac{T}{m} e^{-\gamma|t_1-t_2|} \right] \\ &= \frac{v_0^2}{\gamma^2} (e^{-\gamma t} - e^{-\gamma t'})^2 + \frac{2T}{m} \int_{t'}^t dt_1 \int_{t_1}^t dt_2 e^{-\gamma(t_2-t_1)} \\ &= \frac{v_0^2}{\gamma^2} (e^{-\gamma t} - e^{-\gamma t'})^2 - \frac{2T}{m\gamma} \int_{t'}^t dt_1 (e^{-\gamma(t-t_1)} - 1) \\ &= \frac{v_0^2}{\gamma^2} (e^{-\gamma t} - e^{-\gamma t'})^2 + \frac{2T}{m\gamma} |t - t'| + \frac{2T}{m\gamma^2} (1 - e^{-\gamma|t-t'|}) \end{aligned} \quad (471)$$

for $t' < t$. The initial condition $x(0) = x_0$ gives

$$\langle (x(t) - x_0)^2 \rangle \approx \begin{cases} v_0^2 t^2 & t \ll \gamma^{-1}, \quad \text{ballistic} \\ \frac{v_0^2}{\gamma^2} + \frac{2T}{m\gamma^2} (1 + t\gamma - e^{-\gamma t}) \approx \frac{v_0^2}{\gamma^2} + \frac{2T}{m\gamma} t & t \gg \gamma^{-1}, \quad \text{diffusive} \end{cases} \quad (472)$$

where we can clearly separate the ballistic and diffusive regimes.

F. Fluctuation-dissipation theorem

The relation between the strength of fluctuations and dissipation can easily be seen by considering the long time motion, described by the inhomogeneous solution

$$x(\omega) = \frac{\xi(\omega)}{m(-\omega^2 + \omega_0^2 - i\gamma\omega)}. \quad (473)$$

It generates the correlation function

$$\begin{aligned} C_{xx}(\omega) &= \int dt e^{i\omega t} \langle x(t+\tau)x(\tau) \rangle \\ &= \int dt \frac{d\omega' d\omega''}{(2\pi)^2} e^{i(\omega-\omega')t - i\tau(\omega'+\omega'')} \langle x(\omega')x(\omega'') \rangle \\ &= \int \frac{d\omega''}{2\pi} e^{-i\tau(\omega+\omega'')} \frac{\langle \xi(\omega)\xi(\omega'') \rangle}{m^2(-\omega^2 + \omega_0^2 - i\gamma\omega)(-\omega''^2 + \omega_0^2 - i\gamma\omega'')} \\ &= \int \frac{d\omega''}{2\pi} e^{-i\tau(\omega'+\omega'')} \frac{2\pi\sigma\delta(\omega+\omega'')}{m^2(-\omega^2 + \omega_0^2 - i\gamma\omega)(-\omega''^2 + \omega_0^2 - i\gamma\omega'')} \\ &= \frac{\sigma}{m^2[(\omega^2 - \omega_0^2)^2 + \gamma^2\omega^2]} = \frac{2\gamma T}{m} \frac{1}{(\omega^2 - \omega_0^2)^2 + \gamma^2\omega^2}, \end{aligned} \quad (474)$$

therefore we have a relation between the connected correlation function and the dissipative, imaginary part of the response function,

$$\chi^{(2)}(\omega) = \frac{1}{m} \frac{\gamma\omega}{(\omega_0^2 - \omega^2)^2 + \gamma^2\omega^2} = \frac{\omega}{2T} C_{xx}^{(e)}(\omega), \quad (475)$$

where

$$C_{ab}(t, t') = C_{ab}^{(e)}(t, t') + \langle a(t) \rangle \langle b(t') \rangle. \quad (476)$$

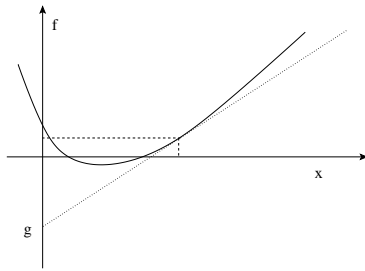


FIG. 32: The Legendre transformation $f(x) \rightarrow g(s) = xf - f(x)$, cf. Eq. (A1).

Appendix A: Legendre transformation

The Legendre transformation $f(x) \rightarrow g(s)$ is useful when we would like to express a function in terms of its derivative $s = f'(x)$ instead of its original variable x . In order to make this transformation well defined we make the map $x \rightarrow s$ invertible by assuming that $f'(x)$ is monotonous function of x , $f''(x) \neq 0$. We assume the existence and smoothness of the second derivative and we restrict ourselves here to the case of convex functions, $f''(x) > 0$.

The Legendre transform $g(s)$ is defined by the equation

$$f(x) + g(s) = xs \quad (\text{A1})$$

where

$$s = f'(x). \quad (\text{A2})$$

When we perform the transformation on $g(s)$ we recover Eq. (A1) due to its symmetrical form for the replacement $x \leftrightarrow s$, $f \leftrightarrow g$ but instead of Eq. (A2) we find

$$\begin{aligned} g'(s) &= \frac{d}{ds}[x(s)s - f(x(s))] \\ &= x'(s)s + x(s) - f'(x(s))x'(s). \\ &= x \end{aligned} \quad (\text{A3})$$

Thus the Legendre transformation is identical with its inverse.

The derivation of Eq. (A1) with respect to x or s yields Eqs. (A2) and (A3). The next derivatives give

$$f''(x) = s'(x), \quad g''(s) = x'(s). \quad (\text{A4})$$

Since $x'(s)s'(x) = 1$ we have an inverse relation between the second derivatives,

$$f''(x)g''(s) = 1. \quad (\text{A5})$$

As a result the Legendre transform is convex, as well.

A convex function can have a single minimum only. The identical form of the Legendre transform and its inverse yields the similar equations

$$f(x_{extr}) + g(0) = f(0) + g(s_{extr}) = 0. \quad (\text{A6})$$

Appendix B: Density matrix

1. Definition, properties

Let us suppose that all we know about our quantum system is that it can be found with probability p_n in the not necessarily orthogonal quantum states $|\psi_n\rangle$, where $\langle\psi_n|\psi_n\rangle = 1$ and $\sum_n p_n = 1$. When an observable A is measured then the expectation value of the result is

$$\langle\langle A \rangle\rangle = \sum_n p_n \langle\psi_n|A|\psi_n\rangle = \text{Tr} A \rho \quad (\text{B1})$$

where we introduced the density matrix

$$\rho = \sum_n |\psi_n\rangle p_n \langle \psi_n| \quad (\text{B2})$$

with the following properties:

1. ρ is hermitian, $\rho^\dagger = \rho$.
2. The trace of ρ is unity, $\text{Tr}\rho = 1$.
3. ρ is positive,

$$\langle \Psi | \rho | \Psi \rangle = \sum_n \langle \Psi | \psi_n \rangle p_n \langle \psi_n | \Psi \rangle = \sum_n p_n |\langle \psi_n | \Psi \rangle|^2 \geq 0. \quad (\text{B3})$$

4. The density matrix, being a hermitian operator is diagonalizable and can be written as

$$\rho = \sum_n |\phi_n\rangle \rho_n \langle \phi_n|, \quad (\text{B4})$$

$\{|\phi_n\rangle\}$ being an orthonormal base. The eigenvalues are real, $0 \leq \rho_n$, and the diagonalization preserves the trace, $\sum_n \rho_n = 1$. The eigenvalue ρ_n can be interpreted as the probability of finding the system in one of the states, $|\phi_n\rangle$ of an orthonormal base.

5. The inequality

$$\text{Tr}\rho^2 = \sum_n \rho_n^2 \leq \sum_n \rho_n = \text{Tr}\rho \quad (\text{B5})$$

becomes an equality for pure states only, $\rho = |\psi\rangle\langle\psi|$. The states with strict inequality are called mixed. The decomposition of the density matrix a mixed state is not unique, there are different systems of non-orthogonal states which equally yield the same density matrix.

Example: The most general density matrix of a two-state system is

$$\rho = \frac{1}{2}(\mathbb{1} + \mathbf{p}\boldsymbol{\sigma}) \quad (\text{B6})$$

where the Pauli-matrices are

$$\boldsymbol{\sigma} = \left(\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \right). \quad (\text{B7})$$

This corresponds to the mixture of two states with probabilities $\frac{1}{2}(1 \pm |\mathbf{p}|)$ and

$$\langle \boldsymbol{\sigma} \rangle = \text{tr}\rho\boldsymbol{\sigma} = \mathbf{p}. \quad (\text{B8})$$

2. Origin

Two, apparently different circumstances, loss of informations and entanglement which require the extension of the basic principles of Quantum Mechanics and to generalize the representation of the state of a system from a vector within a linear space to a certain operator acting on the same space.

Loss of information: One encounters probability in deterministic classical physics as soon as some information is lost. This probability characterizes our limited control of the system. Heisenberg uncertainty relation implies an internal, genuine loss of information about reality what can not be recovered. The resulting probabilistic interpretation is based on such an unavoidable, absolute loss of information. Quantum thermal averages contain both probabilities. The expectation value $\langle \phi_n | A | \phi_n \rangle$ is based on on the probabilistic laws of Quantum Mechanics. The uncertainty, indicated by these probabilities is intrinsic of quantum physics according to the uncertainty principle and can not be reduced. But the probability ρ_n reflects our ignorance and originates from macroscopic physics. Note that the

separation of the quantum and classical probabilities is possible for orthogonal quantum states only, otherwise they are mixed due to the non-uniqueness of the density matrix.

The difference between the two probabilities can clearly be seen in the expectation value

$$\text{Tr}A\rho = \sum_n \rho_n \langle \phi_n | A | \phi_n \rangle \quad (\text{B9})$$

as the the lack of interference terms, $\langle \phi_n | A | \phi_n \rangle$ with $m \neq n$ to the classical probability. The decoherence, the destruction of the coherence among macroscopically different states, is not only the driving force in reaching the macroscopic physics from the microscopic one but it presumably serves as the origin of the universal laws of Statistical Physics. It generates classical probabilities for macroscopically different quantum states.

Entanglement: Let us suppose that our system consists of two sub-systems with bases $|\phi_m\rangle$ and $|\chi_n\rangle$. Any pure state of the complete system can then be written as

$$|\psi\rangle = \sum_{m,n} c_{m,n} |\phi_m\rangle \otimes |\chi_n\rangle. \quad (\text{B10})$$

A state, $|\psi\rangle = |\phi\rangle \otimes |\chi\rangle$, consisting of a single contribution is called factorisable and state which is the sum of more than one factorisable states is called entangled. The properties of a sub-system remain well defined when the whole system is considered as long as this latter is in a factorisable state. In fact, let us consider an observable $A^{(1)}$ of the first sub-system, corresponding to the operator $A = A^{(1)} \otimes \mathbb{1}^{(2)}$ where $\mathbb{1}^{(2)}$ is the identity operator for the second sub-system. Its expectation values in the factorisable state $|\psi\rangle = |\phi\rangle \otimes |\chi\rangle$,

$$\langle \psi | A | \psi \rangle = \langle \phi | A^{(1)} | \phi \rangle, \quad (\text{B11})$$

is indeed determined by the unique state $|\phi\rangle$ of the sub-system.

The expectation value in the entangled state (B10),

$$\langle A \rangle = \sum_{m,n,m'} c_{m,n} c_{m',n}^* \langle \phi_{m'} | A^{(1)} | \phi_m \rangle, \quad (\text{B12})$$

is made up by the matrix elements of $A^{(1)}$ among the different sub-system states $|\phi_m\rangle$, no unique property, characterized by an eigenvalue of $A^{(1)}$ can be recognized. One can show in this case that there is no pure state $|\phi\rangle$ of the subsystem which could reproduce the all expectation value, ie. for all possible choice of the observable $A^{(1)}$.

We are forced to generalize the representation of the states of the sub-system with an entangled pure state from state vectors to density matrices. The density matrix corresponding to a sub-system is called reduced density matrix and can be obtained in the following manner. The density matrix of the full system in the pure state (B10) is

$$\rho = \sum_{m,n,m',n'} c_{m,n} c_{m',n'}^* |\phi_m\rangle \otimes |\chi_n\rangle \langle \phi_{m'}| \otimes \langle \chi_{n'}| \quad (\text{B13})$$

and it is easy to see that the average of our observable of a sub-system can be written as

$$\langle A \rangle = \text{Tr}[\rho A] = \text{Tr}_1[\rho^{(1)} A^{(1)}] \quad (\text{B14})$$

where the trace is taken in the linear space of states of the sub-system 1 and the reduced density matrix is defined by

$$\rho^{(1)} = \sum_{m,n,m'} c_{m,n} c_{m',n}^* |\phi_m\rangle \langle \phi_{m'}|. \quad (\text{B15})$$