

Statistical Thermodynamics

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Statistical physics

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I. PREFACE

Statistical physics considers systems of a large number of entities (particles) such as atoms, molecules, spins, etc. For these system it is impossible and even does not make sense to study the full microscopic dynamics. The only relevant information is, say, how many atoms have a particular energy, then one can calculate the observable thermodynamic values. That is, one has to know the distribution function of the particles over energies that defines the macroscopic properties. This gives the name *statistical physics* and defines the scope of this subject.

The approach outlined above can be used both at and off equilibrium. The branch of physics studying non-equilibrium situations is called *physical kinetics*. In this course, we study only statistical physics at equilibrium. It turns out that at equilibrium the energy distribution function has an explicit general form and the only problem is to calculate the observables. The term *statistical mechanics* means the same as statistical physics. One can call it *statistical thermodynamics* as well.

The formalism of statistical thermodynamics can be developed for both classical and quantum systems. The resulting energy distribution and calculating observables is simpler in the classical case. However, the very formulation of the method is more transparent within the quantum mechanical formalism. In addition, the absolute value of the entropy, including its correct value at $T \rightarrow 0$, can only be obtained in the quantum case. To avoid double work, we will consider only quantum statistical thermodynamics in this course, limiting ourselves to systems without interaction. The more general quantum results will recover their classical forms in the classical limit.

II. MICROSTATES AND MACROSTATES

From quantum mechanics follows that the states of the system do not change continuously (like in classical physics) but are quantized. There is a huge number of discrete quantum states i with corresponding energy values ε_i being the main parameter characterizing these states. In the absence of interaction, each particle has its own set of quantum states which it can occupy. For identical particles these sets of states are identical. One can think of boxes i into which particles are placed, N_i particles in the i th box. The particles can be distributed over the boxes in a number of different ways, corresponding to different *microstates*, in which the state i of each particle is specified. The information contained in the microstates is excessive, and the only meaningful information is provided by the numbers N_i that define the distribution of particles over their quantum states. These numbers N_i specify what in statistical physics is called *macrostate*. If these numbers are known, the energy and other quantities of the system can be found. It should be noted that also the statistical macrostate contains more information than the macroscopic physical quantities that follow from it, as a distribution contains more information than an average over it.

Each macrostate k , specified by the numbers N_i , can be realized by a number w_k of microstates, the so-called *thermodynamic probability*. The latter is typically a large number, unlike the usual probability that changes between 0 and 1. Redistributing the particles over the states i while keeping the same values of N_i generates different microstates within the same macrostate. The basic assumption of statistical mechanics is the equidistribution over microstates. That is, each microstate within a macrostate is equally probable for occupation. Macrostates having a larger w_k are more likely to be realized. As we will see, for large systems, thermodynamic probabilities of different macrostates vary in a wide range and there is the state with the largest value of w that wins over all other macrostates.

If the number of quantum states i is finite, the total number of microstates can be written as

$$\Omega \equiv \sum_k w_k, \quad (1)$$

the sum rule for thermodynamic probabilities. For an isolated system the number of particles N and the energy U are conserved, thus the numbers N_i satisfy the constraints

$$\sum_i N_i = N, \quad (2)$$

$$\sum_i N_i \varepsilon_i = U \quad (3)$$

that limit the variety of the allowed macrostates k .

III. TWO-STATE PARTICLES (COIN TOSSING)

A tossed coin can land in two positions: Head up or tail up. Considering the coin as a particle, one can say that this particle has two “quantum” states, 1 corresponding to the head and 2 corresponding to the tail. If N coins are tossed, this can be considered as a system of N particles with two quantum states each. The microstates of the system are specified by the states occupied by each coin. As each coin has 2 states, there are total

$$\Omega = 2^N \quad (4)$$

microstates. The macrostates of this system are defined by the numbers of particles in each state, N_1 and N_2 . These two numbers satisfy the constraint condition (2), i.e., $N_1 + N_2 = N$. Thus one can take, say, N_1 as the number k labeling macrostates. The number of microstates in one macrostate (that is, the number of different microstates that belong to the same macrostate) is given by the binomial distribution

$$w_{N_1} = \frac{N!}{N_1!(N - N_1)!} = \binom{N}{N_1}. \quad (5)$$

This formula can be derived as follows. We have to pick N_1 particles to be in the state 1, all others will be in the state 2. How many ways are there to do this? The first “0” particle can be picked in N ways, the second one can be picked in $N - 1$ ways since we can choose of $N - 1$ particles only. The third “1” particle can be picked in $N - 2$ different ways etc. Thus one obtains the number of different ways to pick the particles is

$$N \times (N - 1) \times (N - 2) \times \dots \times (N - N_1 + 1) = \frac{N!}{(N - N_1)!}, \quad (6)$$

where the factorial is defined by

$$N! \equiv N \times (N - 1) \times \dots \times 2 \times 1, \quad 0! = 1. \quad (7)$$

The recurrent definition of the factorial is

$$N! = N(N - 1)!, \quad 0! = 1. \quad (8)$$

The expression in Eq. (6) is not yet the thermodynamical probability w_{N_1} because it contains multiple counting of the same microstates. The realizations, in which N_1 “1” particles are picked in different orders, have been counted as different microstates, whereas they are the same microstate. To correct for the multiple counting, one has to divide by the number of permutations $N_1!$ of the N_1 particles that yields Eq. (5). One can check that the condition (1) is satisfied,

$$\sum_{N_1=0}^N w_{N_1} = \sum_{N_1=0}^N \frac{N!}{N_1!(N - N_1)!} = 2^N. \quad (9)$$

The thermodynamic probability w_{N_1} has a maximum at $N_1 = N/2$, half of the coins head and half of the coins tail. This macrostate is the most probable state. Indeed, as for an individual coin the probabilities to land head up and tail up are both equal to 0.5, this is what we expect. For large N the maximum of w_{N_1} on N_1 becomes sharp.

To prove that $N_1 = N/2$ is the maximum of w_{N_1} , one can rewrite Eq. (5) in terms of the new variable $p = N_1 - N/2$ as

$$w_{N_1} = \frac{N!}{(N/2 + p)!(N/2 - p)!}. \quad (10)$$

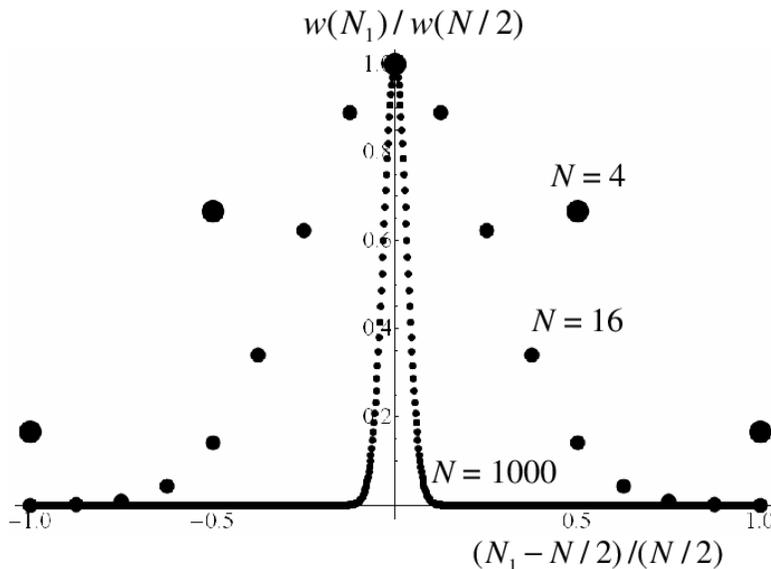


FIG. 1: The binomial distribution for an ensemble of N two-state systems becomes narrow and peaked at $p \equiv N_1 - N/2 = 0$.

One can see that w_p is symmetric around $N_1 = N/2$, i.e., $p = 0$. Using Eq. (8), one obtains

$$\frac{w_{N/2 \pm 1}}{w_{N/2}} = \frac{(N/2)!(N/2)!}{(N/2 + 1)!(N/2 - 1)!} = \frac{N/2}{N/2 + 1} < 1, \quad (11)$$

one can see that $N_1 = N/2$ is indeed the maximum of w_{N_1} . The binomial distribution is shown in Fig. 1 for three different values of N . As the argument, the variable $p/p_{\max} \equiv (N_1 - N/2)/(N/2)$ is used so that one can put all the data on the same plot. One can see that in the limit of large N the binomial distribution becomes narrow and centered at $p = 0$, that is, $N_1 = N/2$. This practically means that if the coin is tossed many times, significant deviations from the 50:50 relation between the numbers of heads and tails will be extremely rare.

IV. STIRLING FORMULA AND THERMODYNAMIC PROBABILITY AT LARGE N

Analysis of expressions with large factorials is simplified by the Stirling formula

$$N! \cong \sqrt{2\pi N} \left(\frac{N}{e}\right)^N. \quad (12)$$

In many important cases, the prefactor $\sqrt{2\pi N}$ is irrelevant, as we will see below. With the Stirling formula substituted, Eq. (10) becomes

$$\begin{aligned} w_{N_1} &\cong \frac{\sqrt{2\pi N} (N/e)^N}{\sqrt{2\pi(N/2+p)} [(N/2+p)/e]^{N/2+p} \sqrt{2\pi(N/2-p)} [(N/2-p)/e]^{N/2-p}} \\ &= \sqrt{\frac{2}{\pi N}} \frac{1}{\sqrt{1 - \left(\frac{2p}{N}\right)^2}} \frac{N^N}{(N/2+p)^{N/2+p} (N/2-p)^{N/2-p}} \\ &= \frac{w_{N/2}}{\sqrt{1 - \left(\frac{2p}{N}\right)^2} \left(1 + \frac{2p}{N}\right)^{N/2+p} \left(1 - \frac{2p}{N}\right)^{N/2-p}}, \end{aligned} \quad (13)$$

where

$$w_{N/2} \cong \sqrt{\frac{2}{\pi N}} 2^N \quad (14)$$

is the maximal value of the thermodynamic probability. Eq. (13) can be expanded for $|p| \ll N$. Since p enters both the bases and the exponents, one has to be careful and expand the logarithm of w_{N_1} rather than w_{N_1} itself. The square root term in Eq. (13) can be discarded as it gives a negligible contribution of order p^2/N^2 . One obtains

$$\begin{aligned}
\ln w_{N_1} &\cong \ln w_{N/2} - \left(\frac{N}{2} + p\right) \ln \left(1 + \frac{2p}{N}\right) - \left(\frac{N}{2} - p\right) \ln \left(1 - \frac{2p}{N}\right) \\
&\cong \ln w_{N/2} - \left(\frac{N}{2} + p\right) \left[\frac{2p}{N} - \frac{1}{2} \left(\frac{2p}{N}\right)^2\right] - \left(\frac{N}{2} - p\right) \left[-\frac{2p}{N} - \frac{1}{2} \left(\frac{2p}{N}\right)^2\right] \\
&\cong \ln w_{N/2} - p - \frac{2p^2}{N} + \frac{p^2}{N} + p - \frac{2p^2}{N} + \frac{p^2}{N} \\
&= \ln w_{N/2} - \frac{2p^2}{N}
\end{aligned} \tag{15}$$

and thus

$$w_{N_1} \cong w_{N/2} \exp\left(-\frac{2p^2}{N}\right). \tag{16}$$

One can see that w_{N_1} becomes very small if $|p| \gtrsim \sqrt{N}$ that for large N does not violate the applicability condition $|p| \ll N$. That is, w_{N_1} is small in the main part of the interval $0 \leq N_1 \leq N$ and is sharply peaked near $N_1 = N/2$.

V. MANY-STATE PARTICLES

The results obtained in Sec. III for two-state particles can be generalized for n -state particles. We are looking for the number of ways to distribute N particles over n boxes so that there are N_i particles in i th box. That is, we look for the number of microstates in the macrostate described by the numbers N_i . The result is given by

$$w = \frac{N!}{N_1!N_2!\dots N_n!} = \frac{N!}{\prod_{i=1}^n N_i!}. \tag{17}$$

This formula can be obtained by using Eq. (5) successively. The number of ways to put N_1 particles in box 1 and the other $N - N_1$ in other boxes is given by Eq. (5). Then the number of ways to put N_2 particles in box 2 is given by a similar formula with $N \rightarrow N - N_1$ (there are only $N - N_1$ particles after N_1 particles have been put in box 1) and $N_1 \rightarrow N_2$. These numbers of ways should multiply. Then one considers box 3 etc. until the last box n . The resulting number of microstates is

$$\begin{aligned}
w &= \frac{N!}{N_1!(N - N_1)!} \times \frac{(N - N_1)!}{N_2!(N - N_1 - N_2)!} \times \frac{(N - N_1 - N_2)!}{N_3!(N - N_1 - N_2 - N_3)!} \times \\
&\dots \times \frac{(N_{n-2} + N_{n-1} + N_n)!}{N_{n-2}!(N_{n-1} + N_n)!} \times \frac{(N_{n-1} + N_n)!}{N_{n-1}!N_n!} \times \frac{N_n!}{N_n!0!}.
\end{aligned} \tag{18}$$

In this formula, all numerators except for the first one and all second terms in the denominators cancel each other, so that Eq. (17) follows.

VI. THERMODYNAMIC PROBABILITY AND ENTROPY

We have seen that different macrostates k can be realized by largely varying numbers of microstates w_k . For large systems, $N \gg 1$, the difference between different thermodynamic probabilities w_k is tremendous, and there is a sharp maximum of w_k at some value of $k = k_{\max}$. The main postulate of statistical physics is that in measurements on large systems, only the most probable macrostate, satisfying the constraints of Eqs. (2) and (3), makes a contribution. For instance, a macrostate of an ideal gas with all molecules in one half of the container is much less probable than the macrostate with the molecules equally distributed over the whole container. (Like the state with all coins landed head up is much less probable than the state with half of the coins landed head up and the other half tail up). For this reason, if the initial state is all molecules in one half of the container, then in the course of evolution the system will come to the most probably state with the molecules equally distributed over the whole container, and will stay in this state forever.

We have seen in thermodynamics that an isolated system, initially in a non-equilibrium state, evolves to the equilibrium state characterized by the maximal entropy. On this way one comes to the idea that entropy S and thermodynamic probability w should be related, one being a monotonic function of the other. The form of this function can be found if one notices that entropy is additive while the thermodynamic probability is multiplicative. If a system consists of two subsystems that weakly interact with each other (that is almost always the case as the intersubsystem interaction is limited to the small region near the interface between them), then $S = S_1 + S_2$ and $w = w_1 w_2$. If one chooses (L. Boltzmann)

$$S = k_B \ln w, \quad (19)$$

then $S = S_1 + S_2$ and $w = w_1 w_2$ are in accord since $\ln(w_1 w_2) = \ln w_1 + \ln w_2$. In Eq. (19) k_B is the Boltzmann constant,

$$k_B = 1.38 \times 10^{-23} \text{ J K}^{-1}. \quad (20)$$

It will be shown that the statistically defined entropy above coincides with the thermodynamic entropy at equilibrium. On the other hand, statistical entropy is well defined for nonequilibrium states as well, where as the thermodynamic entropy is usually undefined off equilibrium.

VII. BOLTZMANN DISTRIBUTION AND CONNECTION WITH THERMODYNAMICS

In this section we obtain the distribution of particles over energy levels i as the most probable macrostate by maximizing its thermodynamic probability w . We label quantum states by the index i and use Eq. (17). The task is to find the maximum of w with respect to all N_i that satisfy the constraints (2) and (3). Practically it is more convenient to maximize $\ln w$ than w itself. Using the method of Lagrange multipliers, one searches for the maximum of the target function

$$\Phi(N_1, N_2, \dots, N_n) = \ln w + \alpha \sum_i N_i - \beta \sum_i \varepsilon_i N_i. \quad (21)$$

Here α and β are Lagrange multipliers with (arbitrary) signs chosen anticipating the final result. The maximum satisfies

$$\frac{\partial \Phi}{\partial N_i} = 0, \quad i = 1, 2, \dots \quad (22)$$

As we are interested in the behavior of macroscopic systems with $N_i \gg 1$, the factorials can be simplified with the help of Eq. (12) that takes the form

$$\ln N! \cong N \ln N - N + \ln \sqrt{2\pi N}. \quad (23)$$

Neglecting the relatively small last term in this expression, one obtains

$$\Phi \cong \ln N! - \sum_j N_j \ln N_j + \sum_j N_j + \alpha \sum_j N_j - \beta \sum_j \varepsilon_j N_j. \quad (24)$$

The first term here is a constant and it won't contribute to the derivatives $\partial \Phi / \partial N_i$. In the latter, the only contribution comes from the terms with $j = i$ in the above expression. One obtains the equations

$$\frac{\partial \Phi}{\partial N_i} = -\ln N_i + \alpha - \beta \varepsilon_i = 0 \quad (25)$$

that yield

$$N_i = e^{\alpha - \beta \varepsilon_i}, \quad (26)$$

the Boltzmann distribution with yet undefined Lagrange multipliers α and β . The latter can be found from Eqs. (2) and (3) in terms of N and U . Summing Eq. (26) over i , one obtains

$$N = e^\alpha \mathcal{Z}, \quad \alpha = \ln(N/\mathcal{Z}), \quad (27)$$

where

$$Z = \sum_i e^{-\beta \varepsilon_i} \quad (28)$$

is the so-called *partition function* (German *Zustandssumme*) that plays a major role in statistical physics. Then, eliminating α from Eq. (26) yields

$$N_i = \frac{N}{Z} e^{-\beta \varepsilon_i}, \quad (29)$$

the Boltzmann distribution. After that for the internal energy U one obtains

$$U = \sum_i \varepsilon_i N_i = \frac{N}{Z} \sum_i \varepsilon_i e^{-\beta \varepsilon_i} = -\frac{N}{Z} \frac{\partial Z}{\partial \beta} \quad (30)$$

or

$$U = -N \frac{\partial \ln Z}{\partial \beta}. \quad (31)$$

This formula implicitly defines the Lagrange multiplier β as a function of U .

The statistical entropy, Eq. (19), within the Stirling approximation becomes

$$S = k_B \ln w = k_B \left(N \ln N - \sum_i N_i \ln N_i \right). \quad (32)$$

Inserting here Eq. (26) and α from Eq. (27), one obtains

$$\frac{S}{k_B} = N \ln N - \sum_i N_i (\alpha - \beta \varepsilon_i) = N \ln N - \alpha N + \beta U = N \ln Z + \beta U. \quad (33)$$

The statistical entropy depends only on the parameter β . Its differential is given by

$$dS = \frac{dS}{d\beta} d\beta = \left(N \frac{\partial \ln Z}{\partial \beta} + U + \beta \frac{dU}{d\beta} \right) d\beta = \beta dU. \quad (34)$$

Comparing this with the thermodynamic relation $dU = T dS$ at $V = 0$, one identifies

$$\beta = \frac{1}{k_B T}. \quad (35)$$

Now, with the help of $dT/d\beta = -k_B T^2$, one can represent the internal energy, Eq. (31), via the derivative with respect to T as

$$U = N k_B T^2 \frac{\partial \ln Z}{\partial T}. \quad (36)$$

Eq. (33) becomes

$$S = N k_B \ln Z + \frac{U}{T}. \quad (37)$$

From here one obtains the statistical formula for the free energy

$$F = U - TS = -N k_B T \ln Z. \quad (38)$$

One can see that the partition function Z contains the complete information of the system's thermodynamics since other quantities such as pressure P follow from F . In particular, one can check $\partial F / \partial T = -S$.

VIII. QUANTUM STATES AND ENERGY LEVELS

A. Stationary Schrödinger equation

In the formalism of quantum mechanics, quantized states and their energies E are the solutions of the *eigenvalue* problem for a matrix or for a differential operator. In the latter case the problem is formulated as the so-called stationary Schrödinger equation

$$\hat{H}\Psi = E\Psi, \quad (39)$$

where $\Psi = \Psi(\mathbf{r})$ is the complex function called *wave function*. The physical interpretation of the wave function is that $|\Psi(\mathbf{r})|^2$ gives the probability for a particle to be found near the space point \mathbf{r} . As above, the number of measurements dN of the total N measurements in which the particle is found in the elementary volume $d^3r = dx dy dz$ around \mathbf{r} is given by

$$dN = N |\Psi(\mathbf{r})|^2 d^3r. \quad (40)$$

The wave function satisfies the normalization condition

$$1 = \int d^3r |\Psi(\mathbf{r})|^2. \quad (41)$$

The operator \hat{H} in Eq. (39) is the so-called Hamilton operator or Hamiltonian. For one particle, it is the sum of kinetic and potential energies

$$\hat{H} = \frac{\hat{\mathbf{p}}^2}{2m} + U(\mathbf{r}), \quad (42)$$

where the classical momentum p is replaced by the operator

$$\hat{\mathbf{p}} = -i\hbar \frac{\partial}{\partial \mathbf{r}}. \quad (43)$$

The Schrödinger equation can be formulated both for single particles and the systems of particles. In this course we will restrict ourselves to single particles. In this case the notation ε will be used for single-particle energy levels instead of E . One can see that Eq. (39) is a second-order linear differential equation. It is an ordinary differential equation in one dimension and partial differential equation in two and more dimensions. If there is a potential energy, this is a linear differential equation with variable coefficients that can be solved analytically only in special cases. In the case $U = 0$ this is a linear differential equation with constant coefficients that is easy to solve analytically.

An important component of the quantum formalism is boundary conditions for the wave function. In particular, for a particle inside a box with rigid walls the boundary condition is $\Psi=0$ at the walls, so that $\Psi(\mathbf{r})$ joins smoothly with the value $\Psi(\mathbf{r}) = 0$ everywhere outside the box. In this case it is also guaranteed that $|\Psi(\mathbf{r})|^2$ is integrable and Ψ can be normalized according to Eq. (41). It turns out that the solution of Eq. (39) that satisfies the boundary conditions exists only for a discrete set of E values that are called *eigenvalues*. The corresponding Ψ are called *eigenfunctions*, and all together is called *eigenstates*. Eigenvalue problems, both for matrices and differential operators, were known in mathematics before the advent of quantum mechanics. The creators of quantum mechanics, mainly Schrödinger and Heisenberg, realised that this mathematical formalism can accurately describe quantization of energy levels observed in experiments. Whereas Schrödinger formulated his famous Schrödinger equation, Heisenberg made a major contribution into description of quantum systems with matrices.

B. Energy levels of a particle in a box

As an illustration, consider a particle in a one-dimensional rigid box, $0 \leq x \leq L$. In this case the momentum becomes

$$\hat{p} = -i\hbar \frac{d}{dx} \quad (44)$$

and Eq. (39) takes the form

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \Psi(x) = \varepsilon \Psi(x) \quad (45)$$

and can be represented as

$$\frac{d^2}{dx^2}\Psi(x) + k^2\Psi(x) = 0, \quad k^2 \equiv \frac{2m\varepsilon}{\hbar^2}. \quad (46)$$

The solution of this equation satisfying the boundary conditions $\Psi(0) = \Psi(L) = 0$ has the form

$$\Psi_\nu(x) = A \sin(k_\nu x), \quad k_\nu = \frac{\pi}{L}\nu, \quad \nu = 1, 2, 3, \dots \quad (47)$$

where eigenstates are labeled by the index ν . The constant A following from Eq. (41) is $A = \sqrt{2/L}$. The energy eigenvalues are given by

$$\varepsilon_\nu = \frac{\hbar^2 k_\nu^2}{2m} = \frac{\pi^2 \hbar^2 \nu^2}{2mL^2}. \quad (48)$$

One can see the the energy ε is quadratic in the momentum $p = \hbar k$ (de Broglie relation), as it should be, but the energy levels are discrete because of the quantization. For very large boxes, $L \rightarrow \infty$, the energy levels become quasicontinuous. The lowest-energy level with $\nu = 1$ is called the *ground state*.

For a three-dimensional box with sides L_x , L_y , and L_z one has to solve the Schrödinger equation

$$-\frac{\hbar^2}{2m} \left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2} \right) \Psi(x) = \varepsilon \Psi(x) \quad (49)$$

with similar boundary conditions. The solution factorizes and has the form

$$\Psi_{\nu_x, \nu_y, \nu_z}(x, y, z) = A \sin(k_{\nu_x} x) \sin(k_{\nu_y} y) \sin(k_{\nu_z} z), \quad k_\alpha = \frac{\pi}{L_\alpha} \nu_\alpha, \quad \nu_\alpha = 1, 2, 3, \dots, \quad (50)$$

where $\alpha = x, y, z$. The energy levels are

$$\varepsilon = \frac{\hbar^2 \mathbf{k}^2}{2m} = \frac{\hbar^2 (k_x^2 + k_y^2 + k_z^2)}{2m} \quad (51)$$

and parametrized by the three quantum numbers ν_α . The ground state is $(\nu_x, \nu_y, \nu_z) = (1, 1, 1)$. One can order the states in increasing ε and number them by the index j , the ground state being $j = 1$. If $L_x = L_y = L_z = L$, then

$$\varepsilon_{\nu_x, \nu_y, \nu_z} = \frac{\pi^2 \hbar^2}{2mL^2} (\nu_x^2 + \nu_y^2 + \nu_z^2) \quad (52)$$

and the same value of ε_j can be realized for different sets of ν_x , ν_y , and ν_z , for instance, $(1, 5, 12)$, $(5, 12, 1)$, etc. The number of different sets of (ν_x, ν_y, ν_z) having the same ε_j is called degeneracy and is denoted as g_j . States with $\nu_x = \nu_y = \nu_z$ have $g_j = 1$ and they are called non-degenerate. If only two of the numbers ν_x , ν_y , and ν_z coincide, the degeneracy is $g_j = 3$. If all numbers are different, $g_j = 3! = 6$. If one sums over the energy levels parametrized by j , one has to multiply the summands by the corresponding degeneracies.

C. Density of states

For systems of a large size and thus very finely quantized states, one can define the density of states $\rho(\varepsilon)$ as the number of energy levels dn in the interval $d\varepsilon$, that is,

$$dn = \rho(\varepsilon) d\varepsilon. \quad (53)$$

It is convenient to start calculation of $\rho(\varepsilon)$ by introducing the number of states dn in the “elementary volume” $d\nu_x d\nu_y d\nu_z$, considering ν_x , ν_y , and ν_z as continuous. The result obviously is

$$dn = d\nu_x d\nu_y d\nu_z, \quad (54)$$

that is, the corresponding density of states is 1. Now one can rewrite the same number of states in terms of the wave vector \mathbf{k} using Eq. (51)

$$dn = \frac{V}{\pi^3} dk_x dk_y dk_z, \quad (55)$$

where $V = L_x L_y L_z$ is the volume of the box. After that one can go over to the number of states within the shell dk , as was done for the distribution function of the molecules over velocities. Taking into account that k_x , k_y , and k_z are all positive, this shell is not a complete spherical shell but $1/8$ of it. Thus

$$dn = \frac{V}{\pi^3} \frac{4\pi}{8} k^2 dk. \quad (56)$$

The last step is to change the variable from k to ε using Eq. (51). With

$$k^2 = \frac{2m}{\hbar^2} \varepsilon, \quad k = \sqrt{\frac{2m}{\hbar^2}} \sqrt{\varepsilon}, \quad \frac{dk}{d\varepsilon} = \frac{1}{2} \sqrt{\frac{2m}{\hbar^2}} \frac{1}{\sqrt{\varepsilon}} \quad (57)$$

one obtains Eq. (53) with

$$\rho(\varepsilon) = \frac{V}{(2\pi)^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \sqrt{\varepsilon}. \quad (58)$$

IX. STATISTICAL THERMODYNAMICS OF THE IDEAL GAS

In this section we demonstrate how the results for the ideal gas, previously obtained within the molecular theory, follow from the more general framework of statistical physics in the preceding section. Consider an ideal gas in a sufficiently large container. In this case the energy levels of the system, see Eq. (51), are quantized so finely that one can introduce the density of states $\rho(\varepsilon)$ defined by Eq. (53). The number of particles in quantum states within the energy interval $d\varepsilon$ is the product of the number of particles in one state $N(\varepsilon)$ and the number of states dn_ε in this energy interval. With $N(\varepsilon)$ given by Eq. (29) one obtains

$$dN_\varepsilon = N(\varepsilon) dn_\varepsilon = \frac{N}{Z} e^{-\beta\varepsilon} \rho(\varepsilon) d\varepsilon. \quad (59)$$

For finely quantized levels one can replace summation in Eq. (28) and similar formulas by integration as

$$\sum_i \dots \Rightarrow \int d\varepsilon \rho(\varepsilon) \dots \quad (60)$$

Thus for the partition function (28) one has

$$Z = \int d\varepsilon \rho(\varepsilon) e^{-\beta\varepsilon}. \quad (61)$$

For quantum particles in a rigid box with the help of Eq. (58) one obtains

$$Z = \frac{V}{(2\pi)^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty d\varepsilon \sqrt{\varepsilon} e^{-\beta\varepsilon} = \frac{V}{(2\pi)^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \frac{\sqrt{\pi}}{2\beta^{3/2}} = V \left(\frac{mk_B T}{2\pi\hbar^2} \right)^{3/2}. \quad (62)$$

Using the classical relation $\varepsilon = mv^2/2$ and thus $d\varepsilon = mv dv$, one can obtain the formula for the number of particles in the speed interval dv

$$dN_v = N f(v) dv, \quad (63)$$

where the speed distribution function $f(v)$ is given by

$$\begin{aligned} f(v) &= \frac{1}{Z} e^{-\beta\varepsilon} \rho(\varepsilon) m v = \frac{1}{V} \left(\frac{2\pi\hbar^2}{mk_B T} \right)^{3/2} \frac{V}{(2\pi)^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \sqrt{\frac{m}{2}} v m v e^{-\beta\varepsilon} \\ &= \left(\frac{m}{2\pi k_B T} \right)^{3/2} 4\pi v^2 \exp\left(-\frac{mv^2}{2k_B T}\right). \end{aligned} \quad (64)$$

This result coincides with the Maxwell distribution function obtained earlier from the molecular theory of gases. The Planck's constant \hbar that links to quantum mechanics disappeared from the final result.

The internal energy of the ideal gas is its kinetic energy

$$U = N\bar{\varepsilon}, \quad (65)$$

$\bar{\varepsilon} = m\bar{v}^2/2$ being the average kinetic energy of an atom. The latter can be calculated with the help of the speed distribution function above, as was done in the molecular theory of gases. The result has the form

$$\bar{\varepsilon} = \frac{f}{2}k_B T, \quad (66)$$

where in our case $f = 3$ corresponding to three translational degrees of freedom. The same result can be obtained from Eq. (31)

$$U = -N \frac{\partial \ln Z}{\partial \beta} = -N \frac{\partial}{\partial \beta} \ln \left[V \left(\frac{m}{2\pi\hbar^2\beta} \right)^{3/2} \right] = \frac{3}{2}N \frac{\partial}{\partial \beta} \ln \beta = \frac{3}{2}N \frac{1}{\beta} = \frac{3}{2}Nk_B T. \quad (67)$$

After that the known result for the heat capacity $C_V = (\partial U/\partial T)_V$ follows.

The pressure P is defined by the thermodynamic formula

$$P = - \left(\frac{\partial F}{\partial V} \right)_T. \quad (68)$$

With the help of Eqs. (38) and (62) one obtains

$$P = Nk_B T \frac{\partial \ln Z}{\partial V} = Nk_B T \frac{\partial \ln V}{\partial V} = \frac{Nk_B T}{V} \quad (69)$$

that amounts to the equation of state of the ideal gas $PV = Nk_B T$.

X. STATISTICAL THERMODYNAMICS OF HARMONIC OSCILLATORS

Consider an ensemble of N identical harmonic oscillators, each of them described by the Hamiltonian

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{kx^2}{2}. \quad (70)$$

Here the momentum operator \hat{p} is given by Eq. (44) and k is the spring constant. This theoretical model can describe, for instance, vibrational degrees of freedom of diatomic molecules. In this case x is the elongation of the chemical bond between the two atoms, relative to the equilibrium bond length. The stationary Schrödinger equation (39) for a harmonic oscillator becomes

$$\left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{kx^2}{2} \right) \Psi(x) = \varepsilon \Psi(x). \quad (71)$$

The boundary conditions for this equation require that $\Psi(\pm\infty) = 0$ and the integral in Eq. (41) converges. In contrast to Eq. (45), this is a linear differential equation with a *variable* coefficient. Such differential equations in general do not have solutions in terms of known functions. In some cases the solution can be expressed through *special functions* such as hypergeometrical, Bessel functions, etc. Solution of Eq. (71) can be found but this task belongs to quantum mechanics courses. The main result that we need here is that the energy eigenvalues of the harmonic oscillator have the form

$$\varepsilon_\nu = \hbar\omega_0 \left(\nu + \frac{1}{2} \right), \quad \nu = 0, 1, 2, \dots, \quad (72)$$

where $\omega_0 = \sqrt{k/m}$ is the frequency of oscillations. The energy level with $\nu = 0$ is the ground state. The ground-state energy $\varepsilon_0 = \hbar\omega_0/2$ is not zero, as would be the case for a classical oscillator. This quantum ground-state energy is called *zero-point energy*. It is irrelevant in the calculation of the heat capacity of an ensemble of harmonic oscillators.

The partition function of a harmonic oscillator is

$$Z = \sum_{\nu=0}^{\infty} e^{-\beta\varepsilon_\nu} = e^{-\beta\hbar\omega_0/2} \sum_{\nu=0}^{\infty} (e^{-\beta\hbar\omega_0})^\nu = \frac{e^{-\beta\hbar\omega_0/2}}{1 - e^{-\beta\hbar\omega_0}} = \frac{1}{e^{\beta\hbar\omega_0/2} - e^{-\beta\hbar\omega_0/2}} = \frac{2}{\sinh(\beta\hbar\omega_0/2)}, \quad (73)$$

where the result for the geometrical progression

$$1 + x + x^2 + x^3 + \dots = (1 - x)^{-1}, \quad x < 1 \quad (74)$$

was used. The hyperbolic functions are defined by

$$\begin{aligned} \sinh(x) &\equiv \frac{e^x - e^{-x}}{2}, & \cosh(x) &\equiv \frac{e^x + e^{-x}}{2} \\ \tanh(x) &\equiv \frac{\sinh(x)}{\cosh(x)}, & \coth(x) &\equiv \frac{\cosh(x)}{\sinh(x)} = \frac{1}{\tanh(x)}. \end{aligned} \quad (75)$$

We will be using the formulas

$$\sinh(x)' = \cosh(x), \quad \cosh(x)' = \sinh(x) \quad (76)$$

and

$$\sinh(x) \cong \begin{cases} x, & x \ll 1 \\ e^x/2, & x \gg 1 \end{cases}, \quad \tanh(x) \cong \begin{cases} x, & x \ll 1 \\ 1, & x \gg 1. \end{cases} \quad (77)$$

The internal (average) energy of the ensemble of oscillators is given by Eq. (31). This yields

$$U = -N \frac{\partial \ln Z}{\partial \beta} = N \frac{\partial \ln \sinh(\beta \hbar \omega_0 / 2)}{\partial \beta} = \frac{N}{\sinh(\beta \hbar \omega_0 / 2)} \frac{\partial \sinh(\beta \hbar \omega_0 / 2)}{\partial \beta} = N \frac{\hbar \omega_0}{2} \coth\left(\frac{\beta \hbar \omega_0}{2}\right) \quad (78)$$

or

$$U = N \frac{\hbar \omega_0}{2} \coth\left(\frac{\hbar \omega_0}{2k_B T}\right). \quad (79)$$

Another way of writing the internal energy is

$$U = N \hbar \omega_0 \left(\frac{1}{e^{\beta \hbar \omega_0} - 1} + \frac{1}{2} \right), \quad (80)$$

where the constant term with 1/2 is the zero-point energy. The limiting low- and high-temperature cases of this formula are

$$U \cong \begin{cases} N \hbar \omega_0 / 2, & k_B T \ll \hbar \omega_0 \\ N k_B T, & k_B T \gg \hbar \omega_0. \end{cases} \quad (81)$$

In the low-temperature case, almost all oscillators are in their ground states, since $e^{-\beta \hbar \omega_0} \ll 1$. Thus the main term that contributes into the partition function in Eq. (73) is $\nu = 0$. Correspondingly, U is the sum of ground-state energies of all oscillators.

At high temperatures, the previously obtained classical result is reproduced. The Planck's constant \hbar that links to quantum mechanics disappears. In this case, $e^{-\beta \hbar \omega_0}$ is only slightly smaller than one, so that very many different n contribute to Z in Eq. (73). In this case one can replace summation by integration, as was done above for the particle in a potential box. In that case one also obtained the classical results.

One can see that the crossover between the two limiting cases corresponds to $k_B T \sim \hbar \omega_0$. In the high-temperature limit $k_B T \gg \hbar \omega_0$, many low-lying energy levels are populated. The top populated level ν^* can be estimated from $k_B T \sim \hbar \omega_0 \nu^*$, so that

$$\nu^* \sim \frac{k_B T}{\hbar \omega_0} \gg 1. \quad (82)$$

Probability to find an oscillator in the states with $\nu \gg \nu^*$ is exponentially small.

The heat capacity is defined by

$$C = \frac{dU}{dT} = N \frac{\hbar \omega_0}{2} \left(-\frac{1}{\sinh^2[\hbar \omega_0 / (2k_B T)]} \right) \left(-\frac{\hbar \omega_0}{2k_B T^2} \right) = N k_B \left(\frac{\hbar \omega_0 / (2k_B T)}{\sinh[\hbar \omega_0 / (2k_B T)]} \right)^2. \quad (83)$$

This formula has limiting cases

$$C \cong \begin{cases} N k_B \left(\frac{\hbar \omega_0}{k_B T} \right)^2 \exp\left(-\frac{\hbar \omega_0}{k_B T}\right), & k_B T \ll \hbar \omega_0 \\ N k_B, & k_B T \gg \hbar \omega_0. \end{cases} \quad (84)$$

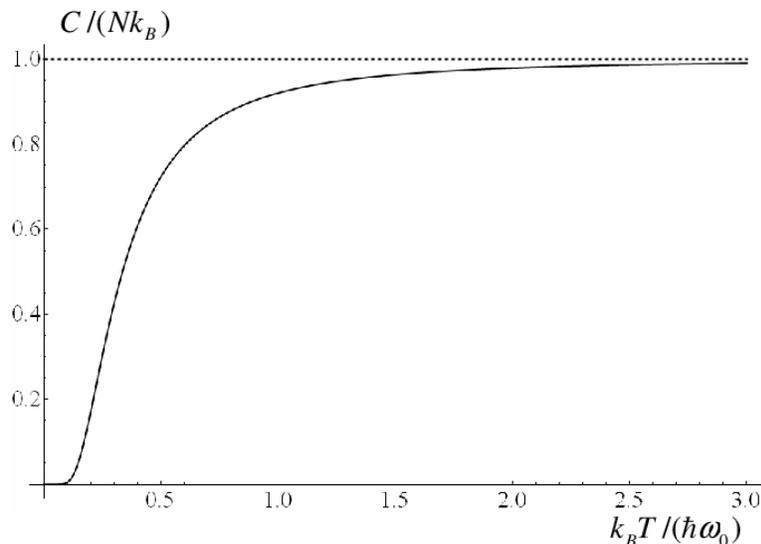


FIG. 2: Heat capacity of harmonic oscillators.

One can see that at high temperatures the heat capacity can be written as

$$C = \frac{f}{2} N k_B, \quad (85)$$

where the effective number of degrees of freedom for an oscillator is $f = 2$. The explanation of the additional factor 2 is that the oscillator has not only the kinetic, but also the potential energy, and the average values of these two energies are the same. Thus the total amount of energy in a vibrational degree of freedom doubles with respect to the translational and rotational degrees of freedom.

At low temperatures the vibrational heat capacity above becomes exponentially small. One says that vibrational degrees of freedom are getting frozen out at low temperatures.

The heat capacity of an ensemble of harmonic oscillators in the whole temperature range, Eq. (83), is plotted in Fig. 2.

The average quantum number of an oscillator is given by

$$n \equiv \langle \nu \rangle = \frac{1}{Z} \sum_{\nu=0}^{\infty} \nu e^{-\beta \varepsilon_{\nu}}. \quad (86)$$

Using Eq. (72), one can calculate this sum as follows

$$n = \frac{1}{Z} \sum_{\nu=0}^{\infty} \left(\frac{1}{2} + \nu \right) e^{-\beta \varepsilon_{\nu}} - \frac{1}{Z} \sum_{\nu=0}^{\infty} \frac{1}{2} e^{-\beta \varepsilon_{\nu}} = \frac{1}{\hbar \omega_0} \frac{1}{Z} \sum_{\nu=0}^{\infty} \varepsilon_{\nu} e^{-\beta \varepsilon_{\nu}} - \frac{Z}{2Z} = -\frac{1}{\hbar \omega_0} \frac{1}{Z} \frac{\partial Z}{\partial \beta} - \frac{1}{2} = \frac{U}{N \hbar \omega_0} - \frac{1}{2}. \quad (87)$$

Finally with the help of Eq. (80), one finds

$$n = \frac{1}{e^{\beta \hbar \omega_0} - 1} = \frac{1}{\exp[\hbar \omega_0 / (k_B T)] - 1}. \quad (88)$$

This is the Bose-Einstein distribution that will be considered later. The meaning of it is the following. Considering the oscillator as a “box” or “mode”, one can ask what is the average number of quanta (that is, “particles” or quasiparticles) in this box at a given temperature. The latter is given by the formula above.

Substituting Eq. (88) into Eq. (80), one obtains a nice formula

$$U = N \hbar \omega_0 \left(n + \frac{1}{2} \right) \quad (89)$$

resembling Eq. (72). At low temperatures, $k_B T \ll \hbar\omega_0$, the average quantum number n becomes exponentially small. This means that the oscillator is predominantly in its ground state, $\nu = 0$. At high temperatures, $k_B T \gg \hbar\omega_0$, Eq. (88) yields

$$n \cong \frac{k_B T}{\hbar\omega_0} \quad (90)$$

that has the same order of magnitude as the top populated quantum level number ν^* given by Eq. (82).

The density of states $\rho(\varepsilon)$ for the harmonic oscillator can be easily found. The number of levels dn_ν in the interval $d\nu$ is

$$dn_\nu = d\nu \quad (91)$$

(that is, there is only one level in the interval $d\nu = 1$). Then, changing the variables with the help of Eq. (72), one finds the number of levels dn_ε in the interval $d\varepsilon$ as

$$dn_\varepsilon = \frac{d\nu}{d\varepsilon} d\varepsilon = \left(\frac{d\varepsilon}{d\nu}\right)^{-1} d\varepsilon = \rho(\varepsilon) d\varepsilon, \quad (92)$$

where

$$\rho(\varepsilon) = \frac{1}{\hbar\omega_0}. \quad (93)$$

To conclude this section, let us reproduce the classical high-temperature results by a simpler method. At high temperatures, many levels are populated and the distribution function $e^{-\beta\varepsilon_\nu}$ only slightly changes from one level to the other. Indeed its relative change is

$$\frac{e^{-\beta\varepsilon_\nu} - e^{-\beta\varepsilon_{\nu+1}}}{e^{-\beta\varepsilon_\nu}} = 1 - e^{-\beta(\varepsilon_{\nu+1} - \varepsilon_\nu)} = 1 - e^{-\beta\hbar\omega_0} \cong 1 - 1 + \beta\hbar\omega_0 = \frac{\hbar\omega_0}{k_B T} \ll 1. \quad (94)$$

In this situation one can replace summation in Eq. (73) by integration over ε using the density of states of Eq. (93):

$$Z = \int_0^\infty d\varepsilon \rho(\varepsilon) e^{-\beta\varepsilon} = \frac{1}{\hbar\omega_0} \int_0^\infty d\varepsilon e^{-\beta\varepsilon} = \frac{1}{\hbar\omega_0 \beta} = \frac{k_B T}{\hbar\omega_0}. \quad (95)$$

Also, one can integrate over ν considering it as continuous and not using the density of states explicitly:

$$Z = \int_0^\infty d\nu e^{-\beta\varepsilon} = \int_0^\infty d\varepsilon \frac{d\nu}{d\varepsilon} e^{-\beta\varepsilon} = \frac{1}{\hbar\omega_0} \int_0^\infty d\varepsilon e^{-\beta\varepsilon} = \frac{1}{\hbar\omega_0 \beta} = \frac{k_B T}{\hbar\omega_0}. \quad (96)$$

The results of this calculation is in accord with Eq. (93). Now the internal energy U is given by

$$U = -N \frac{\partial \ln Z}{\partial \beta} = -N \frac{\partial \ln \frac{1}{\beta} + \dots}{\partial \beta} = N \frac{\partial \ln \beta + \dots}{\partial \beta} = \frac{N}{\beta} = N k_B T \quad (97)$$

that coincides with the second line of Eq. (81).

In 1907 Albert Einstein proposed a theory of thermal properties of solids based on the assumption of the existence therein of independent thermally excited harmonic oscillators. The essential moment was that Einstein applied the Max Planck's idea of quantization, extending it from the electromagnetic radiation (see Chapter XX) to the vibrations of atoms and molecules in solids. Before the Einstein's work, it was a puzzle why the heat capacity is not constant, as predicted by the classical theory (our high-temperature limit) but becomes small at low temperatures. Fig. 2 is the result of the Einstein's theory. This was historically the third application of the idea of quantization, after the seminal 1900 work of Max Planck, and Einstein's theory of the photoeffect of 1905. All these three achievement were accomplished before quantum mechanics was finalized about 1927. Einstein's result at low temperatures is only qualitative as the concept ignores the interaction of the oscillations of different atoms. The accurate theory by Debye, see Chapter XII, leads to the dependence $C_V \propto T^3$ in 3D solids at low temperatures. Still, Figs. 2 and 4 look pretty similar.

XI. STATISTICAL THERMODYNAMICS OF ROTATORS

The rotational kinetic energy of a rigid body, expressed with respect to the *principal axes*, reads

$$E_{\text{rot}} = \frac{1}{2}I_1\omega_1^2 + \frac{1}{2}I_2\omega_2^2 + \frac{1}{2}I_3\omega_3^2. \quad (98)$$

We will restrict our consideration to the axially symmetric body with $I_1 = I_2 = I$, since for the fully asymmetric body the quantum energy levels cannot be found analytically. In this case E_{rot} can be rewritten in terms of the angular momentum components $L_\alpha = I_\alpha\omega_\alpha$, where $\alpha = 1, 2, 3$, as follows

$$E_{\text{rot}} = \frac{L_1^2}{2I_1} + \frac{L_2^2}{2I_2} + \frac{L_3^2}{2I_3} = \frac{\mathbf{L}^2}{2I} + \frac{1}{2} \left(\frac{1}{I_3} - \frac{1}{I} \right) L_3^2, \quad (99)$$

where $\mathbf{L}^2 = L_1^2 + L_2^2 + L_3^2$.

In the important case of a diatomic molecule with two identical atoms, then the center of mass is located between the two atoms at the distance $d/2$ from each, where d is the distance between the atoms. The moment of inertia of the molecule with respect to the 3 axis going through both atoms is zero, $I_3 = 0$. The moments of inertia with respect to the 1 and 2 axis are equal to each other:

$$I_1 = I_2 = I = 2 \times M \left(\frac{d}{2} \right)^2 = \frac{1}{2}Md^2, \quad (100)$$

where M is the mass of the atom. In our case, $I_3 = 0$, there is no kinetic energy associated with rotation around the 3 axis. Then Eq. (99) requires $L_3 = 0$, that is, the angular momentum of a diatomic molecule is perpendicular to its axis.

In quantum mechanics \mathbf{L} and L_3 become operators, and the rotational energy above becomes the Hamiltonian, $E_{\text{rot}} \Rightarrow \hat{H}_{\text{rot}}$. The solution of the stationary Schrödinger equation yields eigenvalues of \mathbf{L}^2 , L_3 in terms of three quantum numbers l , m , and n :

$$\hat{\mathbf{L}}^2 = \hbar^2 l(l+1), \quad l = 0, 1, 2, \dots \quad (101)$$

$$\hat{L}_3 = \hbar n, \quad m, n = -l, -l+1, \dots, l-1, l. \quad (102)$$

Thus, the energy eigenvalues are given by

$$\varepsilon_{l,n} = \frac{\hbar^2 l(l+1)}{2I} + \frac{\hbar^2}{2} \left(\frac{1}{I_3} - \frac{1}{I} \right) n^2 \quad (103)$$

that follows by substitution of Eqs. (101) and (102) into Eq. (99). The quantum number m accounts for the $2l+1$ different orientations of the vector \mathbf{L} in space. As all these orientations are equivalent, the energy does not depend on m . Thus, there are at least $2l+1$ degenerate energy levels. Further, the axis of the molecule can have $2l+1$ different projections on $\hat{\mathbf{L}}$ parametrized by the quantum number n . In the general case $I_3 \neq I$ these states are non-degenerate. However, they become degenerate for the fully symmetric body, $I_1 = I_2 = I_3 = I$. In this case the energy eigenvalues become

$$\varepsilon_l = \frac{\hbar^2 l(l+1)}{2I}, \quad (104)$$

and the degeneracy of the quantum level l is $g_l = (2l+1)^2$. For the diatomic molecule $I_3 = 0$, and the only acceptable value of n is $n = 0$. Thus one obtains Eq. (104) again but with the degeneracy $g_l = 2l+1$.

Below we will consider only the two cases: a) a fully symmetric body and b) diatomic molecule. The rotational partition function for both of them is given by

$$Z = \sum_l g_l e^{-\beta\varepsilon_l}, \quad g_l = (2l+1)^\xi, \quad \xi = \begin{cases} 2, & \text{symmetric body} \\ 1, & \text{diatomic molecule.} \end{cases} \quad (105)$$

In both cases Z cannot be calculated analytically in general. In the general axially-symmetric case $I_1 = I_2 \neq I_3$ with $I_3 \neq 0$ one has to perform a numerical summation over both l and n . However, even the sum over l above cannot be calculated analytically, so that we will consider the limits of low and high temperatures.

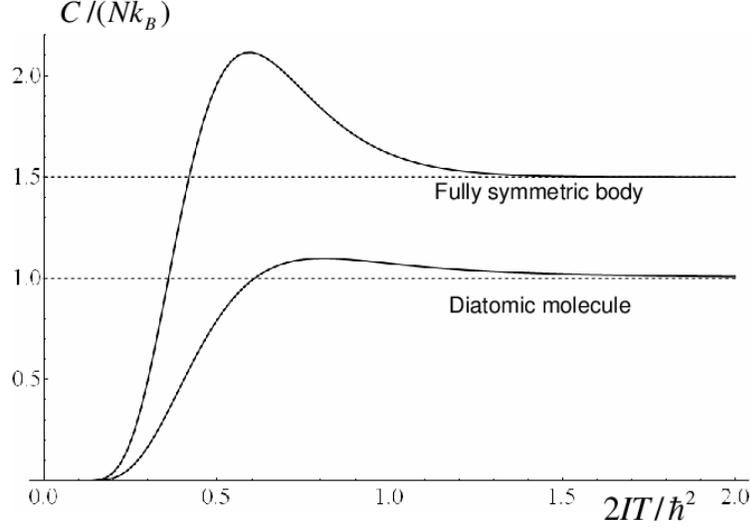


FIG. 3: Rotational heat capacity of a fully symmetric body and a diatomic molecule.

In the low-temperature limit, most of rotators are in their ground state $l = 0$, and very few are in the first excited state $l = 1$. Discarding all other values of l , one obtains

$$Z \cong 1 + 3^\xi \exp\left(-\frac{\beta\hbar^2}{I}\right) \quad (106)$$

at low temperatures. The rotational internal energy is given by

$$U = -N \frac{\partial \ln Z}{\partial \beta} = 3^\xi \frac{\hbar^2}{I} \exp\left(-\frac{\beta\hbar^2}{I}\right) = 3^\xi \frac{\hbar^2}{I} \exp\left(-\frac{\hbar^2}{Ik_B T}\right) \quad (107)$$

and it is exponentially small. The heat capacity is

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = 3^\xi k_B \left(\frac{\hbar^2}{Ik_B T}\right)^2 \exp\left(-\frac{\hbar^2}{Ik_B T}\right) \quad (108)$$

and it is also exponentially small.

In the high-temperature limit, very many energy levels are thermally populated, so that in Eq. (105) one can neglect $1 \ll l$ and replace summation over l by integration. With

$$g_l \cong (2l)^\xi, \quad \varepsilon_l \equiv \varepsilon \cong \frac{\hbar^2 l^2}{2I}, \quad \frac{\partial \varepsilon}{\partial l} = \frac{\hbar^2 l}{I}, \quad \frac{\partial l}{\partial \varepsilon} = \frac{I}{\hbar^2} \sqrt{\frac{\hbar^2}{2I\varepsilon}} = \sqrt{\frac{I}{2\hbar^2 \varepsilon}} \quad (109)$$

one has

$$Z \cong \int_0^\infty dl g_l e^{-\beta \varepsilon_l} \cong 2^\xi \int_0^\infty dl l^\xi e^{-\beta \varepsilon_l} = 2^\xi \int_0^\infty d\varepsilon \frac{\partial l}{\partial \varepsilon} l^\xi e^{-\beta \varepsilon} \quad (110)$$

and further

$$\begin{aligned} Z &\cong 2^\xi \sqrt{\frac{I}{2\hbar^2}} \int_0^\infty d\varepsilon \frac{1}{\sqrt{\varepsilon}} \left(\frac{2I\varepsilon}{\hbar^2}\right)^{\xi/2} e^{-\beta \varepsilon} = 2^{(3\xi-1)/2} \left(\frac{I}{\hbar^2}\right)^{(\xi+1)/2} \int_0^\infty d\varepsilon \varepsilon^{(\xi-1)/2} e^{-\beta \varepsilon} \\ &= 2^{(3\xi-1)/2} \left(\frac{I}{\beta\hbar^2}\right)^{(\xi+1)/2} \int_0^\infty dx x^{(\xi-1)/2} e^{-x} \propto \beta^{-(\xi+1)/2}. \end{aligned} \quad (111)$$

Now the internal energy is given by

$$U = -N \frac{\partial \ln Z}{\partial \beta} = \frac{\xi+1}{2} N \frac{\partial \ln \beta}{\partial \beta} = \frac{\xi+1}{2} N \frac{1}{\beta} = \frac{\xi+1}{2} N k_B T, \quad (112)$$

whereas the heat capacity is

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{\xi + 1}{2} N k_B. \quad (113)$$

In these two formulas, $f = \xi + 1$ is the number of degrees of freedom, $f = 2$ for a diatomic molecule and $f = 3$ for a fully symmetric rotator. This result confirms the principle of equipartition of energy over the degrees of freedom in the classical limit that requires temperatures high enough.

The all-temperature result for the heat capacity of rotators based on the numerical summation in Eq. (105) is shown in Fig. 3. Surprisingly, there is a maximum of the heat capacity in the intermediate temperature region that contrasts the monotonic increase of the heat capacity of the harmonic oscillator shown in Fig. 2.

To conclude this section, let us calculate the partition function classically at high temperatures. The calculation can be performed in the general case of all moments of inertia different. The rotational energy, Eq. (98), can be written as

$$E_{\text{rot}} = \frac{L_1^2}{2I_1} + \frac{L_2^2}{2I_2} + \frac{L_3^2}{2I_3}. \quad (114)$$

The dynamical variables here are the angular momentum components L_1 , L_2 , and L_3 , so that the partition function can be obtained by integration with respect to them

$$\begin{aligned} Z_{\text{class}} &= \int_{-\infty}^{\infty} dL_1 dL_2 dL_3 \exp(-\beta E_{\text{rot}}) \\ &= \int_{-\infty}^{\infty} dL_1 \exp\left(-\frac{\beta L_1^2}{2I_1}\right) \times \int_{-\infty}^{\infty} dL_2 \exp\left(-\frac{\beta L_2^2}{2I_2}\right) \times \int_{-\infty}^{\infty} dL_3 \exp\left(-\frac{\beta L_3^2}{2I_3}\right) \\ &= \sqrt{\frac{2I_1}{\beta}} \times \frac{2I_2}{\beta} \times \frac{2I_3}{\beta} \left(\int_{-\infty}^{\infty} dx e^{-x^2} \right)^3 \propto \beta^{-3/2}. \end{aligned} \quad (115)$$

In fact, Z_{class} contains some additional coefficients, for instance, from the integration over the orientations of the molecule. However, these coefficients are irrelevant in the calculation of the the internal energy and heat capacity. For the internal energy one obtains

$$U = -N \frac{\partial \ln Z}{\partial \beta} = \frac{3}{2} N \frac{\partial \ln \beta}{\partial \beta} = \frac{3}{2} N k_B T \quad (116)$$

that coincides with Eq. (112) with $\xi = 2$. In the case of the diatomic molecule the energy has the form

$$E_{\text{rot}} = \frac{L_1^2}{2I_1} + \frac{L_2^2}{2I_2}. \quad (117)$$

Then the partition function becomes

$$\begin{aligned} Z_{\text{class}} &= \int_{-\infty}^{\infty} dL_1 dL_2 \exp(-\beta E_{\text{rot}}) \\ &= \int_{-\infty}^{\infty} dL_1 \exp\left(-\frac{\beta L_1^2}{2I_1}\right) \times \int_{-\infty}^{\infty} dL_2 \exp\left(-\frac{\beta L_2^2}{2I_2}\right) \\ &= \sqrt{\frac{2I_1}{\beta}} \times \frac{2I_2}{\beta} \left(\int_{-\infty}^{\infty} dx e^{-x^2} \right)^2 \propto \beta^{-1}. \end{aligned} \quad (118)$$

This leads to

$$U = N k_B T, \quad (119)$$

in accordance with Eq. (112) with $\xi = 1$.

XII. STATISTICAL PHYSICS OF VIBRATIONS IN SOLIDS

Above in Sec. X we have studied statistical mechanics of harmonic oscillators. For instance, a diatomic molecule behaves as an oscillator, the chemical bond between the atoms periodically changing its length with time in the

classical description. For molecules consisting of $N \geq 2$ atoms, vibrations become more complicated and, as a rule, involve all N atoms. Still, within the harmonic approximation (the potential energy expanded up to the second-order terms in deviations from the equilibrium positions) the classical equations of motion are linear and can be dealt with matrix algebra. Diagonalizing the dynamical matrix of the system, one can find $3N - 6$ linear combinations of atomic coordinates that dynamically behave as *independent* harmonic oscillators. Such *collective* vibrational modes of the system are called *normal modes*. For instance, a hypothetical triatomic molecule with atoms that are allowed to move along a straight line has 2 normal modes. If the masses of the first and third atoms are the same, one of the normal modes corresponds to antiphase oscillations of the first and third atoms with the second (central) atom being at rest. Another normal mode corresponds to the in-phase oscillations of the first and third atoms with the central atom oscillating in the anti-phase to them. For more complicated molecules normal modes can be found numerically.

Normal modes can be considered quantum mechanically as independent quantum oscillators as in Sec. X. Then the vibrational partition function of the molecule is a product of partition functions of individual normal modes and the internal energy is a sum of internal energies of these modes. The latter is the consequence of the independence of the normal modes.

The solid having a well-defined crystal structure is translationally invariant that simplifies finding normal modes, in spite of a large number of atoms N . In the simplest case of one atom in the unit cell normal modes can be found immediately by making Fourier transformation of atomic deviations. The resulting normal modes are sound waves with different wave vectors \mathbf{k} and polarizations (in the simplest case one longitudinal and two equivalent transverse modes). In the sequel, to illustrate basic principles, we will consider only one type of sound waves (say, the longitudinal wave) but we will count it three times. The results can be then generalized for different kinds of waves. For wave vectors small enough, there is the linear relation between the wave vector and the frequency of the oscillations

$$\omega_k = vk \quad (120)$$

In this formula, ω_k depends only on the magnitude $k = 2\pi/\lambda$ and not on the direction of \mathbf{k} and v is the speed of sound. The acceptable values of \mathbf{k} should satisfy the boundary conditions at the boundaries of the solid body. Obviously, the thermodynamics of a large body is insensitive the shape of the body and to the exact form of these conditions. (Note that the body's surface can be rough and then it is difficult to formulate a model of what exactly happens at the surface!) The simplest possibility is to consider a body of the box shape with dimensions L_x , L_y , and L_z and use the clamped boundary conditions, so that the atoms at the boundary cannot move. These boundary conditions are the same as in the quantum problem of a particle in a potential box. One obtains the atomic displacements in the normal modes of the type $u(x) = u_0 \sin(k_x x)$ etc., and the discrete values of the wave vector components k_α with $\alpha = x, y, z$

$$k_\alpha = \pi \frac{\nu_\alpha}{L_\alpha}, \quad \nu = 1, 2, 3, \dots \quad (121)$$

If the atoms are arranged in a simple cubic lattice with the lattice spacing a , then $L_\alpha = aN_\alpha$, where N_α are the numbers of atoms (or unit cells) in each direction α . Then

$$k_\alpha = \frac{\pi}{a} \frac{\nu_\alpha}{N_\alpha}. \quad (122)$$

Similarly to the problem of the particle in a box, one can introduce the frequency density of normal modes $\rho(\omega)$ via the number of normal modes in the frequency interval $d\omega$

$$dn_\omega = \rho(\omega) d\omega. \quad (123)$$

Using Eq. (56) multiplied by the number of phonon modes 3 and changing from k to ω with the help of Eq. (120) one obtains

$$\rho(\omega) = \frac{3V}{2\pi^2 v^3} \omega^2. \quad (124)$$

The total number of normal modes should be $3N$:

$$3N = 3 \sum_{\mathbf{k}} 1 = 3 \sum_{\nu_x, \nu_y, \nu_z} 1. \quad (125)$$

This equation splits into the three separate equations

$$N_\alpha = \sum_{\nu_\alpha=1}^{\nu_{\alpha,\max}} 1 = \nu_{\alpha,\max}. \quad (126)$$

This defines the maximal value of ν_α and, according to Eq. (122), of k_α that happens to be $k_{\alpha,\max} = \pi/a$ for all α .

As the solid body is macroscopic and there are very many values of the allowed wave vectors, one can replace summation by integration and use the density of states:

$$\sum_{\mathbf{k}} \dots \Rightarrow \int_0^{\omega_{\max}} d\omega \rho(\omega) \dots \quad (127)$$

At large k and thus ω , the linear dependence of Eq. (120) is no longer valid. Moreover, for models with elastic bonds on the lattice at large k there is no purely longitudinal and transverse modes, and the mode frequency depends on the direction of the wave vector. Thus that Eq. (124) becomes invalid as well. Still, one can make a crude approximation assuming that Eqs. (120) and (124) are valid until some maximal frequency of the sound waves in the body. The model based on this assumption is called Debye model. The maximal frequency (or the Debye frequency ω_D) is defined by Eq. (125) that takes the form

$$3N = \int_0^{\omega_D} d\omega \rho(\omega). \quad (128)$$

With the use of Eq. (124) one obtains

$$3N = \int_0^{\omega_D} d\omega \frac{3V}{2\pi^2 v^3} \omega^2 = \frac{V\omega_D^3}{2\pi^2 v^3}, \quad (129)$$

wherefrom

$$\omega_D = (6\pi^2)^{1/3} \frac{v}{a}, \quad (130)$$

where $V/N = v_0 = a^3$, is the unit-cell volume. It is convenient to rewrite Eq. (124) in terms of ω_D as

$$\rho(\omega) = 9N \frac{\omega^2}{\omega_D^3}. \quad (131)$$

The consideration up to this point is completely classical. Now we will consider each \mathbf{k} -mode as an independent harmonic oscillator. The quantum energy levels of the latter are given by Eq. (72). In our case for a \mathbf{k} -oscillator it becomes

$$\varepsilon_{\mathbf{k},\nu_{\mathbf{k}}} = \hbar\omega_{\mathbf{k}} \left(\nu_{\mathbf{k}} + \frac{1}{2} \right), \quad \nu_{\mathbf{k}} = 0, 1, 2, \dots \quad (132)$$

One quant of the energy $\hbar\omega_{\mathbf{k}}$ in the \mathbf{k} -mode is called phonon. The quantum number $\nu_{\mathbf{k}}$ is the number of phonons in the \mathbf{k} -mode. Note the relation

$$\varepsilon = \hbar\omega \quad (133)$$

between the energy of a quant of any wave (phonons, photons) and its frequency.

All the modes contribute additively into the internal energy, thus

$$U = 3 \sum_{\mathbf{k}} \langle \varepsilon_{\mathbf{k},\nu_{\mathbf{k}}} \rangle = 3 \sum_{\mathbf{k}} \hbar\omega_{\mathbf{k}} \left(\langle \nu_{\mathbf{k}} \rangle + \frac{1}{2} \right) = 3 \sum_{\mathbf{k}} \hbar\omega_{\mathbf{k}} \left(n_{\mathbf{k}} + \frac{1}{2} \right), \quad (134)$$

where, similarly to Eq. (88),

$$n_{\mathbf{k}} = \frac{1}{\exp(\beta\hbar\omega_{\mathbf{k}}) - 1}. \quad (135)$$

Replacing summation by integration and rearranging Eq. (134), within the Debye model one obtains

$$U = U_0 + \int_0^{\omega_D} d\omega \rho(\omega) \frac{\hbar\omega}{\exp(\beta\hbar\omega) - 1}, \quad (136)$$

where U_0 is the zero-temperature value of U due to the zero-point motion. The integral term in Eq. (136) can be calculated analytically at low and high temperatures.

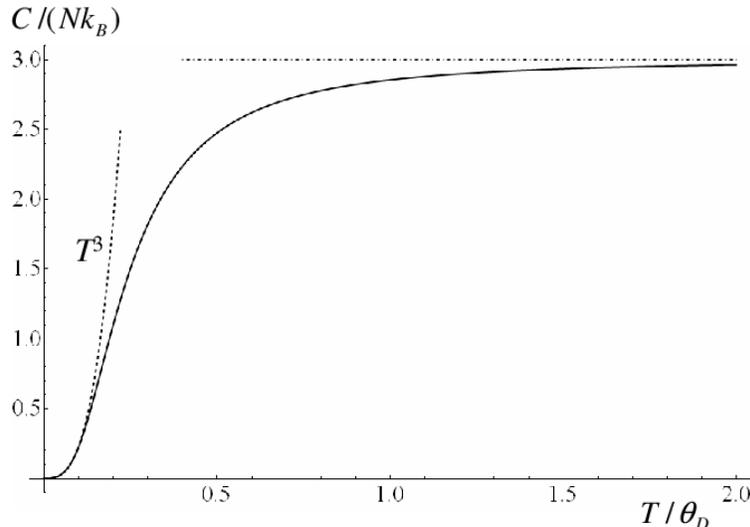


FIG. 4: Temperature dependence of the phonon heat capacity. The low-temperature result $C \propto T^3$ (dashed line) holds only for temperatures much smaller than the Debye temperature θ_D .

For $k_B T \ll \hbar \omega_D$, the integral converges at $\omega \ll \omega_D$, so that one can extend the upper limit of integration to ∞ . One obtains

$$\begin{aligned} U &= U_0 + \int_0^\infty d\omega \rho(\omega) \frac{\hbar \omega}{\exp(\beta \hbar \omega) - 1} = U_0 + \frac{9N}{\omega_D^3} \int_0^\infty d\omega \omega^2 \frac{\hbar \omega}{\exp(\beta \hbar \omega) - 1} \\ &= U_0 + \frac{9N}{(\hbar \omega_D)^3 \beta^4} \int_0^\infty dx \frac{x^3}{e^x - 1} = U_0 + \frac{9N}{(\hbar \omega_D)^3 \beta^4} \frac{\pi^4}{15} = U_0 + \frac{3\pi^4}{5} N k_B T \left(\frac{k_B T}{\hbar \omega_D} \right)^3. \end{aligned} \quad (137)$$

This result can be written in the form

$$U = U_0 + \frac{3\pi^4}{5} N k_B T \left(\frac{T}{\theta_D} \right)^3, \quad (138)$$

where

$$\theta_D = \hbar \omega_D / k_B \quad (139)$$

is the Debye temperature. The heat capacity is given by

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{12\pi^4}{5} N k_B \left(\frac{T}{\theta_D} \right)^3, \quad T \ll \theta_D. \quad (140)$$

Although the Debye temperature enters Eqs. (138) and (140), these results are accurate and insensitive to the Debye approximation.

For $k_B T \gg \hbar \omega_D$, the exponential in Eq. (136) can be expanded for $\beta \hbar \omega \ll 1$. It is, however, convenient to step back and to do the same in Eq. (134). With the help of Eq. (125) one obtains

$$U = U_0 + 3 \sum_{\mathbf{k}} \frac{\hbar \omega_{\mathbf{k}}}{\beta \hbar \omega_{\mathbf{k}}} = U_0 + 3 k_B T \sum_{\mathbf{k}} 1 = U_0 + 3 N k_B T. \quad (141)$$

Note that the phonon spectrum $\omega_{\mathbf{k}}$ that is due to the interactions in the system, disappeared from the formula. For the heat capacity one then obtains

$$C_V = 3 N k_B, \quad (142)$$

k_B per each of approximately $3N$ vibrational modes. One can see that Eqs. (141) and (142) are accurate because they do not use the Debye model. The assumption of the Debye model is really essential at intermediate temperatures, where Eq. (136) is approximate.

The temperature dependence of the photon heat capacity, following from Eq. (136), is shown in Fig. 4 together with its low-temperature asymptote, Eq. (140), and the high-temperature asymptote, Eq. (142). Because of the large numerical coefficient in Eq. (140), the law $C_V \propto T^3$ in fact holds only for the temperatures much smaller than the Debye temperature.

The theory of quantized vibrations in the solid, developed by Debye, improves the more primitive Einstein's model assuming independent oscillators.

XIII. SPINS IN MAGNETIC FIELD

Magnetism of solids is in most cases due to the intrinsic angular momentum of the electron that is called *spin*. In quantum mechanics, spin is an operator represented by a matrix. The value of the electronic angular momentum is $s = 1/2$, so that it is described by a 2×2 matrix and the quantum-mechanical eigenvalue of the square of the electron's angular momentum (in the units of \hbar) is

$$\hat{\mathbf{s}}^2 = s(s+1) = 3/4 \quad (143)$$

c.f. Eq. (101). Eigenvalues of \hat{s}_z , projection of a free spin on any direction z , are given by

$$\hat{s}_z = m, \quad m = \pm 1/2 \quad (144)$$

c.f. Eq. (102). Spin of the electron can be interpreted as circular motion of the charge inside this elementary particle. This results in the magnetis moment of the electron

$$\hat{\boldsymbol{\mu}} = g\mu_B\hat{\mathbf{s}}, \quad (145)$$

where $g = 2$ is the so-called g -factor and μ_B is Bohr's magneton, $\mu_B = e\hbar/(2m_e) = 0.927 \times 10^{-23}$ J/T. Note that the model of circularly moving charges inside the electron leads to the same result with $g = 1$; The true value $g = 2$ follows from the relativistic quantum theory.

The energy (the Hamiltonian) of an electron spin in a magnetic field of the induction \mathbf{B} has the form

$$\hat{H} = -\hat{\boldsymbol{\mu}} \cdot \mathbf{B} = -g\mu_B\hat{\mathbf{s}} \cdot \mathbf{B}, \quad (146)$$

the so-called Zeeman Hamiltonian. One can see that the minimum of the energy corresponds to the spin pointing in the direction of \mathbf{B} . Choosing the z axis in the direction of \mathbf{B} , one obtains

$$\hat{H} = -g\mu_B\hat{s}_z B. \quad (147)$$

Thus the energy eigenvalues of the electronic spin in a magnetic field with the help of Eq. (144) become

$$\varepsilon_m = -g\mu_B m B, \quad (148)$$

where, for the electron, $m = \pm 1/2$.

In an atom, spins of all electrons usually combine into a collective spin S that has half-integer values and is described by an $(2S+1) \times (2S+1)$ matrix. Instead of Eq. (146), one has

$$\hat{H} = -g\mu_B\hat{\mathbf{S}} \cdot \mathbf{B}. \quad (149)$$

Eigenvalues of the projections of $\hat{\mathbf{S}}$ on the direction of \mathbf{B} are given by

$$m = -S, -S+1, \dots, S-1, S, \quad (150)$$

all together $2S+1$ different values, c.f. Eq. (101). The $2S+1$ different energy levels of the spin are given by Eq. (148).

The thermodynamics of the spin is determined by the partition function

$$Z_S = \sum_{m=-S}^S e^{-\beta\varepsilon_m} = \sum_{m=-S}^S e^{m\gamma}, \quad (151)$$

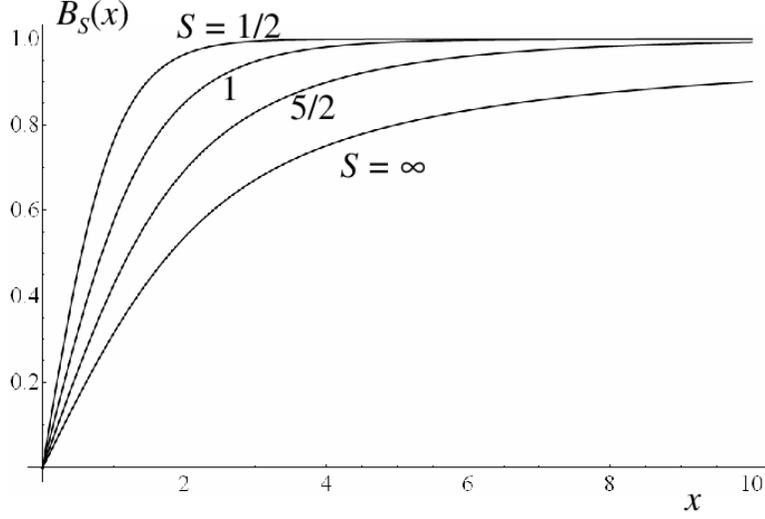


FIG. 5: Brillouin function $B_S(x)$ for different S .

where ε_m is given by Eq. (148) and

$$y \equiv \beta g \mu_B B = \frac{g \mu_B B}{k_B T}. \quad (152)$$

Eq. (151) by the change of the summation index to $k = m + S$ can be reduced to a finite geometrical progression

$$Z_S = e^{-Sy} \sum_{k=0}^{2S} (e^y)^k = e^{-Sy} \frac{e^{(2S+1)y} - 1}{e^y - 1} = \frac{e^{(S+1/2)y} - e^{-(S+1/2)y}}{e^{y/2} - e^{-y/2}} = \frac{\sinh[(S+1/2)y]}{\sinh(y/2)}. \quad (153)$$

For $S = 1/2$ with the help of $\sinh(2x) = 2 \sinh(x) \cosh(x)$ one can transform Eq. (153) to

$$Z_{1/2} = 2 \cosh(y/2). \quad (154)$$

The partition function being found, one can easily obtain thermodynamic quantities.. For instance, the free energy F is given by Eq. (38),

$$F = -N k_B T \ln Z_S = -N k_B T \ln \frac{\sinh[(S+1/2)y]}{\sinh(y/2)}. \quad (155)$$

The average spin polarization is defined by

$$\langle S_z \rangle = \langle m \rangle = \frac{1}{Z} \sum_{m=-S}^S m e^{-\beta \varepsilon_m}. \quad (156)$$

With the help of Eq. (151) one obtains

$$\langle S_z \rangle = \frac{1}{Z} \frac{\partial Z}{\partial y} = \frac{\partial \ln Z}{\partial y}. \quad (157)$$

With the use of Eq. (153) and the derivatives

$$\sinh(x)' = \cosh(x), \quad \cosh(x)' = \sinh(x) \quad (158)$$

one obtains

$$\langle S_z \rangle = b_S(y), \quad (159)$$

where

$$b_S(y) = \left(S + \frac{1}{2}\right) \coth \left[\left(S + \frac{1}{2}\right) y \right] - \frac{1}{2} \coth \left[\frac{1}{2} y \right]. \quad (160)$$

Usually the function $b_S(y)$ is represented in the form $b_S(y) = SB_S(Sy)$, where $B_S(x)$ is the Brillouin function

$$B_S(x) = \left(1 + \frac{1}{2S}\right) \coth \left[\left(1 + \frac{1}{2S}\right) x \right] - \frac{1}{2S} \coth \left[\frac{1}{2S} x \right], \quad (161)$$

(see Fig. 5). One can see that $b_S(\pm\infty) = \pm S$ and $B_S(\pm\infty) = \pm 1$.

For $S = 1/2$ from Eq. (154) one obtains

$$\langle S_z \rangle = b_{1/2}(y) = \frac{1}{2} \tanh \frac{y}{2} \quad (162)$$

and $B_{1/2}(x) = \tanh x$.

In the opposite limit $S \rightarrow \infty$, the Brillouin function becomes the classical Langevin function:

$$B_{1/2}(x) \equiv L(x) = \coth x - \frac{1}{x}. \quad (163)$$

Although atoms never have a really large spin, the classical approximation is very useful as it can strongly simplify calculations and it provides qualitatively reasonable results in most cases.

At zero magnetic field, $y = 0$, the spin polarization should vanish. It is immediately seen in Eq. (162) but not in Eq. (159). To clarify the behavior of $b_S(y)$ at small y , one can use $\coth x \cong 1/x + x/3$ that yields

$$\begin{aligned} b_S(y) &\cong \left(S + \frac{1}{2}\right) \left[\frac{1}{\left(S + \frac{1}{2}\right) y} + \left(S + \frac{1}{2}\right) \frac{y}{3} \right] - \frac{1}{2} \left[\frac{1}{\frac{1}{2} y} + \frac{1}{2} \frac{y}{3} \right] \\ &= \frac{y}{3} \left[\left(S + \frac{1}{2}\right)^2 - \left(\frac{1}{2}\right)^2 \right] = \frac{S(S+1)}{3} y. \end{aligned} \quad (164)$$

In physical units, this means

$$\langle S_z \rangle \cong \frac{S(S+1)}{3} \frac{g\mu_B B}{k_B T}, \quad g\mu_B B \ll k_B T. \quad (165)$$

The average magnetic moment of the spin can be obtained from Eq. (145)

$$\langle \mu_z \rangle = g\mu_B \langle S_z \rangle. \quad (166)$$

The magnetization of the sample M is defined as the magnetic moment per unit volume. If there is one magnetic atom per unit cell and all of them are uniformly magnetized, the magnetization reads

$$M = \frac{\langle \mu_z \rangle}{v_0} = \frac{g\mu_B}{v_0} \langle S_z \rangle, \quad (167)$$

where v_0 is the unit-cell volume.

The internal energy U of a system of N spins can be obtained from the general formula, Eq. (31). The calculation can be, however, avoided since from Eq. (148) simply follows

$$U = N \langle \varepsilon_m \rangle = -Ng\mu_B B \langle m \rangle = -Ng\mu_B B \langle S_z \rangle, \quad (168)$$

where $\langle S_z \rangle$ is given by Eq. (159). In particular, at low magnetic fields (or high temperatures) one has

$$U \cong -N \frac{S(S+1)}{3} \frac{(g\mu_B B)^2}{k_B T}. \quad (169)$$

The magnetic susceptibility per spin is defined by

$$\chi = \frac{\partial \langle \mu_z \rangle}{\partial B}. \quad (170)$$

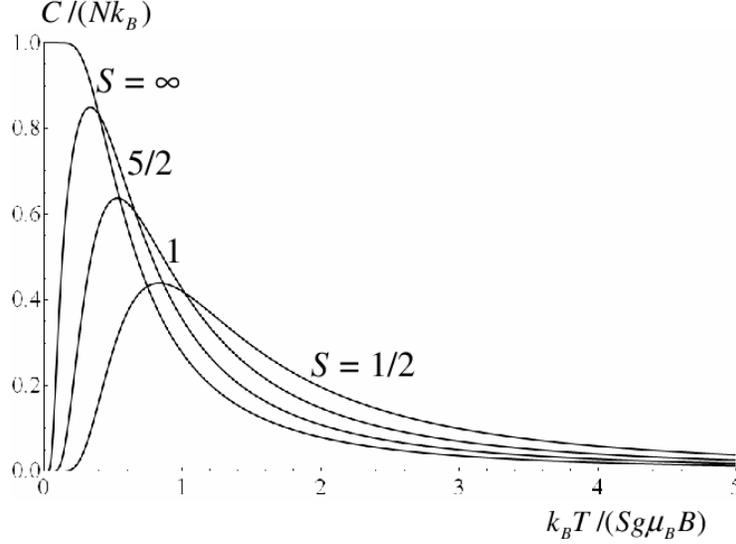


FIG. 6: Temperature dependence of the heat capacity of spins in a magnetic fields with different values of S .

From Eqs. (166) and (159) one obtains

$$\chi = \frac{(g\mu_B)^2}{k_B T} b'_S(y), \quad (171)$$

where

$$b'_S(y) \equiv \frac{db_S(y)}{dy} = - \left(\frac{S+1/2}{\sinh[(S+1/2)y]} \right)^2 + \left(\frac{1/2}{\sinh[y/2]} \right)^2. \quad (172)$$

For $S = 1/2$ from Eq. (162) follows

$$b'_{1/2}(y) = \frac{1}{4 \cosh^2(y/2)}. \quad (173)$$

From Eq. (164) one obtains $b'_S(0) = S(S+1)/3$. Thus in the high-temperature limit (or for $B = 0$)

$$\chi = \frac{S(S+1)}{3} \frac{(g\mu_B)^2}{k_B T}, \quad k_B T \gg g\mu_B B. \quad (174)$$

The susceptibility becomes small at high temperatures as the directions of the spins are strongly disordered by thermal agitation and it is difficult to order them by applying a magnetic field. In the opposite limit $y \gg 1$ the function $b'_S(y)$ and thus the susceptibility also becomes small. The physical reason for this is that at low temperatures, $k_B T \ll g\mu_B B$, the spins are already strongly aligned by the magnetic field, $\langle S_z \rangle \cong S$, so that $\langle S_z \rangle$ becomes hardly sensitive to small changes of B . As a function of temperature, χ has a maximum at intermediate temperatures.

The heat capacity C can be obtained from Eq. (168) as

$$C = \frac{\partial U}{\partial T} = -N g \mu_B B \frac{\partial \langle S_z \rangle}{\partial T} = -N g \mu_B B b'_S(y) \frac{\partial y}{\partial T} = N k_B y^2 b'_S(y). \quad (175)$$

As both the magnetic susceptibility and the heat capacity are expressed via the derivative of the Brillouin function, they are related. The relation has the form

$$\frac{C}{N\chi} = \frac{B^2}{T}. \quad (176)$$

One can see that C also has a maximum at intermediate temperatures, $y \sim 1$. At high temperatures C decreases as $1/T^2$:

$$C \cong Nk_B \frac{S(S+1)}{3} \left(\frac{g\mu_B B}{k_B T} \right)^2, \quad (177)$$

and at low temperatures C becomes exponentially small, except for the case $S = \infty$ (see Fig. 6). The finite value of the heat capacity in the limit $T \rightarrow 0$ contradicts the third law of thermodynamics. Thus the classical spin model fails in this limit.

XIV. PHASE TRANSITIONS AND THE MEAN-FIELD APPROXIMATION

As explained in thermodynamics, with changing thermodynamic parameters such as temperature, pressure, etc., the system can undergo phase transitions. In the first-order phase transitions, the chemical potentials μ of the two competing phases become equal at the phase transition line, while on each side of this line they are unequal and only one of the phases is thermodynamically stable. The first-order transition is switching between two different phases (as, for instance, between water and ice) and is thus abrupt. To the contrast, second-order transitions are gradual: The so-called order parameter continuously grows from zero as the phase-transition line is crossed. Thermodynamic quantities are singular at second-order transitions.

Phase transitions are complicated phenomena that arise due to interaction between particles in many-particle systems in the thermodynamic limit $N \rightarrow \infty$. It can be shown that thermodynamic quantities of finite systems are non-singular and, in particular, there are no second-order phase transitions. Up to now in this course we studied systems without interaction. Including the latter requires an extension of the formalism of statistical mechanics that is done in Sec. XVI. In such an extended formalism, one has to calculate partition functions over the energy levels of the whole system that, in general, depend on the interaction. In some cases these energy levels are known exactly but they are parametrized by many quantum numbers over which summation has to be carried out. In most of the cases, however, the energy levels are not known analytically and their calculation is a huge quantum-mechanical problem. In both cases calculation of the partition function is a very serious task. There are some models for which thermodynamic quantities had been calculated exactly, including models that possess second-order phase transitions. For other models, approximate numerical methods had been developed that allow calculating phase transition temperatures and critical indices. It was shown that there are no phase transitions in one-dimensional systems with short-range interactions.

It is most convenient to illustrate the physics of phase transitions considering magnetic systems, or the systems of spins introduced in Sec. XIII. The simplest forms of interaction between different spins are Ising interaction $-J_{ij}\hat{S}_{iz}\hat{S}_{jz}$ including only z components of the spins and Heisenberg interaction $-J_{ij}\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j$. The *exchange interaction* J_{ij} follows from quantum mechanics of atoms and is of electrostatic origin. In most cases practically there is only interaction J between spins of the neighboring atoms in a crystal lattice, because J_{ij} decreases exponentially with distance. For the Ising model, all energy levels of the whole system are known exactly while for the Heisenberg model they are not. In the case $J > 0$ neighboring spins have the lowest interaction energy when they are collinear, and the state with all spins pointing in the same direction is the exact ground state of the system. For the Ising model, all spins in the ground state are parallel or antiparallel with the z axis, that is, it is double-degenerate. For the Heisenberg model the spins can point in any direction in the ground state, so that the ground state has a continuous degeneracy. In both cases, Ising and Heisenberg, the ground state for $J > 0$ is *ferromagnetic*.

The nature of the interaction between spins considered above suggests that at $T \rightarrow 0$ the system should fall into its ground state, so that thermodynamic averages of all spins approach their maximal values, $\left| \langle \hat{\mathbf{S}}_i \rangle \right| \rightarrow S$. With increasing temperature, excited levels of the system become populated and the average spin value decreases, $\left| \langle \hat{\mathbf{S}}_i \rangle \right| < S$. At high temperatures all energy levels become populated, so that neighboring spins can have all possible orientations with respect to each other. In this case, if there is no external magnetic field acting on the spins (see Sec. XIII), the average spin value should be exactly zero, because there as many spins pointing in one direction as there are the spins pointing in the other direction. This is why the high-temperature state is called *symmetric state*. If now the temperature is lowered, there should be a phase transition temperature T_C (the Curie temperature for ferromagnets) below which the order parameter (average spin value) becomes nonzero. Below T_C the symmetry of the state is *spontaneously* broken. This state is called *ordered state*. Note that if there is an applied magnetic field, it will break the symmetry by creating a nonzero spin average at all temperatures, so that there is no sharp phase transition, only a gradual increase of $\left| \langle \hat{\mathbf{S}}_i \rangle \right|$ as the temperature is lowered.

Although the scenario outlined above looks persuasive, there are subtle effects that may preclude ordering and ensure $\left| \langle \hat{\mathbf{S}}_i \rangle \right| = 0$ at all nonzero temperatures. As said above, ordering does not occur in one dimension (spin chains)

for both Ising and Heisenberg models. In two dimensions, Ising model shows a phase transition, and the analytical solution of the problem exists and was found by Lars Onsager. However, two-dimensional Heisenberg model does not order. In three dimensions, both Ising and Heisenberg models show a phase transition and no analytical solution is available.

A. The mean-field approximation for ferromagnets

While a rigorous solution of the problem of phase transition is very difficult, there is a simple approximate solution that captures the physics of phase transitions as described above and provides qualitatively correct results in most cases, including three-dimensional systems. The idea of this approximate solution is to reduce the original many-spin problem to an effective self-consistent one-spin problem by considering one spin (say i) and replacing other spins in the interaction by their average thermodynamic values, $-J_{ij}\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j \Rightarrow -J_{ij}\hat{\mathbf{S}}_i \cdot \langle \hat{\mathbf{S}}_j \rangle$. One can see that now the interaction term has mathematically the same form as the term describing interaction of a spin with the applied magnetic field, Eq. (149). Thus one can use the formalism of Sec. (XIII) to solve the problem analytically. This approach is called mean field approximation (MFA) or molecular field approximation and it was first suggested by Weiss for ferromagnets.

The effective one-spin Hamiltonian within the MFA is similar to Eq: (149) and has the form

$$\hat{H} = -\hat{\mathbf{S}} \cdot \left(g\mu_B \mathbf{B} + Jz \langle \hat{\mathbf{S}} \rangle \right) + \frac{1}{2} Jz \langle \hat{\mathbf{S}} \rangle^2, \quad (178)$$

where z is the number of nearest neighbors for a spin in the lattice ($z = 6$ for the simple cubic lattice). Here the last term ensures that the replacement $\hat{\mathbf{S}} \Rightarrow \langle \hat{\mathbf{S}} \rangle$ in \hat{H} yields $\hat{H} = -\langle \hat{\mathbf{S}} \rangle \cdot g\mu_B \mathbf{B} - (1/2)Jz \langle \hat{\mathbf{S}} \rangle^2$ that becomes the correct ground-state energy at $T = 0$ where $|\langle \hat{\mathbf{S}} \rangle| = S$. For the Heisenberg model, in the presence of a whatever weak applied field \mathbf{B} the ordering will occur in the direction of \mathbf{B} . Choosing the z axis in this direction, one can simplify Eq. (178) to

$$\hat{H} = -\left(g\mu_B B + Jz \langle \hat{S}_z \rangle \right) \hat{S}_z + \frac{1}{2} Jz \langle \hat{S}_z \rangle^2. \quad (179)$$

The same mean-field Hamiltonian is valid for the Ising model as well, if the magnetic field is applied along the z axis. Thus, within the MFA (but not in general!) Ising and Heisenberg models are equivalent. The energy levels corresponding to Eq. (179) are

$$\varepsilon_m = -\left(g\mu_B B + Jz \langle \hat{S}_z \rangle \right) m + \frac{1}{2} Jz \langle \hat{S}_z \rangle^2, \quad m = -S, -S+1, \dots, S-1, S. \quad (180)$$

Now, after calculation of the partition function \mathcal{Z} , Eq. (151), one arrives at the free energy per spin

$$F = -k_B T \ln Z = \frac{1}{2} Jz \langle \hat{S}_z \rangle^2 - k_B T \ln \frac{\sinh[(S+1/2)y]}{\sinh(y/2)}, \quad (181)$$

where

$$y \equiv \frac{g\mu_B B + Jz \langle \hat{S}_z \rangle}{k_B T}. \quad (182)$$

To find the actual value of the order parameter $\langle \hat{S}_z \rangle$ at any temperature T and magnetic field B , one has to minimize F with respect to $\langle \hat{S}_z \rangle$, as explained in thermodynamics. One obtains the equation

$$0 = \frac{\partial F}{\partial \langle \hat{S}_z \rangle} = Jz \langle \hat{S}_z \rangle - Jz b_S(y), \quad (183)$$

where $b_S(y)$ is defined by Eq. (160). Rearranging terms one arrives at the transcendental Curie-Weiss equation

$$\langle \hat{S}_z \rangle = b_S \left(\frac{g\mu_B B + Jz \langle \hat{S}_z \rangle}{k_B T} \right) \quad (184)$$

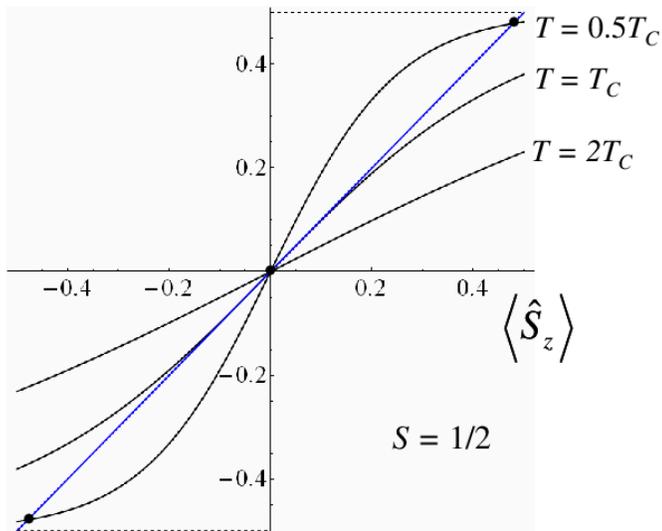
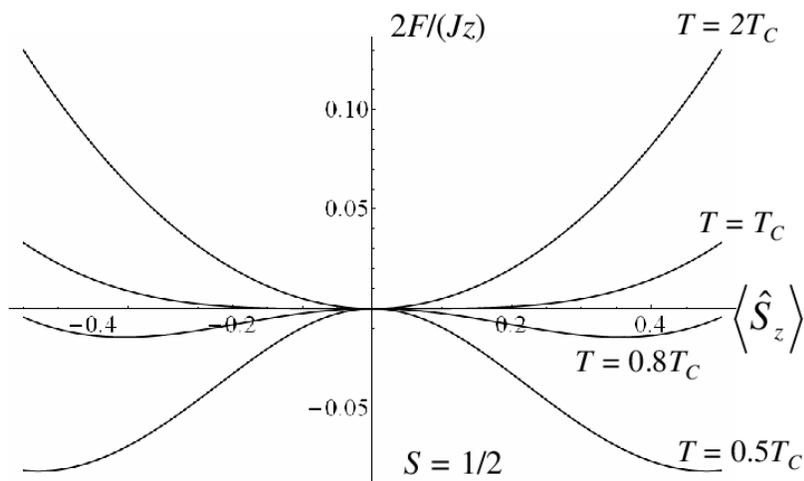


FIG. 7: Graphic solution of the Curie-Weiss equation.

FIG. 8: Free energy of a ferromagnet vs $\langle \hat{S}_z \rangle$ within the MFA. (Arbitrary vertical shift.)

that defines $\langle \hat{S}_z \rangle$. In fact, this equation could be obtained in a shorter way by using the modified argument, Eq. (182), in Eq. (159).

For $B = 0$, Eq. (184) has the only solution $\langle \hat{S}_z \rangle = 0$ at high temperatures. As $b_S(y)$ has the maximal slope at $y = 0$, it is sufficient that this slope (with respect to $\langle \hat{S}_z \rangle$) becomes smaller than 1 to exclude any solution other than $\langle \hat{S}_z \rangle = 0$. Using Eq. (164), one obtains that the only solution $\langle \hat{S}_z \rangle = 0$ is realized for $T \geq T_C$, where

$$T_C = \frac{S(S+1)}{3} \frac{Jz}{k_B} \quad (185)$$

is the Curie temperature within the mean-field approximation. Below T_C the slope of $b_S(y)$ with respect to $\langle \hat{S}_z \rangle$ exceeds 1, so that there are three solutions for $\langle \hat{S}_z \rangle$: One solution $\langle \hat{S}_z \rangle = 0$ and two symmetric solutions $\langle \hat{S}_z \rangle \neq 0$ (see Fig. 7). The latter correspond to the lower free energy than the solution $\langle \hat{S}_z \rangle = 0$ thus they are thermodynamically stable (see Fig. 8). These solutions describe the ordered state below T_C .

Slightly below T_C the value of $\langle \hat{S}_z \rangle$ is still small and can be found by expanding $b_S(y)$ up to y^3 . In particular, for $S = 1/2$ one has

$$b_{1/2}(y) = \frac{1}{2} \tanh \frac{y}{2} \cong \frac{1}{4}y - \frac{1}{48}y^3. \quad (186)$$

Using $T_C = (1/4)Jz/k_B$ and thus $Jz = 4k_B T_C$ for $S = 1/2$, one can rewrite Eq. (184) with $B = 0$ in the form

$$\langle \hat{S}_z \rangle = \frac{T_C}{T} \langle \hat{S}_z \rangle - \frac{4}{3} \left(\frac{T_C}{T} \right)^3 \langle \hat{S}_z \rangle^3. \quad (187)$$

One of the solutions is $\langle \hat{S}_z \rangle = 0$ while the other two solutions are

$$\frac{\langle \hat{S}_z \rangle}{S} = \pm \frac{T}{T_C} \sqrt{3 \left(1 - \frac{T}{T_C} \right)}, \quad S = \frac{1}{2}. \quad (188)$$

As this result is only valid for T near T_C , one can discard the factor in front of the square root and simplify this formula to

$$\frac{\langle \hat{S}_z \rangle}{S} = \pm \sqrt{3 \left(1 - \frac{T}{T_C} \right)}, \quad S = \frac{1}{2}, \quad (189)$$

Although obtained near T_C , in this form the result is only by the factor $\sqrt{3}$ off at $T = 0$. The singularity of the order parameter near T_C is square root, so that for the magnetization critical index defined as

$$\langle \hat{S}_z \rangle \propto M \propto (T_C - T)^\beta \quad (190)$$

one has $\beta = 1/2$. Results of the numerical solution of the Curie-Weiss equation with $B = 0$ for different S are shown in Fig. 9. Note that the magnetization is related to the spin average by Eq. (167).

Let us now consider the magnetic susceptibility per spin χ defined by Eq. (170) above T_C . Linearizing Eq. (184) with the use of Eq. (164), one obtains

$$\langle \hat{S}_z \rangle = \frac{S(S+1)}{3} \frac{g\mu_B B + Jz \langle \hat{S}_z \rangle}{k_B T} = \frac{S(S+1)}{3} \frac{g\mu_B B}{k_B T} + \frac{T_C}{T} \langle \hat{S}_z \rangle. \quad (191)$$

From this equation one obtains

$$\langle \hat{S}_z \rangle = \frac{S(S+1)}{3} \frac{g\mu_B B}{k_B T} \frac{1}{1 - T_C/T} = \frac{S(S+1)}{3} \frac{g\mu_B B}{k_B (T_C - T)}. \quad (192)$$

Then the magnetic susceptibility can be calculated by differentiation:

$$\chi = \frac{\partial \langle \mu_z \rangle}{\partial B} = g\mu_B \frac{\partial \langle \hat{S}_z \rangle}{\partial B} = \frac{S(S+1)}{3} \frac{(g\mu_B)^2}{k_B (T - T_C)}. \quad (193)$$

In contrast to non-interacting spins, Eq. (174), the susceptibility diverges at $T = T_C$ rather than at $T = 0$. The inverse susceptibility χ^{-1} is a straight line crossing the T axis at T_C . In the theory of phase transitions the critical index for the susceptibility γ is defined as.

$$\chi \propto (T - T_C)^{-\gamma}. \quad (194)$$

One can see that $\gamma = 1$ within the MFA.

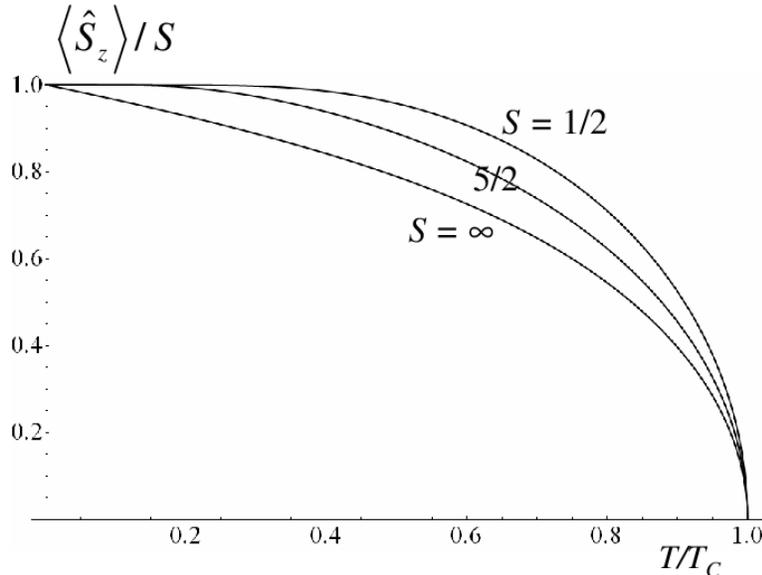


FIG. 9: Temperature dependences of normalized spin averages $\langle \hat{S}_z \rangle / S$ for $S = 1/2, 5/2, \infty$ obtained from the numerical solution of the Curie-Weiss equation.

At $T = T_C$, there is no linear susceptibility, and the magnetization is a singular function of the magnetic field, that defines another critical index, δ . In this case, the Curie-Weiss equation can be expanded for small $\langle \hat{S}_z \rangle$ and small B . Using Eq. (186), at $T = T_C$ one obtains

$$0 = \frac{g\mu_B B}{4k_B T} - \frac{4}{3} \langle \hat{S}_z \rangle^3, \quad (195)$$

c.f. Eq. (187). Thus,

$$\langle \hat{S}_z \rangle = \left(\frac{3g\mu_B B}{16k_B T} \right)^{1/3} \quad S = \frac{1}{2}. \quad (196)$$

The critical isotherm index δ is defined by

$$\langle \hat{S}_z \rangle \propto B^{1/\delta}, \quad (197)$$

thus within the mean-field approximation $\delta = 3$.

More precise methods than the MFA yield smaller values of β and larger values of γ and δ , depending on the details of the model such as the number of interacting spin components (1 for the Ising and 3 for the Heisenberg) and the dimension of the lattice. Critical indices are insensitive to such factors as lattice structure and the value of the spin S . On the other hand, the value of T_C does not possess such *universality* and depends on all parameters of the problem. Accurate values of T_C are by up to 25% lower than their mean-field values in three dimensions.

XV. 1D ISING MODEL

The 1D Ising model is a chain of magnetic atoms with spins $S = 1/2$ interacting with their nearest neighbors in the chain via the coupling of their z -components. The Hamiltonian of the 1D Ising model reads

$$\hat{H} = -J \sum_{i=1}^{N-1} \hat{S}_{iz} \hat{S}_{i+1,z} - g\mu_B B \sum_{i=1}^N \hat{S}_{iz}, \quad (198)$$

where N is the number of atoms in the chain, the exchange coupling $J > 0$ for the ferromagnetic interaction, and B is the magnetic field applied along the z -axis. The quantum energy levels of the Ising model are trivial and correspond

to the values of \hat{S}_{iz} equal to $m_i = \pm 1/2$. (In the presence of a transverse field or a coupling of other spin components the quantum problem becomes non-trivial.) Thus, the energy of the system divided by the temperature that enters the partition function can be written as

$$\beta E \equiv \frac{E}{k_B T} = -\theta \sum_{i=1}^{N-1} m_i m_{i+1} - \rho \sum_{i=1}^N m_i, \quad (199)$$

where we have introduced the dimensionless exchange and field parameters

$$\theta \equiv \beta J = \frac{J}{k_B T}, \quad \rho \equiv \frac{g\mu_B B}{k_B T}. \quad (200)$$

One can calculate the partition function analytically if one considers the ring instead of the open chain. In the thermodynamic limit, there should be no difference between the two model variants but for the ring the analytical calculation exists for any N . Thus to βE we add the term $-\theta m_N m_1$ (the last spin is coupled with the first one). The partition function for the Ising ring is given by

$$Z = \sum_{m_1, m_2, \dots, m_N} \exp(\theta m_1 m_2 + \rho m_1 + \theta m_2 m_3 + \rho m_2 + \dots + \theta m_N m_1 + \rho m_N). \quad (201)$$

It is convenient to make a trick that allows representing the partition function as a product of matrices. For this, we redistribute the field terms:

$$Z = \sum_{m_1, m_2, \dots, m_N} \exp\left(\theta m_1 m_2 + \frac{\rho}{2}(m_1 + m_2) + \theta m_2 m_3 + \frac{\rho}{2}(m_2 + m_3) + \dots + \theta m_N m_1 + \frac{\rho}{2}(m_N + m_1)\right). \quad (202)$$

Then,

$$Z = \sum_{m_1, m_2, \dots, m_N} A_{m_1 m_2} A_{m_2 m_3} \dots A_{m_{N-1} m_N} A_{m_N m_1} = \sum_{m_1} (\mathbb{A}^N)_{m_1 m_1} = \text{Tr}(\mathbb{A}^N) \quad (203)$$

is the trace of the N th power of the 2×2 matrix with matrix elements

$$A_{mk} = \exp\left(\theta mk + \frac{\rho}{2}(m+k)\right), \quad m, k = \pm 1/2 \quad (204)$$

that is,

$$\mathbb{A} = \begin{pmatrix} \exp(\theta/4 - \rho/2) & \exp(-\theta/4) \\ \exp(-\theta/4) & \exp(\theta/4 + \rho/2) \end{pmatrix}. \quad (205)$$

It can be easily shown that the trace of a matrix is invariant under the unitary transformation. If \mathbb{U} is the unitary matrix, then the unitary transformation reads

$$\mathbb{B} = \mathbb{U}^{-1} \mathbb{A} \mathbb{U}, \quad (206)$$

where the inverse unitary matrix \mathbb{U}^{-1} is just transposed and complex conjugate of \mathbb{U} . As one can make a cyclic permutation of matrices under the Tr operator, one can write

$$\text{Tr}(\mathbb{A}^N) = \text{Tr}(\mathbb{A}^N \mathbb{U} \mathbb{U}^{-1}) = \text{Tr}(\mathbb{U}^{-1} \mathbb{A}^N \mathbb{U}) = \text{Tr}(\mathbb{U}^{-1} \mathbb{A} \mathbb{U} \mathbb{U}^{-1} \mathbb{A} \mathbb{U} \dots \mathbb{U}^{-1} \mathbb{A} \mathbb{U}) = \text{Tr}(\mathbb{B}^N). \quad (207)$$

One can choose the unitary transformation that diagonalizes \mathbb{A} , in this case

$$\mathbb{B} = \begin{pmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{pmatrix}, \quad \mathbb{B}^N = \begin{pmatrix} \lambda_1^N & 0 \\ 0 & \lambda_2^N \end{pmatrix}. \quad (208)$$

Thus, the problem reduced to calculating the eigenvalues of \mathbb{A} above. The secular equation has the form

$$0 = \begin{vmatrix} \exp(\theta/4 - \rho/2) - \lambda & \exp(-\theta/4) \\ \exp(-\theta/4) & \exp(\theta/4 + \rho/2) - \lambda \end{vmatrix} = [\exp(\theta/4 - \rho/2) - \lambda][\exp(\theta/4 + \rho/2) - \lambda] - \exp(-\theta/2) \quad (209)$$

or

$$\lambda^2 - e^{\theta/4} (e^{\rho/2} + e^{-\rho/2}) \lambda + e^{\theta/2} - e^{-\theta/2} = 0 \quad (210)$$

or, finally,

$$\lambda^2 - 2e^{\theta/4} \cosh \frac{\rho}{2} \lambda + 2 \sinh \frac{\theta}{2} = 0. \quad (211)$$

The solution of this quadratic equations are

$$\begin{aligned} \lambda_{1,2} &= e^{\theta/4} \cosh \frac{\rho}{2} \pm \sqrt{e^{\theta/2} \cosh^2 \frac{\rho}{2} - 2 \sinh \frac{\theta}{2}} = e^{\theta/4} \cosh \frac{\rho}{2} \pm \sqrt{e^{\theta/2} \cosh^2 \frac{\rho}{2} - e^{\theta/2} + e^{-\theta/2}} \\ &= e^{\theta/4} \left(\cosh \frac{\rho}{2} \pm \sqrt{\sinh^2 \frac{\rho}{2} + e^{-\theta}} \right). \end{aligned} \quad (212)$$

Now the partition function is

$$Z = \lambda_1^N + \lambda_2^N \Rightarrow e^{N\theta/4} \left(\cosh \frac{\rho}{2} + \sqrt{\sinh^2 \frac{\rho}{2} + e^{-\theta}} \right)^N, \quad (213)$$

where we have discarded the smaller eigenvalue that makes a negligible contribution for large N . One can see that Z does not have any singularities, so that in the 1D Ising model there are no phase transitions.

1D Ising model with an arbitrary S can be solved in a similar way by diagonalizing an $(2S+1) \times (2S+1)$ matrix. However, this solution is cumbersome and can be done only numerically, in general. There is no phase transition for any S , including $S \rightarrow \infty$.

All thermodynamic quantities can be obtained from Z . Let us first calculate the internal energy in zero field. In this case $\rho = 0$ and

$$Z = e^{N\theta/4} (1 + e^{-\theta/2})^N = (e^{\theta/4} + e^{-\theta/4})^N = 2^N \cosh^N \frac{\theta}{4}. \quad (214)$$

The energy is given by

$$U = -\frac{\partial \ln Z}{\partial \beta} = -J \frac{\partial \ln Z}{\partial \theta} = -NJ \frac{\partial \ln \cosh \frac{\theta}{4}}{\partial \theta} = -\frac{1}{4} NJ \tanh \frac{\theta}{4} = -\frac{1}{4} NJ \tanh \frac{J}{4k_B T}. \quad (215)$$

In the limit $T \rightarrow 0$ ($\theta \rightarrow \infty$) one has

$$U = -\frac{1}{4} NJ \quad (216)$$

that can be obtained directly as the ground state of the Hamiltonian, Eq. (198). In the opposite limit, $k_B T \gg J$ ($\theta \ll 1$) the energy behaves as

$$U \cong -\frac{1}{16} NJ \theta = -\frac{1}{16} N \frac{J^2}{k_B T}. \quad (217)$$

The heat capacity is given by

$$C = \frac{\partial U}{\partial T} = Nk_B \left(\frac{J}{4k_B T} \right)^2 / \cosh^2 \frac{J}{4k_B T}. \quad (218)$$

This is exponentially small at $k_B T \ll J$ and behaves as

$$C = Nk_B \left(\frac{J}{4k_B T} \right)^2 \quad (219)$$

for $k_B T \gg J$. At $k_B T \sim J$ the heat capacity has a broad maximum.

The magnetization of the Ising model per spin is given by the standard formula, Eq. (166). The spin polarization $\langle \hat{S}_z \rangle$ is defined by

$$\langle \hat{S}_z \rangle = \frac{1}{N} \left\langle \sum_{i=1}^N m_i \right\rangle = \frac{1}{N} \frac{1}{Z} \sum_{m_1, m_2, \dots, m_N} \left(\sum_{i=1}^N m_i \right) \exp \left(\theta m_1 m_2 + \theta m_2 m_3 + \dots + \theta m_N m_1 + \rho \sum_{i=1}^N m_i \right) \quad (220)$$

that can be expressed as

$$\langle \hat{S}_z \rangle = \frac{1}{N} \frac{1}{Z} \frac{\partial Z}{\partial \rho} = \frac{1}{N} \frac{\partial \ln Z}{\partial \rho}. \quad (221)$$

From Eq. (213) one obtains

$$\langle \hat{S}_z \rangle = \frac{\partial}{\partial \rho} \ln \left(\cosh \frac{\rho}{2} + \sqrt{\sinh^2 \frac{\rho}{2} + e^{-\theta}} \right) = \frac{\frac{1}{2} \sinh \frac{\rho}{2} + \frac{1}{2} \frac{\sinh \frac{\rho}{2} \cosh \frac{\rho}{2}}{\sqrt{\sinh^2 \frac{\rho}{2} + e^{-\theta}}}}{\cosh \frac{\rho}{2} + \sqrt{\sinh^2 \frac{\rho}{2} + e^{-\theta}}} \quad (222)$$

that simplifies to

$$\langle \hat{S}_z \rangle = \frac{1}{2} \frac{\sinh \frac{\rho}{2}}{\sqrt{\sinh^2 \frac{\rho}{2} + e^{-\theta}}}. \quad (223)$$

One can see that the spin polarization vanishes in the limit $B \rightarrow 0$ ($\rho \rightarrow 0$), thus there is no spontaneous ordering in this model. In the high-field limit, $\rho \rightarrow \infty$, one has $\langle \hat{S}_z \rangle = 1/2$, the full alignment of the spins. The magnetic susceptibility per spin is given by

$$\chi = \frac{\partial \langle \mu_z \rangle}{\partial B} = g\mu_B \frac{\partial \langle \hat{S}_z \rangle}{\partial B} = \frac{(g\mu_B)^2}{k_B T} \frac{\partial \langle \hat{S}_z \rangle}{\partial \rho}. \quad (224)$$

Using the formula above, one obtains

$$\chi = \frac{(g\mu_B)^2}{k_B T} \frac{1}{4} \left(\frac{\cosh \frac{\rho}{2}}{\sqrt{\sinh^2 \frac{\rho}{2} + e^{-\theta}}} - \frac{\sinh \frac{\rho}{2} \cosh \frac{\rho}{2}}{(\sinh^2 \frac{\rho}{2} + e^{-\theta})^{3/2}} \right) = \frac{(g\mu_B)^2}{k_B T} \frac{\cosh \frac{\rho}{2}}{4 (\sinh^2 \frac{\rho}{2} + e^{-\theta})^{3/2}} \left[\sinh^2 \frac{\rho}{2} + e^{-\theta} - \sinh \frac{\rho}{2} \right]. \quad (225)$$

In zero field, $\rho = 0$, this becomes

$$\chi = \frac{(g\mu_B)^2}{4k_B T} e^{\theta/2} = \frac{(g\mu_B)^2}{4k_B T} \exp \frac{J}{2k_B T}. \quad (226)$$

One can see that the magnetic susceptibility exponentially diverges at $T = 0$ that is the most interesting result for the 1D Ising model. At high temperatures, the exponential term tends to 1 and the result is the susceptibility of noninteracting spins, a particular case of Eq. (174) for $S = 1/2$.

XVI. THE GRAND CANONICAL ENSEMBLE

In the previous chapters we considered statistical properties of systems of non-interacting and *distinguishable* particles. Assigning a quantum state for one such a particle is independent from assigning the states for other particles, these processes are *statistically independent*. Particle 1 in state 1 and particle 2 in state 2, the microstate (1,2), and the microstate (2,1) are counted as different microstates within the same macrostate. However, quantum-mechanical particles such as electrons are indistinguishable from each other. Thus microstates (1,2) and (2,1) should be counted as a single microstate, one particle in state 1 and one in state 2, without specifying with particle is in which state. This means that assigning quantum states for different particles, as we have done above, is not statistically independent. Accordingly, the method based on the minimization of the Boltzmann entropy of a large system, Eq. (19), becomes invalid. This changes the foundations of statistical description of such systems.

In addition to indistinguishability of quantum particles, it follows from the relativistic quantum theory that particles with half-integer spin, called *fermions*, cannot occupy a quantum state more than once. There is no place for more than one fermion in any quantum state, the so-called *exclusion principle*. An important example of fermions is electron. To the contrary, particles with integer spin, called *bosons*, can be put into a quantum state in unlimited numbers. Examples of bosons are Helium and other atoms with an integer spin. Note that in the case of fermions, even for a large system, one cannot use the Stirling formula, Eq. (12), to simplify combinatorial expressions, since the occupation numbers of quantum states can be only 0 and 1. This is an additional reason why the Boltzmann formalism does not work here.

Finally, the Boltzmann formalism of quantum statistics does not work for systems with interaction because the quantum states of such systems are quantum states of the system as the whole rather than one-particle quantum states.

To construct the statistical mechanics of systems of indistinguishable particles and/or systems with interaction, one has to consider the *grand canonical ensemble* of \mathcal{N} systems. The quantum states of a system are labeled by ξ , and the ensemble contains any numbers \mathcal{N}_ξ of systems in states ξ . The total number of systems in the ensemble is

$$\mathcal{N} = \sum_{\xi} \mathcal{N}_\xi. \quad (227)$$

The number of particles in the states is not fixed, each state ξ has N_ξ particles. We require that the average number of particles in the system and the average energy of the system over the ensemble are fixed:

$$N = \frac{1}{\mathcal{N}} \sum_{\xi} N_\xi \mathcal{N}_\xi, \quad U = \frac{1}{\mathcal{N}} \sum_{\xi} E_\xi \mathcal{N}_\xi. \quad (228)$$

Do not confuse \mathcal{N}_ξ with N_ξ ! The number of ways \mathcal{W} in which the ensemble of systems, specified by \mathcal{N}_ξ , can be realized (i.e., the number of microstates or thermodynamic probability) can be calculated in exactly the same way as it was done above in the case of Boltzmann statistics. As the systems we are considering are distinguishable, one obtains

$$\mathcal{W} = \frac{\mathcal{N}!}{\prod_{\xi} \mathcal{N}_\xi!}. \quad (229)$$

Since the number of systems in the ensemble \mathcal{N} and thus all \mathcal{N}_ξ can be arbitrary high, the actual state of the ensemble is that maximizing \mathcal{W} under the constraints of Eq. (228). Within the method of Lagrange multipliers, one has to maximize the target function

$$\Phi(\mathcal{N}_1, \mathcal{N}_2, \dots) = \ln \mathcal{W} + \alpha \sum_{\xi} \mathcal{N}_\xi \mathcal{N}_\xi - \beta \sum_{\xi} E_\xi \mathcal{N}_\xi \quad (230)$$

[c.f. Eq. (21) and below]. Using the Stirling formula, Eq. (12), one obtains

$$\Phi \cong \ln \mathcal{N}! - \sum_{\xi} \mathcal{N}_\xi \ln \mathcal{N}_\xi + \sum_{\xi} \mathcal{N}_\xi + \alpha \sum_{\xi} \mathcal{N}_\xi \mathcal{N}_\xi - \beta \sum_{\xi} E_\xi \mathcal{N}_\xi. \quad (231)$$

Minimizing with respect to \mathcal{N}_ξ , considering \mathcal{N} as a constant, one obtains the equations

$$\frac{\partial \Phi}{\partial \mathcal{N}_\xi} = -\ln \mathcal{N}_\xi + \alpha \mathcal{N}_\xi - \beta E_\xi = 0 \quad (232)$$

that yield

$$\mathcal{N}_\xi = e^{\alpha \mathcal{N}_\xi - \beta E_\xi}, \quad (233)$$

the Gibbs distribution of the so-called grand canonical ensemble.

The total number of systems \mathcal{N} is given by

$$\mathcal{N} = \sum_{\xi} \mathcal{N}_\xi = \sum_{\xi} e^{\alpha \mathcal{N}_\xi - \beta E_\xi} = \mathcal{Z}. \quad (234)$$

where \mathcal{Z} is the partition function of the grand canonical ensemble. The coefficients α and β are defined from the conditions for the average number of particles and average energy over the ensemble, Eq. (228). For the average number of particles, one obtains

$$N = \frac{1}{\mathcal{N}} \sum_{\xi} N_\xi \mathcal{N}_\xi = \frac{1}{\mathcal{Z}} \sum_{\xi} N_\xi e^{\alpha \mathcal{N}_\xi - \beta E_\xi} = \frac{\partial \ln \mathcal{Z}}{\partial \alpha}. \quad (235)$$

The ensemble average of the internal energy becomes

$$U = \frac{1}{\mathcal{Z}} \sum_{\xi} E_\xi e^{\alpha \mathcal{N}_\xi - \beta E_\xi} = -\frac{\partial \ln \mathcal{Z}}{\partial \beta}. \quad (236)$$

In contrast to Eq. (31), this formula does not contain N explicitly since the average number of particles in a system is encapsulated in \mathcal{Z} .

We define the statistical entropy per system as

$$S = \frac{1}{\mathcal{N}} k_B \ln \mathcal{W} = \frac{1}{\mathcal{N}} k_B \ln \frac{\mathcal{N}!}{\prod_{\xi} \mathcal{N}_{\xi}!}. \quad (237)$$

Using the Stirling formula, Eq. (12) without the irrelevant prefactor, one obtains

$$\frac{S}{k_B} = \ln \mathcal{N} - 1 - \frac{1}{\mathcal{N}} \sum_{\xi} \mathcal{N}_{\xi} \ln \mathcal{N}_{\xi} + \frac{1}{\mathcal{N}} \sum_{\xi} \mathcal{N}_{\xi} = \ln \mathcal{N} - \frac{1}{\mathcal{N}} \sum_{\xi} \mathcal{N}_{\xi} \ln \mathcal{N}_{\xi}. \quad (238)$$

Inserting here the Gibbs distribution, Eq. (233), results in

$$\frac{S}{k_B} = \ln \mathcal{N} - \frac{1}{\mathcal{N}} \sum_{\xi} \mathcal{N}_{\xi} (\alpha \mathcal{N}_{\xi} - \beta E_{\xi}) = \ln \mathcal{Z} - \alpha N + \beta U. \quad (239)$$

To clarify the physical meaning of the parameters α and β , one can calculate the differential dS with respect to these parameters and compare the result with the thermodynamic formula for the systems with a variable number of particles and $V = \text{const}$,

$$dS = \frac{1}{T} dU - \frac{\mu}{T} dN, \quad (240)$$

where μ is the chemical potential. One obtains

$$\begin{aligned} \frac{1}{k_B} \frac{\partial S}{\partial \alpha} &= \frac{\partial \ln \mathcal{Z}}{\partial \alpha} - N - \alpha \frac{\partial N}{\partial \alpha} + \beta \frac{\partial U}{\partial \alpha} = -\alpha \frac{\partial N}{\partial \alpha} + \beta \frac{\partial U}{\partial \alpha} \\ \frac{1}{k_B} \frac{\partial S}{\partial \beta} &= \frac{\partial \ln \mathcal{Z}}{\partial \beta} + U - \alpha \frac{\partial N}{\partial \beta} + \beta \frac{\partial U}{\partial \beta} = -\alpha \frac{\partial N}{\partial \beta} + \beta \frac{\partial U}{\partial \beta}. \end{aligned} \quad (241)$$

Combining these formulas and using

$$dN = \frac{\partial N}{\partial \alpha} d\alpha + \frac{\partial N}{\partial \beta} d\beta, \quad dU = \frac{\partial U}{\partial \alpha} d\alpha + \frac{\partial U}{\partial \beta} d\beta, \quad (242)$$

one obtains

$$dS = k_B \frac{\partial S}{\partial \alpha} d\alpha + k_B \frac{\partial S}{\partial \beta} d\beta = -k_B \alpha dN + k_B \beta dU. \quad (243)$$

Comparing this formula with Eq. (240), one identifies

$$\beta = \frac{1}{k_B T}, \quad \alpha = \frac{\mu}{k_B T} = \beta \mu. \quad (244)$$

Thus Eq. (236) can be rewritten as

$$U = -\frac{\partial \ln \mathcal{Z}}{\partial T} \frac{\partial T}{\partial \beta} = k_B T^2 \frac{\partial \ln \mathcal{Z}}{\partial T}. \quad (245)$$

Substituting the values of α and β into Eq. (239), one obtains

$$-k_B T \ln \mathcal{Z} = U - TS - \mu N. \quad (246)$$

Using the thermodynamical formulas

$$\mu N = G = U - TS + PV, \quad (247)$$

one finally obtains

$$-k_B T \ln \mathcal{Z} = -PV = \Omega, \quad (248)$$

where $\Omega(T, V, \mu)$ is the Ω -potential. Using the main thermodynamic relation for Ω , one can obtain all thermodynamic quantities from $\ln \mathcal{Z}$.

XVII. STATISTICS OF NON-INTERACTING INDISTINGUISHABLE PARTICLES

The Gibbs distribution looks similar to the Boltzmann distribution, Eq. (26). However, this is a distribution of systems of particles in the grand canonical ensemble, rather than the distribution of particles over their individual energy levels. For systems of non-interacting particles, the individual energy levels i exist and the distribution of particles over them can be found. For these systems, the state ξ is specified by the set $\{N_i\}$ of particles' population numbers satisfying

$$N_\xi = \sum_i N_i, \quad E_\xi = \sum_i \varepsilon_i N_i. \quad (249)$$

State obtained by redistribution of the particles over the one-particle states i does not count as new states, only the numbers N_i matter. This implies that within the approach of the grand canonical ensemble the particles are considered as indistinguishable.

The average of N_i over the grand canonical ensemble is given by

$$\bar{N}_i = \frac{1}{\mathcal{Z}} \sum_\xi N_i \mathcal{N}_\xi = \frac{1}{\mathcal{Z}} \sum_\xi N_i e^{\alpha N_\xi - \beta E_\xi}, \quad (250)$$

where \mathcal{Z} is defined by Eq. (234). As both N_ξ and E_ξ are additive in N_i , see Eqs. (249), the summand of Eq. (234) is multiplicative:

$$\mathcal{Z} = \sum_{N_1} e^{(\alpha - \beta \varepsilon_1) N_1} \times \sum_{N_2} e^{(\alpha - \beta \varepsilon_2) N_2} \times \dots = \prod_j \mathcal{Z}_j. \quad (251)$$

As similar factorization occurs in Eq. (250), all factors except the factor containing N_i cancel each other leading to

$$\bar{N}_i = \frac{1}{\mathcal{Z}_i} \sum_{N_i} N_i e^{(\alpha - \beta \varepsilon_i) N_i} = \frac{\partial \ln \mathcal{Z}_i}{\partial \alpha}. \quad (252)$$

The partition functions for quantum states i have different forms for bosons and fermions. For fermions N_i take the values 0 and 1 only, thus

$$\mathcal{Z}_i = 1 + e^{\alpha - \beta \varepsilon_i}. \quad (253)$$

For bosons, N_i take any values from 0 to ∞ . Thus

$$\mathcal{Z}_i = \sum_{N_i=0}^{\infty} e^{(\alpha - \beta \varepsilon_i) N_i} = \frac{1}{1 - e^{\alpha - \beta \varepsilon_i}}. \quad (254)$$

Now \bar{N}_i can be calculated from Eq. (252). Discarding the bar over N_i , one obtains

$$N_i = \frac{1}{e^{\beta \varepsilon_i - \alpha} \pm 1} = \frac{1}{e^{\beta(\varepsilon_i - \mu)} \pm 1}, \quad (255)$$

where (+) corresponds to fermions and (-) corresponds to bosons and α was expressed via μ using Eq. (244). In the first case the distribution is called Fermi-Dirac distribution and in the second case the Bose-Einstein distribution. Eq. (255) should be compared with the Boltzmann distribution, Eq. (26). The chemical potential μ is defined by the normalization condition

$$N = \sum_i \frac{1}{e^{\beta(\varepsilon_i - \mu)} \pm 1} \quad (256)$$

Replacing summation by integration, this can be rewritten as

$$N = \int_0^\infty d\varepsilon \rho(\varepsilon) f(\varepsilon, \mu), \quad f(\varepsilon, \mu) = \frac{1}{e^{\beta(\varepsilon - \mu)} \pm 1}. \quad (257)$$

The internal energy U is given by

$$U = \sum_i \frac{\varepsilon_i}{e^{\beta(\varepsilon_i - \mu)} \pm 1} \Rightarrow \int_0^\infty d\varepsilon \rho(\varepsilon) \varepsilon f(\varepsilon, \mu). \quad (258)$$

At high temperatures μ becomes large negative, so that $-\beta\mu \gg 1$. In this case one can neglect ± 1 in the denominator in comparison to the large exponential, and the Bose-Einstein and Fermi-Dirac distributions simplify to the Boltzmann distribution. Replacing summation by integration, one obtains

$$N = e^{\beta\mu} \int_0^\infty d\varepsilon \rho(\varepsilon) e^{-\beta\varepsilon} = e^{\beta\mu} Z. \quad (259)$$

Using the result for the one-particle partition function for particles in a box, Eqs. (62), yields

$$e^{-\beta\mu} = \frac{Z}{N} = \frac{1}{n} \left(\frac{mk_B T}{2\pi\hbar^2} \right)^{3/2} \gg 1 \quad (260)$$

and our calculation is self-consistent. At low temperatures ± 1 in the denominator of Eq. (257) cannot be neglected, and the system is called *degenerate*.

The Ω -potential is given by Eq. (248) that upon substituting Eqs. (251), (253), and (254) becomes

$$\Omega = -k_B T \ln \mathcal{Z} = -k_B T \sum_i \ln \mathcal{Z}_i = \mp k_B T \sum_i \ln \left(1 \pm e^{\beta(\mu - \varepsilon_i)} \right), \quad (261)$$

where the upper and lower signs correspond to the Fermi and Bose statistics. Replacing summation by integration, one obtains

$$\Omega = \mp k_B T \int d\varepsilon \rho(\varepsilon) \ln \left(1 \pm e^{\beta(\mu - \varepsilon)} \right). \quad (262)$$

For the density of states in the form of a power of the energy, $\rho(\varepsilon) = \rho_0 \varepsilon^m$, one can integrate by parts:

$$\Omega = \mp k_B T \frac{\rho_0 \varepsilon^{m+1}}{m+1} \ln \left(1 \pm e^{\beta(\mu - \varepsilon)} \right) \Big|_0^\infty - \int d\varepsilon \frac{\rho_0 \varepsilon^{m+1}}{m+1} \frac{1}{e^{\beta(\varepsilon - \mu)} \pm 1}. \quad (263)$$

Here the first term vanishes and the second term is proportional to the energy given by Eq. (258):

$$\Omega = -\frac{1}{m+1} U. \quad (264)$$

For non-relativistic particles, $m = 1/2$, see Eq. (58), so that one obtains the relation

$$PV = \frac{2}{3} U. \quad (265)$$

In particular, for the Maxwell-Boltzmann gas $U = (3/2) N k_B T$, so that the equation of state $PV = N k_B T$ results. For ultra-relativistic particles there is a linear relation between the energy and momentum, as for phonons and photons. This implies $m = 2$, see Eq. (124) keeping in mind $\varepsilon = \hbar\omega$. In this case one obtains the relation

$$PV = \frac{1}{3} U. \quad (266)$$

XVIII. BOSE-EINSTEIN GAS

In the macroscopic limit $N \rightarrow \infty$ and $V \rightarrow \infty$, so that the concentration of particles $n = N/V$ is constant, the energy levels of the system become so finely quantized that they become quasicontinuous. In this case summation in Eq. (256) can be replaced by integration. However, it turns out that in 3D below some temperature T_B the ideal Bose-gas undergoes the so-called Bose condensation. The latter means that a macroscopic number of particles $N_0 \sim N$ falls into the ground state. These particles are called *Bose condensate*. Setting the energy of the ground state to zero (that always can be done) from Eq. (257) one obtains

$$N_0 = \frac{1}{e^{-\beta\mu} - 1}. \quad (267)$$

Resolving this for μ , one obtains

$$\mu = -k_B T \ln \left(1 + \frac{1}{N_0} \right) \cong -\frac{k_B T}{N_0}. \quad (268)$$

Since N_0 is very large, one has practically $\mu = 0$ below the Bose condensation temperature. Having $\mu = 0$, one can easily calculate the number of particles in the excited states N_{ex} by integration as

$$N_{\text{ex}} = \int_0^\infty d\varepsilon \frac{\rho(\varepsilon)}{e^{\beta\varepsilon} - 1}. \quad (269)$$

The total number of particles is then

$$N = N_0 + N_{\text{ex}}. \quad (270)$$

In 3D, using the density of states $\rho(\varepsilon)$ given by Eq. (58), one obtains

$$N_{\text{ex}} = \frac{V}{(2\pi)^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty d\varepsilon \frac{\sqrt{\varepsilon}}{e^{\beta\varepsilon} - 1} = \frac{V}{(2\pi)^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \frac{1}{\beta^{3/2}} \int_0^\infty dx \frac{\sqrt{x}}{e^x - 1}. \quad (271)$$

The integral here is a number, a particular case of the general integral

$$\int_0^\infty dx \frac{x^{s-1}}{e^x - 1} = \Gamma(s)\zeta(s), \quad (272)$$

where $\Gamma(s)$ is the gamma-function satisfying

$$\Gamma(n+1) = n\Gamma(n) = n! \quad (273)$$

$$\Gamma(1/2) = \sqrt{\pi}, \quad \Gamma(3/2) = \sqrt{\pi}/2 \quad (274)$$

and $\zeta(s)$ is the Riemann zeta function

$$\zeta(s) \equiv \sum_{k=1}^{\infty} k^{-s} \quad (275)$$

having the values

$$\zeta(1) = \infty, \quad \zeta(3/2) = 2.612, \quad \zeta(5/2) = 1.341, \quad \frac{\zeta(5/2)}{\zeta(3/2)} = 0.5134. \quad (276)$$

Thus Eq. (271) yields

$$N_{\text{ex}} = \frac{V}{(2\pi)^2} \left(\frac{2mk_B T}{\hbar^2} \right)^{3/2} \Gamma(3/2)\zeta(3/2) \quad (277)$$

increasing with temperature. At $T = T_B$ one has $N_{\text{ex}} = N$ that is,

$$N = \frac{V}{(2\pi)^2} \left(\frac{2mk_B T_B}{\hbar^2} \right)^{3/2} \Gamma(3/2)\zeta(3/2), \quad (278)$$

and thus the condensate disappears, $N_0 = 0$. From the equation above follows

$$k_B T_B = \frac{\hbar^2}{2m} \left(\frac{(2\pi)^2 n}{\Gamma(3/2)\zeta(3/2)} \right)^{2/3}, \quad n = \frac{N}{V}, \quad (279)$$

that is, $T_B \propto n^{2/3}$. In typical situations $T_B < 0.1$ K that is a very low temperature that can be obtained by special methods such as laser cooling. Now, obviously, Eq. (277) can be rewritten as

$$\frac{N_{\text{ex}}}{N} = \left(\frac{T}{T_B} \right)^{3/2}, \quad T \leq T_B \quad (280)$$

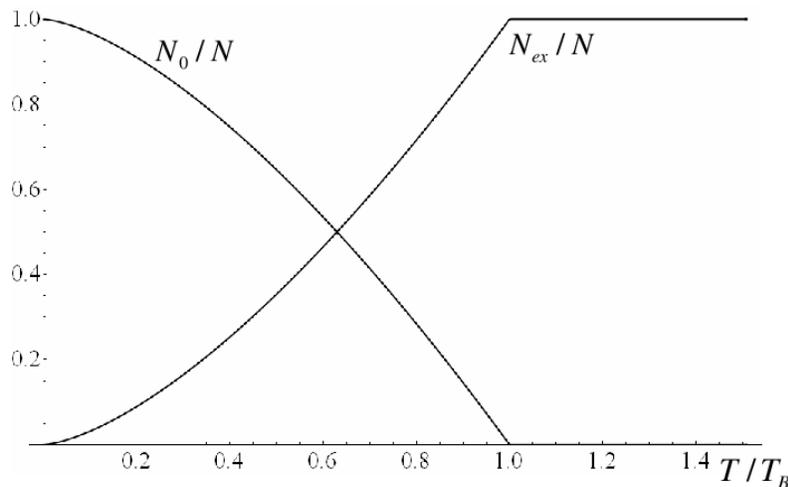


FIG. 10: Condensate fraction $N_0(T)/N$ and the fraction of excited particles $N_{\text{ex}}(T)/N$ for the ideal Bose-Einstein gas.

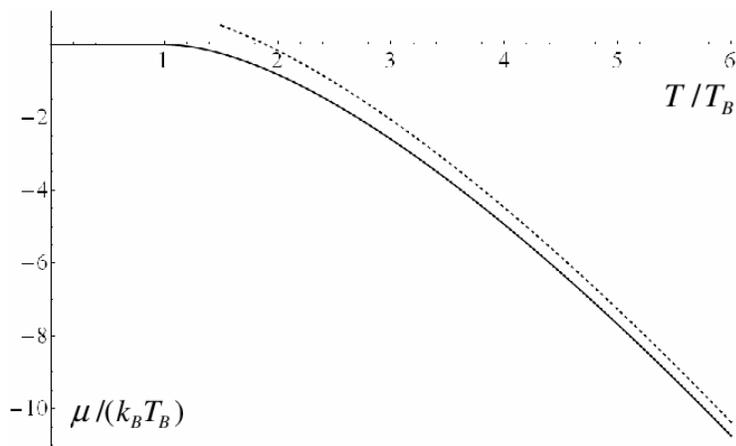


FIG. 11: Chemical potential $\mu(T)$ of the ideal 3D Bose-Einstein gas ($\mu = 0$ for $T < T_B$ and was computed numerically by solving Eq. (282) for $T > T_B$). Dashed line: High-temperature asymptote corresponding to the Boltzmann statistics, Eq. (260).

The temperature dependence of the Bose-condensate is given by

$$\frac{N_0}{N} = 1 - \frac{N_{\text{ex}}}{N} = 1 - \left(\frac{T}{T_B}\right)^{3/2}, \quad T \leq T_B. \quad (281)$$

One can see that at $T = 0$ all bosons are in the Bose condensate, while at $T = T_B$ the Bose condensate disappears. Indeed, in the whole temperature range $0 \leq T \leq T_B$ one has $N_0 \sim N$ and our calculations using $\mu = 0$ in this temperature range are self-consistent. The results above are shown in Fig. 10.

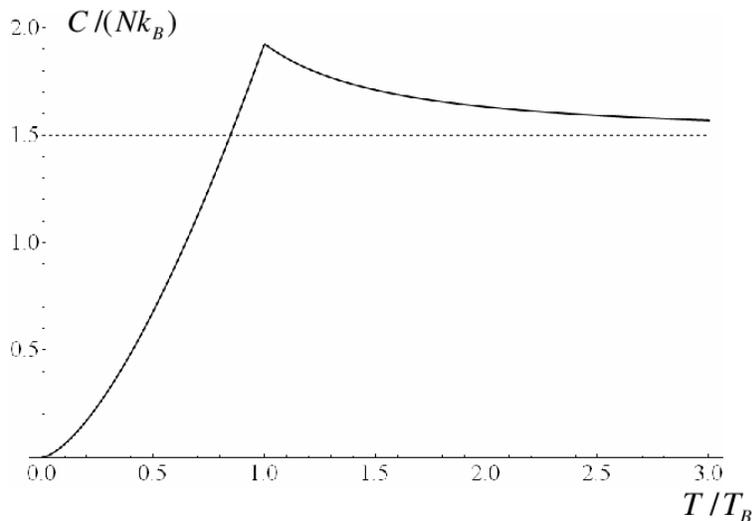


FIG. 12: Heat capacity $C_V(T)$ of the ideal 3D Bose-Einstein gas.

Above T_B there is no Bose condensate, thus $\mu \neq 0$ and is defined by the equation

$$N = \int_0^\infty d\varepsilon \frac{\rho(\varepsilon)}{e^{\beta(\varepsilon-\mu)} - 1}. \quad (282)$$

This is a nonlinear equation that has no general analytical solution. The result of its numerical solution is shown in Fig. 11. At high temperatures the Bose-Einstein (and also Fermi-Dirac) distribution simplifies to the Boltzmann distribution and μ can be easily found. Equation (260) with the help of Eq. (279) can be rewritten in the form

$$e^{-\beta\mu} = \frac{1}{\zeta(3/2)} \left(\frac{T}{T_B} \right)^{3/2} \gg 1, \quad (283)$$

so that the high-temperature limit implies $T \gg T_B$.

Let us consider now the energy of the ideal Bose gas. Since the energy of the condensate is zero, in the thermodynamic limit one has

$$U = \int_0^\infty d\varepsilon \frac{\varepsilon \rho(\varepsilon)}{e^{\beta(\varepsilon-\mu)} - 1} \quad (284)$$

in the whole temperature range. At high temperatures, $T \gg T_B$, the Boltzmann distribution applies, so that U is given by Eq. (67) and the heat capacity is a constant, $C_V = (3/2) Nk_B$. For $T < T_B$ one has $\mu = 0$, thus

$$U = \int_0^\infty d\varepsilon \frac{\varepsilon \rho(\varepsilon)}{e^{\beta\varepsilon} - 1} \quad (285)$$

that in three dimensions becomes

$$U = \frac{V}{(2\pi)^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty d\varepsilon \frac{\varepsilon^{3/2}}{e^{\beta\varepsilon} - 1} = \frac{V}{(2\pi)^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \Gamma(5/2) \zeta(5/2) (k_B T)^{5/2}. \quad (286)$$

With the help of Eq. (278) this can be expressed in the form

$$U = Nk_B T \left(\frac{T}{T_B} \right)^{3/2} \frac{\Gamma(5/2) \zeta(5/2)}{\Gamma(3/2) \zeta(3/2)} = Nk_B T \left(\frac{T}{T_B} \right)^{3/2} \frac{3}{2} \frac{\zeta(5/2)}{\zeta(3/2)}, \quad T \leq T_B. \quad (287)$$

The corresponding heat capacity is

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = Nk_B \left(\frac{T}{T_B} \right)^{3/2} \frac{15}{4} \frac{\zeta(5/2)}{\zeta(3/2)}. \quad (288)$$

To find the heat capacity at $T > T_B$, one has first to find $\mu(T)$ numerically from Eq. (282), then substitute it into Eq. (284) to find the energy, and then differentiate the result with respect to T . The result for the heat capacity of the 3D bose gas in the whole range of the temperature is shown in Fig. 12.

To calculate the pressure of the ideal bose-gas, one can start with the entropy that below T_B is given by

$$S = \int_0^T dT' \frac{C_V(T')}{T'} = \frac{2}{3} C_V = N k_B \left(\frac{T}{T_B} \right)^{3/2} \frac{5 \zeta(5/2)}{2 \zeta(3/2)}. \quad (289)$$

Differentiating the free energy

$$F = U - TS = -N k_B T \left(\frac{T}{T_B} \right)^{3/2} \frac{\zeta(5/2)}{\zeta(3/2)}, \quad (290)$$

one obtains the pressure

$$P = - \left(\frac{\partial F}{\partial V} \right)_T = - \left(\frac{\partial F}{\partial T_B} \right)_T \left(\frac{\partial T_B}{\partial V} \right)_T = - \left(-\frac{3}{2} \frac{F}{T_B} \right) \left(-\frac{2}{3} \frac{T_B}{V} \right) = -\frac{F}{V}, \quad (291)$$

i.e. the equation of state

$$PV = N k_B T \left(\frac{T}{T_B} \right)^{3/2} \frac{\zeta(5/2)}{\zeta(3/2)}, \quad T \leq T_B, \quad (292)$$

compared to $PV = N k_B T$ at high temperatures. In fact, this result can be obtained immediately from the pressure-energy relation, Eq. (265).

One can see that the pressure of the ideal bose gas with the condensate contains an additional factor $(T/T_B)^{3/2} < 1$, the fraction of particles in the excited states. This is because the particles in the condensate are not thermally agitated and thus they do not contribute into the pressure. Using Eq. (280), one can rewrite the equation of state of the 3D bose gas at $T \leq T_B$ as

$$PV = N_{\text{ex}}(T) k_B T \frac{\zeta(5/2)}{\zeta(3/2)}. \quad (293)$$

Other thermodynamic functions above can be rewritten in this way, too. Combining this with Eq. (277), one can see that the volume cancels out in the equation of state and the pressure is a function of the temperature alone:

$$P = P_B(T) \equiv \frac{\Gamma(3/2)\zeta(5/2)}{(2\pi)^2} \left(\frac{2mk_B T}{\hbar^2} \right)^{3/2} k_B T. \quad (294)$$

This is the same behavior as that of the saturated vapor. One can see that one cannot define the heat capacity at constant pressure C_P as one cannot change T keeping $P = \text{const}$. Also, one cannot define the meaningful thermal expansion coefficient and compressibility for the Bose-gas below T_B . If the external pressure exceed the pressure of the gas above, the gas will be compressed to zero volume. In the opposite case, the gas will expand until the condensate disappears, and then the volume stabilizes at some finite value.

XIX. FERMI-DIRAC GAS

Properties of the Fermi gas [plus sign in Eq. (257)] are different from those of the Bose gas because the exclusion principle prevents multi-occupancy of quantum states. As a result, no condensation at the ground state occurs at low temperatures. For a macroscopic system, the chemical potential can be found from the equation

$$N = \int_0^\infty d\varepsilon \rho(\varepsilon) f(\varepsilon) = \int_0^\infty d\varepsilon \frac{\rho(\varepsilon)}{e^{\beta(\varepsilon-\mu)} + 1} \quad (295)$$

at all temperatures. This is a nonlinear equation for μ that in general can be solved only numerically. The result of the numerical solution for $\mu(T)$ is shown in Fig. 13. The Fermi-Dirac distribution function for different temperatures is shown in Fig. 14.

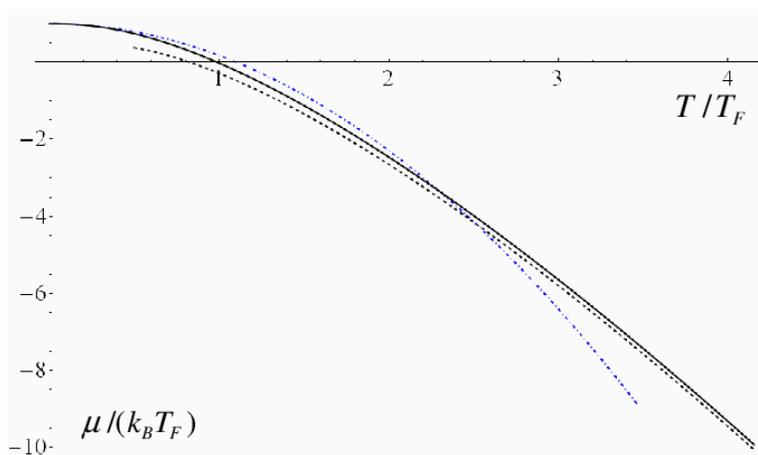


FIG. 13: Chemical potential $\mu(T)$ of the ideal Fermi-Dirac gas. Dashed line: High-temperature asymptote corresponding to the Boltzmann statistics, Eq. (260). Dashed-dotted line: Low-temperature asymptote, Eq. (310).

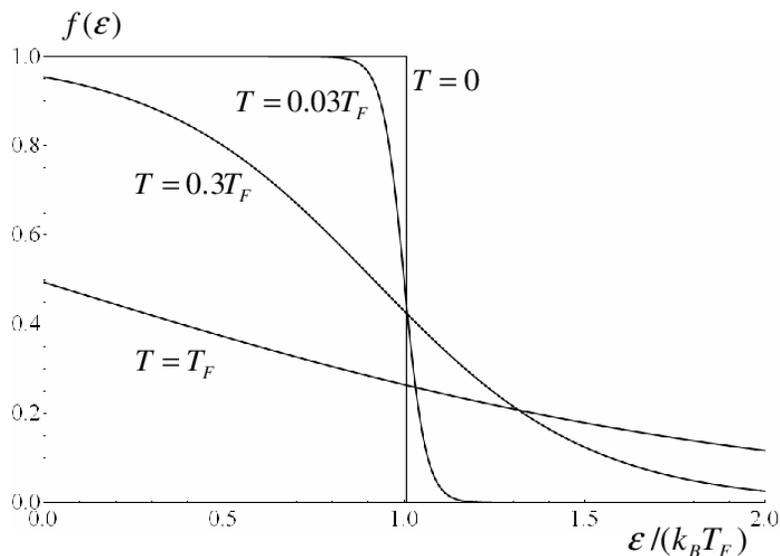


FIG. 14: Fermi-Dirac distribution function at different temperatures.

In the limit $T \rightarrow 0$ fermions fill the certain number of low-lying energy levels to minimize the total energy while obeying the exclusion principle. As we will see, the chemical potential of fermions is positive at low temperatures, $\mu > 0$. For $T \rightarrow 0$ (i. e., $\beta \rightarrow \infty$) one has $e^{\beta(\varepsilon-\mu)} \rightarrow 0$ if $\varepsilon < \mu$ and $e^{\beta(\varepsilon-\mu)} \rightarrow \infty$ if $\varepsilon > \mu$. Thus Eq. (295) becomes

$$f(\varepsilon) = \begin{cases} 1, & \varepsilon < \mu \\ 0, & \varepsilon > \mu. \end{cases} \quad (296)$$

The zero-temperature value of μ that we call the Fermi energy ε_F , is defined by the equation

$$N = \int_0^{\varepsilon_F} d\varepsilon \rho(\varepsilon). \quad (297)$$

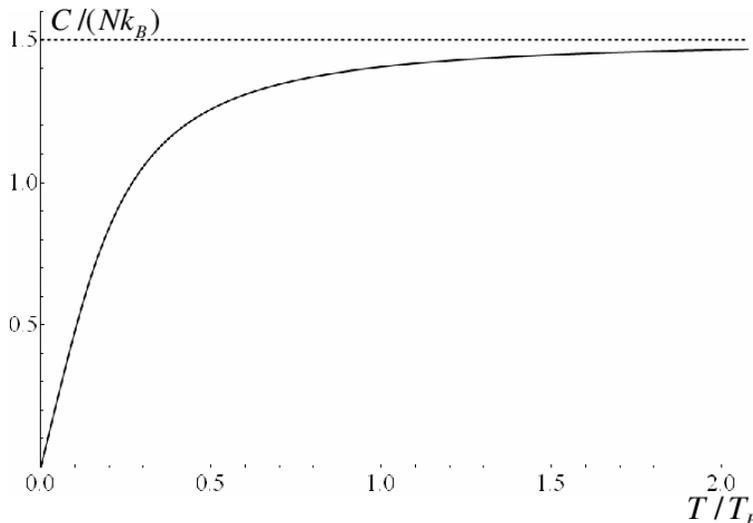


FIG. 15: Heat capacity $C(T)$ of the ideal Fermi-Dirac gas.

Fermions are mainly electrons having spin 1/2 and correspondingly degeneracy 2 because of the two states of the spin. In three dimensions, using Eq. (58) with an additional factor 2 for the degeneracy one obtains

$$N = \frac{2V}{(2\pi)^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^{\varepsilon_F} d\varepsilon \sqrt{\varepsilon} = \frac{2V}{(2\pi)^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \frac{2}{3} \varepsilon_F^{3/2}. \quad (298)$$

From here one obtains

$$\varepsilon_F = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3}. \quad (299)$$

It is convenient also to introduce the Fermi temperature as

$$k_B T_F = \varepsilon_F. \quad (300)$$

One can see that T_F has the same structure as T_B defined by Eq. (279). In typical metals, $T_F \sim 10^5$ K, so that at room temperatures $T \ll T_F$ and the electron gas is degenerate. It is convenient to express the density of states in three dimensions, Eq. (58), in terms of ε_F :

$$\rho(\varepsilon) = \frac{3}{2} N \frac{\sqrt{\varepsilon}}{\varepsilon_F^{3/2}}. \quad (301)$$

Let us now calculate the internal energy U at $T = 0$:

$$U = \int_0^{\mu_0} d\varepsilon \rho(\varepsilon) \varepsilon = \frac{3}{2} \frac{N}{\varepsilon_F^{3/2}} \int_0^{\varepsilon_F} d\varepsilon \varepsilon^{3/2} = \frac{3}{2} \frac{N}{\varepsilon_F^{3/2}} \frac{2}{5} \varepsilon_F^{5/2} = \frac{3}{5} N \varepsilon_F. \quad (302)$$

One cannot calculate the heat capacity C_V from this formula as it requires taking into account small temperature-dependent corrections in U . This will be done later. One can calculate the pressure at low temperatures since in this region the entropy S should be small and $F = U - TS \cong U$. One obtains

$$P = - \left(\frac{\partial F}{\partial V} \right)_{T=0} \cong - \left(\frac{\partial U}{\partial V} \right)_{T=0} = - \frac{3}{5} N \frac{\partial \varepsilon_F}{\partial V} = - \frac{3}{5} N \left(- \frac{2}{3} \frac{\varepsilon_F}{V} \right) = \frac{2}{5} n \varepsilon_F = \frac{\hbar^2}{2m} \frac{2}{5} (3\pi^2)^{2/3} n^{5/3}. \quad (303)$$

To calculate the heat capacity at low temperatures, one has to find temperature-dependent corrections to Eq. (302). We will need the integral of a general type

$$M_\eta = \int_0^\infty d\varepsilon \varepsilon^\eta f(\varepsilon) = \int_0^\infty d\varepsilon \frac{\varepsilon^\eta}{e^{(\varepsilon-\mu)/(k_B T)} + 1} \quad (304)$$

that enters Eq. (295) for N and the similar equation for U . With the use of Eq. (301) one can write

$$N = \frac{3}{2} \frac{N}{\varepsilon_F^{3/2}} M_{1/2}, \quad (305)$$

$$U = \frac{3}{2} \frac{N}{\varepsilon_F^{3/2}} M_{3/2}. \quad (306)$$

It will be shown at the end of this section that for $k_B T \ll \mu$ the expansion of M_η up to quadratic terms has the form

$$M_\eta = \frac{\mu^{\eta+1}}{\eta+1} \left[1 + \frac{\pi^2 \eta (\eta+1)}{6} \left(\frac{k_B T}{\mu} \right)^2 \right]. \quad (307)$$

Now Eq. (305) takes the form

$$\varepsilon_F^{3/2} = \mu^{3/2} \left[1 + \frac{\pi^2}{8} \left(\frac{k_B T}{\mu} \right)^2 \right] \quad (308)$$

that defines $\mu(T)$ up to the terms of order T^2 :

$$\mu = \varepsilon_F \left[1 + \frac{\pi^2}{8} \left(\frac{k_B T}{\mu} \right)^2 \right]^{-2/3} \cong \varepsilon_F \left[1 - \frac{\pi^2}{12} \left(\frac{k_B T}{\mu} \right)^2 \right] \cong \varepsilon_F \left[1 - \frac{\pi^2}{12} \left(\frac{k_B T}{\varepsilon_F} \right)^2 \right] \quad (309)$$

or, with the help of Eq. (300),

$$\mu = \varepsilon_F \left[1 - \frac{\pi^2}{12} \left(\frac{T}{T_F} \right)^2 \right]. \quad (310)$$

It is not surprising that the chemical potential decreases with temperature because at high temperatures it takes large negative values, see Eq. (260). Equation (306) becomes

$$U = \frac{3}{2} \frac{N}{\varepsilon_F^{3/2}} \frac{\mu^{5/2}}{(5/2)} \left[1 + \frac{5\pi^2}{8} \left(\frac{k_B T}{\mu} \right)^2 \right] \cong \frac{3}{5} N \frac{\mu^{5/2}}{\varepsilon_F^{3/2}} \left[1 + \frac{5\pi^2}{8} \left(\frac{k_B T}{\varepsilon_F} \right)^2 \right]. \quad (311)$$

Using Eq. (310), one obtains

$$\begin{aligned} U &= \frac{3}{5} N \varepsilon_F \left[1 - \frac{\pi^2}{12} \left(\frac{T}{T_F} \right)^2 \right]^{5/2} \left[1 + \frac{5\pi^2}{8} \left(\frac{T}{T_F} \right)^2 \right] \\ &\cong \frac{3}{5} N \varepsilon_F \left[1 - \frac{5\pi^2}{24} \left(\frac{T}{T_F} \right)^2 \right] \left[1 + \frac{5\pi^2}{8} \left(\frac{T}{T_F} \right)^2 \right] \end{aligned} \quad (312)$$

that yields

$$U = \frac{3}{5} N \varepsilon_F \left[1 + \frac{5\pi^2}{12} \left(\frac{T}{T_F} \right)^2 \right]. \quad (313)$$

At $T = 0$ this formula reduces to Eq. (302). Now one obtains

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = N k_B \frac{\pi^2}{2} \frac{T}{T_F} \quad (314)$$

that is small at $T \ll T_F$. The numerically found heat capacity in the whole temperature range is shown in Fig. 15. In the high-temperature limit it tends to the classical result $C_V = (3/2) N k_B$.

Let us now derive Eq. (307). Integrating Eq. (304) by parts, one obtains

$$M_\eta = \frac{\varepsilon^{\eta+1}}{\eta+1} f(\varepsilon) \Big|_0^\infty - \int_0^\infty d\varepsilon \frac{\varepsilon^{\eta+1}}{\eta+1} \frac{\partial f(\varepsilon)}{\partial \varepsilon}. \quad (315)$$

The first term of this formula is zero. At low temperatures $f(\varepsilon)$ is close to a step function fast changing from 1 to 0 in the vicinity of $\varepsilon = \mu$. Thus

$$\frac{\partial f(\varepsilon)}{\partial \varepsilon} = \frac{\partial}{\partial \varepsilon} \frac{1}{e^{\beta(\varepsilon-\mu)} + 1} = -\frac{\beta e^{\beta(\varepsilon-\mu)}}{[e^{\beta(\varepsilon-\mu)} + 1]^2} = -\frac{\beta}{4 \cosh^2 [\beta(\varepsilon - \mu)/2]} \quad (316)$$

has a sharp negative peak at $\varepsilon = \mu$. To the contrary, $\varepsilon^{\eta+1}$ is a slow function of ε that can be expanded in the Taylor series in the vicinity of $\varepsilon = \mu$. Up to the second order one has

$$\begin{aligned} \varepsilon^{\eta+1} &= \mu^{\eta+1} + \left. \frac{\partial \varepsilon^{\eta+1}}{\partial \varepsilon} \right|_{\varepsilon=\mu} (\varepsilon - \mu) + \frac{1}{2} \left. \frac{\partial^2 \varepsilon^{\eta+1}}{\partial \varepsilon^2} \right|_{\varepsilon=\mu} (\varepsilon - \mu)^2 \\ &= \mu^{\eta+1} + (\eta + 1) \mu^\eta (\varepsilon - \mu) + \frac{1}{2} \eta (\eta + 1) \mu^{\eta-1} (\varepsilon - \mu)^2. \end{aligned} \quad (317)$$

Introducing $x \equiv \beta(\varepsilon - \mu)/2$ and formally extending integration in Eq. (315) from $-\infty$ to ∞ , one obtains

$$M_\eta = \frac{\mu^{\eta+1}}{\eta + 1} \int_{-\infty}^{\infty} dx \left[\frac{1}{2} + \frac{\eta + 1}{\beta \mu} x + \frac{\eta(\eta + 1)}{\beta^2 \mu^2} x^2 \right] \frac{1}{\cosh^2(x)}. \quad (318)$$

The contribution of the linear x term vanishes by symmetry. Using the integrals

$$\int_{-\infty}^{\infty} dx \frac{1}{\cosh^2(x)} = 2, \quad \int_{-\infty}^{\infty} dx \frac{x^2}{\cosh^2(x)} = \frac{\pi^2}{6}, \quad (319)$$

one arrives at Eq. (307).

XX. ELECTROMAGNETIC RADIATION (PHOTON GAS)

The heat propagating away from hot objects is electromagnetic radiation. It was experimentally established that in a cavity withing a body there is electromagnetic radiation at equilibrium with the body whose intensity and the average frequency increase with the temperature of the body. If a small hole is bored in the body connecting the cavity with the outside world, a stream of electromagnetic radiation goes out and can be analyzed. Analysis of its intensity and frequency distribution lead to the introduction of the concept of quantization in physics by Max Planck in 1900.

The properties of the equilibrium electromagnetic radiation are similar to those of elastic vibrations in solids. Quanta of the latter are called *phonons* while those of the former are called *photons*. So, instead of electromagnetic radiation one can speak of the phonon gas. It is clear that the properties of the photon gas do not depend of the shape of the cavity (that also was proven experimentally). Thus, one can consider a cavity in the form of a box with the sizes L_x , L_y , and L_z , applying boundary conditions at the borders of the cavity. The most natural boundary conditions, plausible in the case of metals, require that the electric field in the electromagnetic wave be zero at the borders, otherwise a strong current will be induced. This boundary condition leads to the normal modes in a form of standing plane waves with the wave vectors $\mathbf{k} = \{k_x, k_y, k_z\}$ given by

$$k_\alpha = \frac{\pi}{L_\alpha} \nu_\alpha, \quad \nu_\alpha = 1, 2, 3, \dots, \quad \alpha = x, y, z. \quad (320)$$

This formula is similar to those for a quantum particle in a box, Eq. (50) and for a clamped elastic body, Eq. (121). An important difference with the elastic problem is that the values of the wave vectors are unlimited.

The frequency density of the modes can be obtained in the same way as it was done for the elastic waves. There is only two transverse polarizations of the electromagnetic waves instead of three polarizations of the elastic waves. Taking this into account and using $\omega = ck$, where c is the speed of light, one obtains

$$\rho(\omega) = \frac{V}{\pi^2 c^3} \omega^2, \quad (321)$$

where $V = L_x L_y L_z$ is the volume of the cavity.

In fact, the properties of the electromagnetic radiation (also called *black-body radiation*) were experimentally investigated before those of the elastic system. First, the problem was considered classically and it was supposed that there

is the energy equal to $k_B T$ in each mode. Multiplying the formula above by $k_B T$ and dividing it by V , one obtains the spectral energy density

$$\rho_E(\omega) = \frac{k_B T}{\pi^2 c^3} \omega^2, \quad (322)$$

the Rayleigh-Jeans formula. The integral of Eq. (322) over the frequencies, with the upper bound equal to infinity, is diverging, that is termed the *ultraviolet catastrophe*. Experiments, however, showed that this formula is valid only at low frequencies. The experimentally found spectral energy density had a maximum at some frequency, dependent on the temperature, and decreased exponentially at high frequencies. Trying to understand this, Max Planck came up with the idea of quantization of the energy of a harmonic oscillator, in this case of the energy of an electromagnetic wave. Within the classical statistical physics, the energy of the oscillator obeys the Boltzmann statistics with the continuous values of the oscillator's energy, and the partition function of the oscillator is given by

$$Z = \int_0^{\infty} d\varepsilon e^{-\beta\varepsilon} = \frac{1}{\beta}. \quad (323)$$

(There is no density of states $\rho(\varepsilon)$ here as a single oscillator is considered.) Then, the oscillator's thermal energy becomes

$$E = -\frac{\partial \ln Z}{\partial \beta} = \frac{1}{\beta} = k_B T \quad (324)$$

that leads to the Rayleigh-Jeans formula, Eq. (322). Planck tried quantized values of the oscillator's energies, $\varepsilon = \hbar\omega\nu$ with $\nu = 0, 1, 2, \dots$, and ω being the oscillator's frequency. In this case the partition function is a geometrical progression:

$$Z = \sum_{\nu=0}^{\infty} (e^{-\beta\hbar\omega})^{\nu} = \frac{1}{1 - e^{-\beta\hbar\omega}} \quad (325)$$

and the oscillator's thermal energy becomes

$$E = -\frac{\partial \ln Z}{\partial \beta} = \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}. \quad (326)$$

At high temperatures, $\beta\hbar\omega \ll 1$, the classical result $E = k_B T$ is recovered. In this case, $e^{-\beta\hbar\omega}$ is close to one and summation can be replaced by integration. In general, one obtains the Planck's formula

$$\rho_E(\omega) = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\beta\hbar\omega} - 1} \quad (327)$$

that perfectly describes the experiment. In particular, the maximum of the spectral energy density satisfies the transcendental equation

$$3(1 - e^{-\beta\hbar\omega}) = \beta\hbar\omega, \quad (328)$$

thus $\omega_{\max} \propto k_B T / \hbar$. In this way the Planck's constant has been introduced in physics and could be measured. Planck has empirically found quantum energy levels of the harmonic oscillator before quantum mechanics was created. From Planck's finding it follows that the energy of the electromagnetic field is split into discrete portions, quanta, with the energy $\hbar\omega$. These quanta of electromagnetic energy are called *photons*. Photons and phonons are examples of *quasiparticles* - excitations having some properties of particles.

The derivation above repeats that for the quantum harmonic oscillator starting from Eq. (72). The only difference is that the zero-point energy is absent in the Planck's derivation. However, as this energy cannot be released, it cannot be measured and has to be discarded in interpreting the energy of the black-body radiation. Integrating the spectral energy density over the frequencies, one obtains the energy of the photon gas:

$$U = u(T)V, \quad u(T) = \int_0^{\infty} d\omega \rho_E(\omega) = \frac{\pi^2}{15c^3\hbar^3} (k_B T)^4 \quad (329)$$

that is similar to Eq. (138) for the phonon gas in the elastic body.

Let us calculate the pressure of the photon gas. The heat capacity is given by

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{4\pi^2 V k_B}{15c^3 \hbar^3} (k_B T)^3. \quad (330)$$

The entropy can be obtained by the integration:

$$S = \int_0^T dT' \frac{C_V(T')}{T'} = \frac{1}{3} C_V = \frac{4\pi^2 V k_B}{45c^3 \hbar^3} (k_B T)^3. \quad (331)$$

Then, the free energy becomes

$$F = U - TS = U - \frac{4}{3}U = -\frac{1}{3}U = -\frac{1}{3}u(T)V. \quad (332)$$

Now, the equation of state is given by

$$P = - \left(\frac{\partial F}{\partial V} \right)_T = \frac{1}{3}u(T), \quad (333)$$

in accordance with Eq. (266) for ultra-relativistic particles. One can see that the photon gas behaves as saturated vapor – it can be compressed without any pressure increase because of condensation. Indeed, one can calculate the number of photons in the photon gas and it turns out to be proportional to the volume and depending on the temperature. Thus, the number of photons is not conserved, unlike that of the ordinary particles. The pressure of the photons is small, 2.4×10^{-6} N/m² at $T = 300$ K, much smaller than the atmospheric pressure 10^5 N/m², still it can be demonstrated in a high-school experiment.

The electromagnetic radiation at equilibrium can be considered in a different way using the statistics of indistinguishable particles based on the grand canonical ensemble. In the description of harmonic oscillators, phonons and photons above, we considered equidistant quantum energy levels of harmonic oscillators, or normal modes that behave like harmonic oscillators, and we applied the Boltzmann statistics to find the numbers of the oscillators in each of their quantum states. The oscillators or normal modes are obviously distinguishable, so they are considered as such. Now we take another point of view and consider normal modes as quantum states, asking how many excitations (quasiparticles such as phonons or photons) are in each mode, that is, in each quantum state in the new sense. Obviously, the number of excitations in each state is unlimited and the excitations are indistinguishable by definition. Thus, one can apply the method of the grand canonical ensemble and use the Bose-Einstein distribution for the numbers of excitations in each state. The total number of excitations N is obviously not conserved. Thus, in the grand canonical ensemble there is no constraint on the number of particles and thus no Lagrange parameter α and no chemical potential μ . As a result, one can use the Bose distribution function with $\mu = 0$

$$n(\omega) = \frac{1}{e^{\beta \hbar \omega} - 1} \quad (334)$$

for the number of excitations in the mode (state) with the frequency ω . This is Eq. (88) obtained for the harmonic oscillator by summing up the geometrical progression. Multiplying this by the density of modes (now states) $\rho(\omega)$ of Eq. (321) for photons and by the energy of the mode (now state) $\hbar\omega$, one arrives at the Planck's formula, Eq. (327).

It should be stressed that the quasiparticle picture of the excited states of the modes is only possible if the excitation spectrum of the mode is equidistant. Then the energy of the mode is proportional to the number of excitations and one can use the energy constraint in the form of Eqs. (3) or (249). If the energy levels are not equidistant, as is the case for the anharmonic oscillator, rotator, or even a particle in a box, one cannot use these formulas for the energy within the quasiparticle description. Still, the approach based on the Boltzmann statistics is working in these cases.