

Statistical Thermodynamics - Fall 2009

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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 *kinetics*. The equilibrium situations are within the scope of statistical physics in the narrow sense that belongs to this course. 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 formalism of statistical physics 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 physics 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 in which it can be at the moment, and 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. 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 allowed macroscopic states 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

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

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 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,

$$\sum_{N_1=0}^N w_{N_1} = \sum_{N_1=0}^N \frac{N!}{N_1!(N - N_1)!} = 2^N. \quad (8)$$

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

$$w_{N_1} = \frac{N!}{(N/2 + p)!(N/2 - p)!}. \quad (9)$$

One can see that w_p is symmetric around $N_1 = N/2$, i.e., $p = 0$. Working out the ratio

$$\frac{w_{N/2 \pm 1}}{w_{N/2}} = \frac{(N/2)!(N/2)!}{(N/2 + 1)!(N/2 - 1)!} = \frac{N/2}{N/2 + 1} < 1, \quad (10)$$

one can see that $N_1 = N/2$ is indeed the maximum of w_{N_1} .

IV. STIRLING FORMULA AND THERMODYNAMIC PROBABILITY AT LARGE N

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

$$N! \cong \sqrt{2\pi N} \left(\frac{N}{e}\right)^N. \quad (11)$$

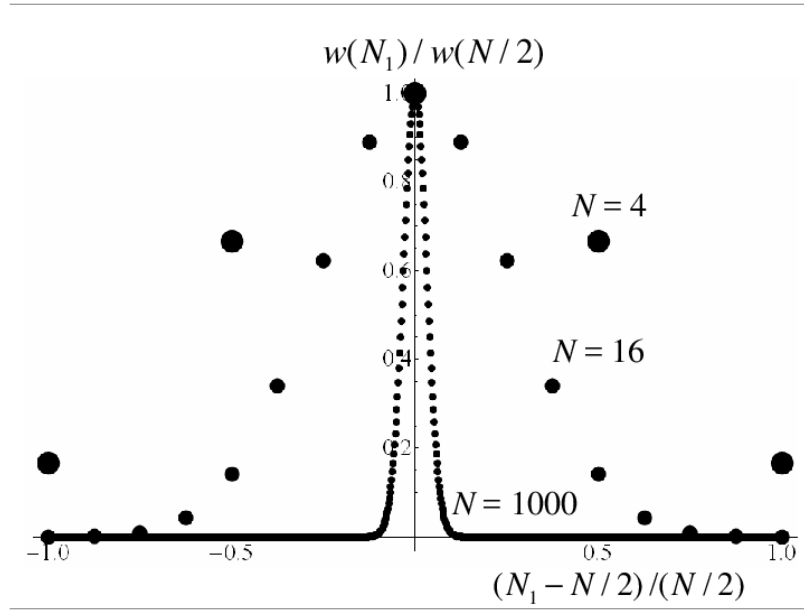


FIG. 1: Binomial distribution for an ensemble of N two-state systems.

In particular, Eq. (9) becomes

$$\begin{aligned}
 w_{N_1} &\cong \frac{\sqrt{2\pi N} (N/e)^N}{\sqrt{2\pi (N/2+p)} [(N/2+p)/e]^{N/2+p} \sqrt{2\pi (N/2-p)} [(N/2-p)/e]^{N/2-p}} \\
 &= \sqrt{\frac{2}{\pi N}} \frac{1}{\sqrt{1 - \left(\frac{2p}{N}\right)^2}} \frac{N^N}{(N/2+p)^{N/2+p} (N/2-p)^{N/2-p}} \\
 &= \frac{w_{N/2}}{\sqrt{1 - \left(\frac{2p}{N}\right)^2} \left(1 + \frac{2p}{N}\right)^{N/2+p} \left(1 - \frac{2p}{N}\right)^{N/2-p}}, \tag{12}
 \end{aligned}$$

where

$$w_{N/2} \cong \sqrt{\frac{2}{\pi N}} 2^N \tag{13}$$

is the maximal value of the thermodynamic probability. Eq. (12) 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. (12) can be discarded as it gives a negligible contribution of order p^2/N^2 . One obtains

$$\begin{aligned}
 \ln w_{N_1} &\cong \ln w_{N/2} - \left(\frac{N}{2} + p\right) \ln \left(1 + \frac{2p}{N}\right) - \left(\frac{N}{2} - p\right) \ln \left(1 - \frac{2p}{N}\right) \\
 &\cong \ln w_{N/2} - \left(\frac{N}{2} + p\right) \left[\frac{2p}{N} - \frac{1}{2} \left(\frac{2p}{N}\right)^2\right] - \left(\frac{N}{2} - p\right) \left[-\frac{2p}{N} - \frac{1}{2} \left(\frac{2p}{N}\right)^2\right] \\
 &\cong \ln w_{N/2} - p - \frac{2p^2}{N} + \frac{p^2}{N} + p - \frac{2p^2}{N} + \frac{p^2}{N} \\
 &= \ln w_{N/2} - \frac{2p^2}{N} \tag{14}
 \end{aligned}$$

and thus

$$w_{N_1} \cong w_{N/2} \exp \left(-\frac{2p^2}{N} \right). \tag{15}$$

One can see that w_{N_1} becomes very small if $|p| \equiv |N_1 - N/2| \gtrsim \sqrt{N}$ that is much smaller than N for large 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

$$w = \frac{N!}{N_1!N_2!\dots N_n!} = \frac{N!}{\prod_{i=1}^n N_i!}. \quad (16)$$

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

$$\begin{aligned} w = & \frac{N!}{N_1!(N - N_1)!} \times \frac{(N - N_1)!}{N_2!(N - N_1 - N_2)!} \times \frac{(N - N_1 - N_2)!}{N_3!(N - N_1 - N_2 - N_3)!} \times \\ & \dots \times \frac{(N_{n-2} + N_{n-1} + N_n)!}{N_{n-2}!(N_{n-1} + N_n)!} \times \frac{(N_{n-1} + N_n)!}{N_{n-1}!N_n!} \times \frac{N_n!}{N_n!0!}. \end{aligned} \quad (17)$$

In this formula, all numerators except for the first one and all second terms in the denominators cancel each other, so that Eq. (16) 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 probable 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)

$$S = k_B \ln w, \quad (18)$$

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. (18) k_B is the Boltzmann constant,

$$k_B = 1.38 \times 10^{-23} \text{ J K}^{-1}. \quad (19)$$

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. (16). 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

$$\Phi(N_1, N_2, \dots, N_n) = \ln w + \alpha \sum_i N_i - \beta \sum_i \varepsilon_i N_i. \quad (20)$$

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

$$\frac{\partial \Phi}{\partial N_i} = 0, \quad i = 1, 2, \dots \quad (21)$$

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. (11) that takes the form

$$\ln N! \cong N \ln N - N + \ln \sqrt{2\pi N}. \quad (22)$$

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

$$\Phi \cong \ln N! - \sum_j N_j \ln N_j + \sum_j N_j + \alpha \sum_j N_j - \beta \sum_j \varepsilon_j N_j. \quad (23)$$

In the derivatives $\partial \Phi / \partial N_i$, the only contribution comes from the terms with $j = i$ in the above expression. One obtains the equations

$$\frac{\partial \Phi}{\partial N_i} = -\ln N_i + \alpha - \beta \varepsilon_i = 0 \quad (24)$$

that yield

$$N_i = e^{\alpha - \beta \varepsilon_i}, \quad (25)$$

the Boltzmann distribution.

The Lagrange multipliers can be found from Eqs. (2) and (3) in terms of N and U . Summing Eq. (25) over i , one obtains

$$N = e^\alpha Z, \quad \alpha = \ln(N/Z), \quad (26)$$

where

$$Z = \sum_i e^{-\beta \varepsilon_i} \quad (27)$$

is the so-called *partition function* (German *Zustandssumme*) that plays a major role in statistical physics. Then, eliminating α from Eq. (25) yields

$$N_i = \frac{N}{Z} e^{-\beta \varepsilon_i}. \quad (28)$$

After that for the internal energy U one obtains

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

or

$$U = -N \frac{\partial \ln Z}{\partial \beta}. \quad (30)$$

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

The statistical entropy, Eq. (18), within the Stirling approximation becomes

$$S = k_B \ln w = k_B \left(N \ln N - \sum_i N_i \ln N_i \right). \quad (31)$$

Inserting here Eq. (25) and α from Eq. (26), one obtains

$$\frac{S}{k_B} = N \ln N - \sum_i N_i (\alpha - \beta \varepsilon_i) = N \ln N - \alpha N + \beta U = N \ln Z + \beta U, \quad (32)$$

Let us show now that β is related to the temperature. To this purpose, we differentiate S with respect to U keeping $N = \text{const}$:

$$\frac{1}{k_B} \frac{\partial S}{\partial U} = N \frac{\partial \ln Z}{\partial U} + U \frac{\partial \beta}{\partial U} + \beta = N \frac{\partial \ln Z}{\partial \beta} \frac{\partial \beta}{\partial U} + U \frac{\partial \beta}{\partial U} + \beta. \quad (33)$$

Here according to Eq. (30) the first and second terms cancel each other leading to

$$\frac{\partial S}{\partial U} = k_B \beta. \quad (34)$$

Note that the energies of quantum states ε_i depend on the geometry of the system. In particular, for quantum particles in a box ε_i depend on L_x , L_y , and L_z according to Eq. (48). In the differentiation over U above, ε_i were kept constant. From the thermodynamical point of view, this amounts to differentiating over U with the constant volume V . Recalling the thermodynamic formula

$$\left(\frac{\partial S}{\partial U} \right)_V = \frac{1}{T} \quad (35)$$

and comparing it with Eq. (34), one identifies

$$\beta = \frac{1}{k_B T}. \quad (36)$$

Thus Eq. (30) actually defines the internal energy as a function of the temperature. Now from Eq. (32) one obtains the statistical formula for the free energy

$$F = U - TS = -N k_B T \ln Z. \quad (37)$$

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 .

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

$$\hat{H}\Psi = E\Psi, \quad (38)$$

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

$$dN = N |\Psi(\mathbf{r})|^2 d^3r. \quad (39)$$

The wave function satisfies the normalization condition

$$1 = \int d^3r |\Psi(\mathbf{r})|^2. \quad (40)$$

The operator \hat{H} in Eq. (38) is the so-called Hamilton operator or Hamiltonian. For one particle, it is the sum of kinetic and potential energies

$$\hat{H} = \frac{\hat{\mathbf{p}}^2}{2m} + U(\mathbf{r}), \quad (41)$$

where the classical momentum p is replaced by the operator

$$\hat{\mathbf{p}} = -i\hbar \frac{\partial}{\partial \mathbf{r}}. \quad (42)$$

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. (38) 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. (40). It turns out that the solution of Eq. (38) 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

$$\hat{p} = -i\hbar \frac{d}{dx} \quad (43)$$

and Eq. (38) takes the form

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \Psi(x) = \varepsilon \Psi(x) \quad (44)$$

and can be represented as

$$\frac{d^2}{dx^2} \Psi(x) + k^2 \Psi(x) = 0, \quad k^2 \equiv \frac{2m\varepsilon}{\hbar^2}. \quad (45)$$

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

$$\Psi_\nu(x) = A \sin(k_\nu x), \quad k_\nu = \frac{\pi}{L} \nu, \quad \nu = 1, 2, 3, \dots \quad (46)$$

where eigenstates are labeled by the index ν . The constant A following from Eq. (40) is $A = \sqrt{2/L}$. The energy eigenvalues are given by

$$\varepsilon_\nu = \frac{\hbar^2 k_\nu^2}{2m} = \frac{\pi^2 \hbar^2 \nu^2}{2mL^2}. \quad (47)$$

One can see that 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 a similar calculation yields the energy levels parametrized by the three quantum numbers ν_x , ν_y , and ν_z :

$$\varepsilon = \frac{\hbar^2 \mathbf{k}^2}{2m} = \frac{\hbar^2 (k_x^2 + k_y^2 + k_z^2)}{2m}, \quad k_\alpha = \frac{\pi}{L_\alpha} \nu_\alpha, \quad \nu_\alpha = 1, 2, 3, \dots \quad (48)$$

and $\alpha = x, y, z$. Here the ground state corresponds to $\nu_x = \nu_y = \nu_z = 1$. 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

$$\varepsilon_{\nu_x, \nu_y, \nu_z} = \frac{\pi^2 \hbar^2}{2mL^2} (\nu_x^2 + \nu_y^2 + \nu_z^2) \quad (49)$$

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,

$$dn = \rho(\varepsilon)d\varepsilon. \quad (50)$$

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

$$dn = d\nu_x d\nu_y d\nu_z, \quad (51)$$

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. (48)

$$dn = \frac{V}{\pi^3} dk_x dk_y dk_z, \quad (52)$$

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

$$dn = \frac{V}{\pi^3} \frac{4\pi}{8} k^2 dk. \quad (53)$$

The last step is to change the variable from k to ε using Eq. (48). With

$$k^2 = \frac{2m}{\hbar^2} \varepsilon, \quad k = \sqrt{\frac{2m}{\hbar^2}} \sqrt{\varepsilon}, \quad \frac{dk}{d\varepsilon} = \frac{1}{2} \sqrt{\frac{2m}{\hbar^2}} \frac{1}{\sqrt{\varepsilon}} \quad (54)$$

one obtains Eq. (50) with

$$\rho(\varepsilon) = \frac{V}{(2\pi)^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \sqrt{\varepsilon}. \quad (55)$$

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. (48), are quantized so finely that one can introduce the density of states $\rho(\varepsilon)$ defined by Eq. (50). 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. (28) one obtains

$$dN_\varepsilon = N(\varepsilon) dn_\varepsilon = \frac{N}{Z} e^{-\beta\varepsilon} \rho(\varepsilon) d\varepsilon. \quad (56)$$

For finely quantized levels one can replace summation in Eq. (27) and similar formulas by integration as

$$\sum_i \dots \Rightarrow \int d\varepsilon \rho(\varepsilon) \dots \quad (57)$$

Thus for the partition function (27) one has

$$Z = \int d\varepsilon \rho(\varepsilon) e^{-\beta\varepsilon}. \quad (58)$$

For quantum particles in a rigid box with the help of Eq. (55) one obtains

$$Z = \frac{V}{(2\pi)^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty d\varepsilon \sqrt{\varepsilon} e^{-\beta\varepsilon} = \frac{V}{(2\pi)^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \frac{\sqrt{\pi}}{2\beta^{3/2}} = V \left(\frac{mk_B T}{2\pi\hbar^2} \right)^{3/2}. \quad (59)$$

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

$$dN_v = N f(v) dv, \quad (60)$$

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

$$\begin{aligned} f(v) &= \frac{1}{Z} e^{-\beta\varepsilon} \rho(\varepsilon) mv = \frac{1}{V} \left(\frac{2\pi\hbar^2}{mk_B T} \right)^{3/2} \frac{V}{(2\pi)^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \sqrt{\frac{m}{2}} v mv e^{-\beta\varepsilon} \\ &= \left(\frac{m}{2\pi k_B T} \right)^{3/2} 4\pi v^2 \exp\left(-\frac{mv^2}{2k_B T}\right). \end{aligned} \quad (61)$$

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

The internal energy of the ideal gas is its kinetic energy

$$U = N\bar{\varepsilon}, \quad (62)$$

$\bar{\varepsilon} = m\bar{v}^2/2$ 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

$$\bar{\varepsilon} = \frac{f}{2} k_B T, \quad (63)$$

where in our case $f = 3$ corresponding to three translational degrees of freedom. The same result can be obtained from Eq. (30)

$$U = -N \frac{\partial \ln Z}{\partial \beta} = -N \frac{\partial}{\partial \beta} V \ln \left(\frac{m}{2\pi\hbar^2\beta} \right)^{3/2} = \frac{3}{2} N \frac{\partial}{\partial \beta} \ln \beta = \frac{3}{2} N \frac{1}{\beta} = \frac{3}{2} N k_B T. \quad (64)$$

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

$$P = - \left(\frac{\partial F}{\partial V} \right)_T. \quad (65)$$

With the help of Eqs. (37) and (59) one obtains

$$P = N k_B T \frac{\partial \ln Z}{\partial V} = N k_B T \frac{\partial \ln V}{\partial V} = \frac{N k_B T}{V} \quad (66)$$

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

X. STATISTICAL THERMODYNAMICS OF HARMONIC OSCILLATORS

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

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{kx^2}{2}. \quad (67)$$

Here the momentum operator \hat{p} is given by Eq. (43) 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 (38) for a harmonic oscillator becomes

$$\left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{kx^2}{2} \right) \Psi(x) = \varepsilon \Psi(x). \quad (68)$$

The boundary conditions for this equation require that $\Psi(\pm\infty) = 0$ and the integral in Eq. (40) converges. In contrast to Eq. (44), 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. (68) 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

$$\varepsilon_\nu = \hbar\omega_0 \left(\nu + \frac{1}{2} \right), \quad \nu = 0, 1, 2, \dots, \quad (69)$$

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

$$Z = \sum_{\nu=0}^{\infty} e^{-\beta\varepsilon_\nu} = e^{-\beta\hbar\omega_0/2} \sum_{\nu=0}^{\infty} (e^{-\beta\hbar\omega_0})^\nu = \frac{e^{-\beta\hbar\omega_0/2}}{1 - e^{-\beta\hbar\omega_0}} = \frac{1}{e^{\beta\hbar\omega_0/2} - e^{-\beta\hbar\omega_0/2}} = \frac{2}{\sinh(\beta\hbar\omega_0/2)}, \quad (70)$$

where the result for the geometrical progression

$$1 + x + x^2 + x^3 + \dots = (1 - x)^{-1}, \quad x < 1 \quad (71)$$

was used. The hyperbolic functions are defined by

$$\begin{aligned} \sinh(x) &\equiv \frac{e^x - e^{-x}}{2}, & \cosh(x) &\equiv \frac{e^x + e^{-x}}{2} \\ \tanh(x) &\equiv \frac{\sinh(x)}{\cosh(x)}, & \coth(x) &\equiv \frac{\cosh(x)}{\sinh(x)} = \frac{1}{\tanh(x)}. \end{aligned} \quad (72)$$

We will be using the formulas

$$\sinh(x)' = \cosh(x), \quad \cosh(x)' = \sinh(x) \quad (73)$$

and

$$\sinh(x) \cong \begin{cases} x, & x \ll 1 \\ e^x/2, & x \gg 1 \end{cases}, \quad \tanh(x) \cong \begin{cases} x, & x \ll 1 \\ 1, & x \gg 1. \end{cases} \quad (74)$$

The internal (average) energy of the ensemble of oscillators is given by Eq. (30). This yields

$$U = -N \frac{\partial \ln Z}{\partial \beta} = -N \sinh(\beta\hbar\omega_0/2) \frac{\partial}{\partial \beta} \frac{1}{\sinh(\beta\hbar\omega_0/2)} = N \frac{\hbar\omega_0}{2} \coth\left(\frac{\beta\hbar\omega_0}{2}\right) \quad (75)$$

or

$$U = N \frac{\hbar\omega_0}{2} \coth\left(\frac{\hbar\omega_0}{2k_B T}\right). \quad (76)$$

Another way of writing the internal energy is

$$U = N\hbar\omega_0 \left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega_0} - 1} \right) \quad (77)$$

or the similar in terms of T . The limiting low- and high-temperature cases of this formula are

$$U \cong \begin{cases} N\hbar\omega_0/2, & k_B T \ll \hbar\omega_0 \\ Nk_B T, & k_B T \gg \hbar\omega_0. \end{cases} \quad (78)$$

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. (70) is $\nu = 0$. Correspondingly, U is the sum of ground-state energies of all oscillators.

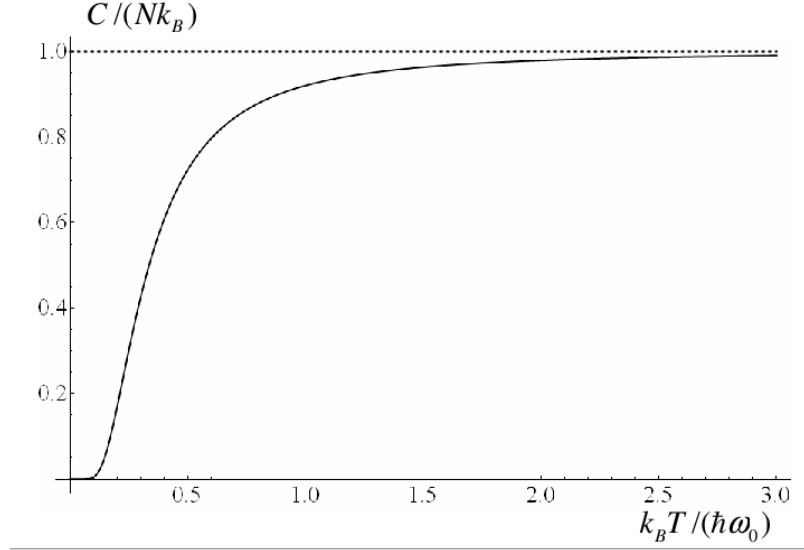


FIG. 2: Heat capacity of harmonic oscillators.

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. (70). 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

$$\nu^* \sim \frac{k_B T}{\hbar\omega_0} \gg 1. \quad (79)$$

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

The heat capacity is defined by

$$C = \frac{dU}{dT} = N \frac{\hbar\omega_0}{2} \left(-\frac{1}{\sinh^2 [\hbar\omega_0/(2k_B T)]} \right) \left(-\frac{\hbar\omega_0}{2k_B T^2} \right) = N k_B \left(\frac{\hbar\omega_0/(2k_B T)}{\sinh [\hbar\omega_0/(2k_B T)]} \right)^2. \quad (80)$$

This formula has limiting cases

$$C \cong \begin{cases} N k_B \left(\frac{\hbar\omega_0}{k_B T} \right)^2 \exp \left(-\frac{\hbar\omega_0}{k_B T} \right), & k_B T \ll \hbar\omega_0 \\ N k_B, & k_B T \gg \hbar\omega_0. \end{cases} \quad (81)$$

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

$$C = \frac{f}{2} N k_B, \quad (82)$$

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 average quantum number of an oscillator is given by

$$n \equiv \langle \nu \rangle = \frac{1}{Z} \sum_{\nu=0}^{\infty} \nu e^{-\beta \epsilon_{\nu}}. \quad (83)$$

Using Eq. (69), one can calculate this sum as follows

$$n = \frac{1}{Z} \sum_{\nu=0}^{\infty} \left(\frac{1}{2} + \nu \right) e^{-\beta \varepsilon_{\nu}} - \frac{1}{Z} \sum_{\nu=0}^{\infty} \frac{1}{2} e^{-\beta \varepsilon_{\nu}} = \frac{1}{\hbar \omega_0} \frac{1}{Z} \sum_{\nu=0}^{\infty} \varepsilon_{\nu} e^{-\beta \varepsilon_{\nu}} - \frac{Z}{2Z} = -\frac{1}{\hbar \omega_0} \frac{1}{Z} \frac{\partial Z}{\partial \beta} - \frac{1}{2} = \frac{U}{N \hbar \omega_0} - \frac{1}{2}. \quad (84)$$

Finally with the help of Eq. (77), one finds

$$n = \frac{1}{e^{\beta \hbar \omega_0} - 1} = \frac{1}{\exp[\hbar \omega_0 / (k_B T)] - 1} \quad (85)$$

so that

$$U = N \hbar \omega_0 \left(\frac{1}{2} + n \right). \quad (86)$$

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. (85) yields

$$n \cong \frac{k_B T}{\hbar \omega_0} \quad (87)$$

that has the same order of magnitude as the top populated quantum level number ν^* given by Eq. (79).

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

$$dn_{\nu} = d\nu \quad (88)$$

(that is, there is only one level in the interval $d\nu = 1$). Then, changing the variables with the help of Eq. (69), one finds the number of levels dn_{ε} in the interval $d\varepsilon$ as

$$dn_{\varepsilon} = \frac{d\nu}{d\varepsilon} d\varepsilon = \left(\frac{d\varepsilon}{d\nu} \right)^{-1} d\varepsilon = \rho(\varepsilon) d\varepsilon, \quad (89)$$

where

$$\rho(\varepsilon) = \frac{1}{\hbar \omega_0}. \quad (90)$$

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

$$\frac{e^{-\beta \varepsilon_{\nu}} - e^{-\beta \varepsilon_{\nu+1}}}{e^{-\beta \varepsilon_{\nu}}} = 1 - e^{-\beta(\varepsilon_{\nu+1} - \varepsilon_{\nu})} = 1 - e^{-\beta \hbar \omega_0} \cong 1 - 1 + \beta \hbar \omega_0 = \frac{\hbar \omega_0}{k_B T} \ll 1. \quad (91)$$

In this situation one can replace summation in Eq. (70) by integration using the rule in Eq. (57). One can integrate over ε using the density of states of Eq. (90). Also one can integrate directly over ν considering it as continuous:

$$Z = \int_0^{\infty} d\nu e^{-\beta \varepsilon} = \int_0^{\infty} d\varepsilon \frac{d\nu}{d\varepsilon} e^{-\beta \varepsilon} = \frac{1}{\hbar \omega_0} \int_0^{\infty} d\varepsilon e^{-\beta \varepsilon} = \frac{1}{\hbar \omega_0 \beta} = \frac{k_B T}{\hbar \omega_0}. \quad (92)$$

The results of this calculation is in accord with Eq. (90). Now the internal energy U is given by

$$U = -N \frac{\partial \ln Z}{\partial \beta} = -N \frac{\partial \ln \frac{1}{\beta} + \dots}{\partial \beta} = N \frac{\partial \ln \beta + \dots}{\partial \beta} = \frac{N}{\beta} = N k_B T \quad (93)$$

that coincides with the second line of Eq. (78).

XI. STATISTICAL THERMODYNAMICS OF ROTATORS

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

$$E_{\text{rot}} = \frac{1}{2}I_1\omega_1^2 + \frac{1}{2}I_2\omega_2^2 + \frac{1}{2}I_3\omega_3^2. \quad (94)$$

We will restrict our consideration to the axially symmetric body with $I_1 = I_2 = I$. In this case E_{rot} can be rewritten in terms of the angular momentum components $L_\alpha = I_\alpha\omega_\alpha$ as follows

$$E_{\text{rot}} = \frac{\mathbf{L}^2}{2I} + \frac{1}{2} \left(\frac{1}{I_3} - \frac{1}{I} \right) L_3^2. \quad (95)$$

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:

$$I_1 = I_2 = I = 2 \times m \left(\frac{d}{2} \right)^2 = \frac{1}{2}md^2, \quad (96)$$

where m is the mass of an atom. In our case, $I_3 = 0$, there is no kinetic energy associated with rotation around the 3 axis. Then Eq. (95) 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. The solution of the stationary Schrödinger equation yields eigenvalues of \mathbf{L}^2 , L_3 , and E_{rot} in terms of three quantum numbers l , m , and n . These eigenvalues are given by

$$\hat{\mathbf{L}}^2 = \hbar^2 l(l+1), \quad l = 0, 1, 2, \dots \quad (97)$$

$$\hat{L}_3 = \hbar n, \quad m, n = -l, -l+1, \dots, l-1, l \quad (98)$$

and

$$E_{\text{rot}} = \frac{\hbar^2 l(l+1)}{2I} + \frac{\hbar^2}{2} \left(\frac{1}{I_3} - \frac{1}{I} \right) n^2 \quad (99)$$

that follows by substitution of Eqs. (97) and (98) into Eq. (95). One can see that the results do not depend on the quantum number m and there are $2l+1$ degenerate levels because of this. Indeed, the angular momentum of the molecule $\hat{\mathbf{L}}$ can have $2l+1$ different projections on any axis and this is the reason for the degeneracy. 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

$$E_{\text{rot}} = \frac{\hbar^2 l(l+1)}{2I} \quad (100)$$

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. (100) again but with the degeneracy $g_l = 2l+1$.

The rotational partition function both for the symmetric body and for a diatomic molecule is given by

$$Z = \sum_l g_l e^{-\beta \varepsilon_l}, \quad g_l = (2l+1)^\xi, \quad \xi = \begin{cases} 2, & \text{symmetric body} \\ 1, & \text{diatomic molecule,} \end{cases} \quad (101)$$

where $\varepsilon_l \equiv E_{\text{rot}}$. In both cases Z cannot be calculated analytically in general. In the general case $I_1 = I_2 \neq I_3$ with $I_3 \neq 0$ one has to perform summation over both l and n .

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

$$Z \cong 1 + 3^\xi \exp \left(-\frac{\beta \hbar^2}{I} \right) \quad (102)$$

at low temperatures. The rotational internal energy is given by

$$U = -N \frac{\partial \ln Z}{\partial \beta} = 3^\xi \frac{\hbar^2}{I} \exp \left(-\frac{\beta \hbar^2}{I} \right) = 3^\xi \frac{\hbar^2}{I} \exp \left(-\frac{\hbar^2}{Ik_B T} \right) \quad (103)$$

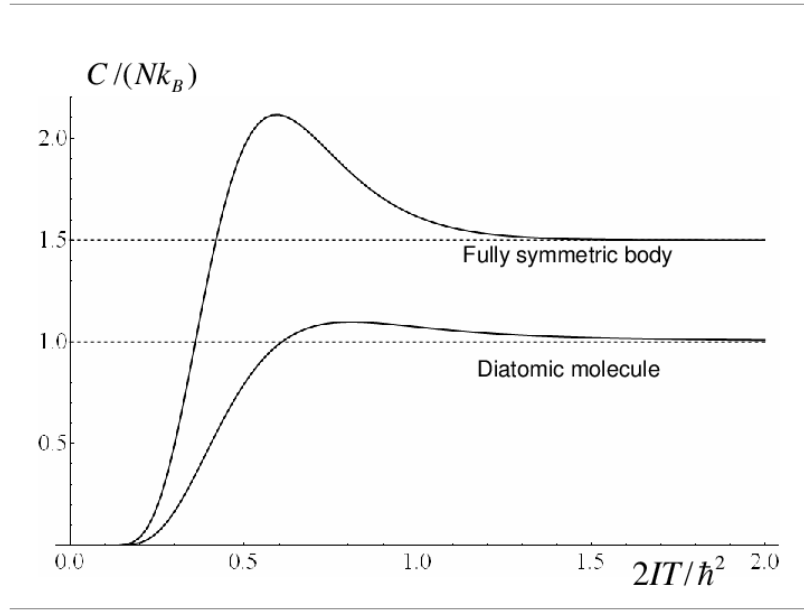


FIG. 3: Rotational heat capacity of a fully symmetric body and a diatomic molecule.

and it is exponentially small. The heat capacity is

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = 3\xi k_B \left(\frac{\hbar^2}{Ik_B T} \right)^2 \exp \left(-\frac{\hbar^2}{Ik_B T} \right) \quad (104)$$

and it is also exponentially small.

In the high-temperature limit, very many energy levels are thermally populated, so that in Eq. (101) one can replace summation by integration. With

$$g_l \cong (2l)^\xi, \quad \varepsilon_l \equiv \varepsilon \cong \frac{\hbar^2 l^2}{2I}, \quad \frac{\partial \varepsilon}{\partial l} = \frac{\hbar^2 l}{I}, \quad \frac{\partial l}{\partial \varepsilon} = \frac{I}{\hbar^2} \sqrt{\frac{\hbar^2}{2I\varepsilon}} = \sqrt{\frac{I}{2\hbar^2 \varepsilon}} \quad (105)$$

one has

$$Z \cong \int_0^\infty dl g_l e^{-\beta \varepsilon_l} \cong 2^\xi \int_0^\infty dl l^\xi e^{-\beta \varepsilon_l} = 2^\xi \int_0^\infty d\varepsilon \frac{\partial l}{\partial \varepsilon} l^\xi e^{-\beta \varepsilon} \quad (106)$$

and further

$$\begin{aligned} Z &\cong 2^\xi \sqrt{\frac{I}{2\hbar^2}} \int_0^\infty d\varepsilon \frac{1}{\sqrt{\varepsilon}} \left(\frac{2I\varepsilon}{\hbar^2} \right)^{\xi/2} e^{-\beta \varepsilon} = 2^{(3\xi-1)/2} \left(\frac{I}{\hbar^2} \right)^{(\xi+1)/2} \int_0^\infty d\varepsilon \varepsilon^{(\xi-1)/2} e^{-\beta \varepsilon} \\ &= 2^{(3\xi-1)/2} \left(\frac{I}{\beta \hbar^2} \right)^{(\xi+1)/2} \int_0^\infty dx x^{(\xi-1)/2} e^{-x} \propto \beta^{-(\xi+1)/2}. \end{aligned} \quad (107)$$

Now the internal energy is given by

$$U = -N \frac{\partial \ln Z}{\partial \beta} = \frac{\xi+1}{2} N \frac{\partial \ln \beta}{\partial \beta} = \frac{\xi+1}{2} N \frac{1}{\beta} = \frac{\xi+1}{2} N k_B T, \quad (108)$$

whereas the heat capacity is

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{\xi+1}{2} N k_B. \quad (109)$$

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.

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. (94), can be written as

$$E_{\text{rot}} = \frac{L_1^2}{2I_1} + \frac{L_2^2}{2I_2} + \frac{L_3^2}{2I_3}. \quad (110)$$

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

$$\begin{aligned} Z_{\text{class}} &= \int_{-\infty}^{\infty} dL_1 dL_2 dL_3 \exp(-\beta E_{\text{rot}}) \\ &= \int_{-\infty}^{\infty} dL_1 \exp\left(-\frac{\beta L_1^2}{2I_1}\right) \times \int_{-\infty}^{\infty} dL_2 \exp\left(-\frac{\beta L_2^2}{2I_2}\right) \times \int_{-\infty}^{\infty} dL_3 \exp\left(-\frac{\beta L_3^2}{2I_3}\right) \\ &= \sqrt{\frac{2I_1}{\beta}} \times \frac{2I_2}{\beta} \times \frac{2I_3}{\beta} \left(\int_{-\infty}^{\infty} dx e^{-x^2}\right)^3 \propto \beta^{-3/2}. \end{aligned} \quad (111)$$

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

$$U = -N \frac{\partial \ln Z}{\partial \beta} = \frac{3}{2} N \frac{\partial \ln \beta}{\partial \beta} = \frac{3}{2} N k_B T \quad (112)$$

that coincides with Eq. (108) with $\xi = 2$. In the case of the diatomic molecule the energy has the form

$$E_{\text{rot}} = \frac{L_1^2}{2I_1} + \frac{L_2^2}{2I_2}. \quad (113)$$

Then the partition function becomes

$$\begin{aligned} Z_{\text{class}} &= \int_{-\infty}^{\infty} dL_1 dL_2 \exp(-\beta E_{\text{rot}}) \\ &= \int_{-\infty}^{\infty} dL_1 \exp\left(-\frac{\beta L_1^2}{2I_1}\right) \times \int_{-\infty}^{\infty} dL_2 \exp\left(-\frac{\beta L_2^2}{2I_2}\right) \\ &= \sqrt{\frac{2I_1}{\beta}} \times \frac{2I_2}{\beta} \left(\int_{-\infty}^{\infty} dx e^{-x^2}\right)^2 \propto \beta^{-1}. \end{aligned} \quad (114)$$

This leads to

$$U = N k_B T, \quad (115)$$

in accordance with Eq. (108) with $\xi = 1$.

XII. STATISTICAL PHYSICS OF VIBRATIONS IN SOLIDS

Above in Sec. X we have studied statistical mechannics 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 hypothetic 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

$$\omega_k = vk \quad (116)$$

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. Similarly to the quantum problem of a particle in a potential box with dimensions L_x , L_y , and L_z , one obtains the quantized values of the wave vector components k_α with $\alpha = x, y, z$

$$k_\alpha = \pi \frac{\nu_\alpha}{L_\alpha}, \quad \nu = 1, 2, 3, \dots \quad (117)$$

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

$$dn_\omega = \rho(\omega) d\omega. \quad (118)$$

Using Eq. (53) multiplied by the number of phonon modes 3 and changing from k to ω with the help of Eq. (116) one obtains

$$\rho(\omega) = \frac{3V}{2\pi^2 v^3} \omega^2. \quad (119)$$

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

$$3N = 3 \sum_{\mathbf{k}} 1 = 3 \sum_{k_x, k_y, k_z} 1. \quad (120)$$

For a body of a box shape $N = N_x N_y N_z$, so that the above equation splits into the three separate equations

$$N_\alpha = \sum_{k_\alpha=1}^{k_{\alpha,\max}} 1 \cong \nu_{\alpha,\max} \quad (121)$$

for $\alpha = x, y, z$. This results in

$$k_{\alpha,\max} = \pi \frac{N_\alpha}{L_\alpha} = \pi a, \quad (122)$$

where a is the lattice spacing, that is, the distance between the atoms.

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

$$\sum_{\mathbf{k}} \dots \Rightarrow \int_0^{\omega_{\max}} d\omega \rho(\omega) \dots \quad (123)$$

At large k and thus ω , the linear dependence of Eq. (116) is no longer valid, so that Eq. (119) becomes invalid as well. Still, one can make a crude approximation assuming that Eqs. (116) and (119) 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. (120) that takes the form

$$3N = \int_0^{\omega_D} d\omega \rho(\omega). \quad (124)$$

With the use of Eq. (119) one obtains

$$3N = \int_0^{\omega_D} d\omega \frac{3V}{2\pi^2 v^3} \omega^2 = \frac{V\omega_D^3}{2\pi^2 v^3}, \quad (125)$$

wherefrom

$$\omega_D = (6\pi^2)^{1/3} \frac{v}{a}, \quad (126)$$

where we used $(V/N)^{1/3} = v_0^{1/3} = a$, and v_0 is the unit-cell volume. It is convenient to rewrite Eq. (119) in terms of ω_D as

$$\rho(\omega) = 9N \frac{\omega^2}{\omega_D^3}. \quad (127)$$

The quantum energy levels of a harmonic oscillator are given by Eq. (69). In our case for a \mathbf{k} -oscillator it becomes

$$\varepsilon_{\mathbf{k}, \nu_{\mathbf{k}}} = \hbar\omega_k \left(\nu_{\mathbf{k}} + \frac{1}{2} \right), \quad \nu = 0, 1, 2, \dots \quad (128)$$

All the \mathbf{k} -oscillators contribute additively into the internal energy,

$$U = 3 \sum_{\mathbf{k}} \langle \varepsilon_{\mathbf{k}, \nu_{\mathbf{k}}} \rangle = 3 \sum_{\mathbf{k}} \hbar\omega_k \left(\langle \nu_{\mathbf{k}} \rangle + \frac{1}{2} \right) = 3 \sum_{\mathbf{k}} \hbar\omega_k \left(n_{\mathbf{k}} + \frac{1}{2} \right), \quad (129)$$

where, similarly to Eq. (85),

$$n_{\mathbf{k}} = \frac{1}{\exp(\beta\hbar\omega_k) - 1}. \quad (130)$$

Replacing summation by integration and rearranging Eq. (129), within the Debye model one obtains

$$U = U_0 + \int_0^{\omega_D} d\omega \rho(\omega) \frac{\hbar\omega}{\exp(\beta\hbar\omega) - 1}, \quad (131)$$

where U_0 is the zero-temperature value of U due to the zero-point motion. The integral term in Eq. (131) can be calculated analytically at low and high temperatures.

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

$$\begin{aligned} U &= U_0 + \int_0^{\infty} d\omega \rho(\omega) \frac{\hbar\omega}{\exp(\beta\hbar\omega) - 1} = U_0 + \frac{9N}{\omega_D^3} \int_0^{\infty} d\omega \omega^2 \frac{\hbar\omega}{\exp(\beta\hbar\omega) - 1} \\ &= U_0 + \frac{9N}{(\hbar\omega_D)^3 \beta^4} \int_0^{\infty} dx \frac{x^3}{e^x - 1} = U_0 + \frac{9N}{(\hbar\omega_D)^3 \beta^4} \frac{\pi^4}{15} = U_0 + \frac{3\pi^4}{5} N k_B T \left(\frac{k_B T}{\hbar\omega_D} \right)^3. \end{aligned} \quad (132)$$

This result can be written in the form

$$U = U_0 + \frac{3\pi^4}{5} N k_B T \left(\frac{T}{\theta_D} \right)^3, \quad (133)$$

where

$$\theta_D = \hbar\omega_D / k_B \quad (134)$$

is the Debye temperature. The heat capacity is given by

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{12\pi^4}{5} N k_B \left(\frac{T}{\theta_D} \right)^3, \quad T \ll \theta_D. \quad (135)$$

Although the Debye temperature enters Eqs. (133) and (135), these results are accurate and insensitive to the Debye approximation.

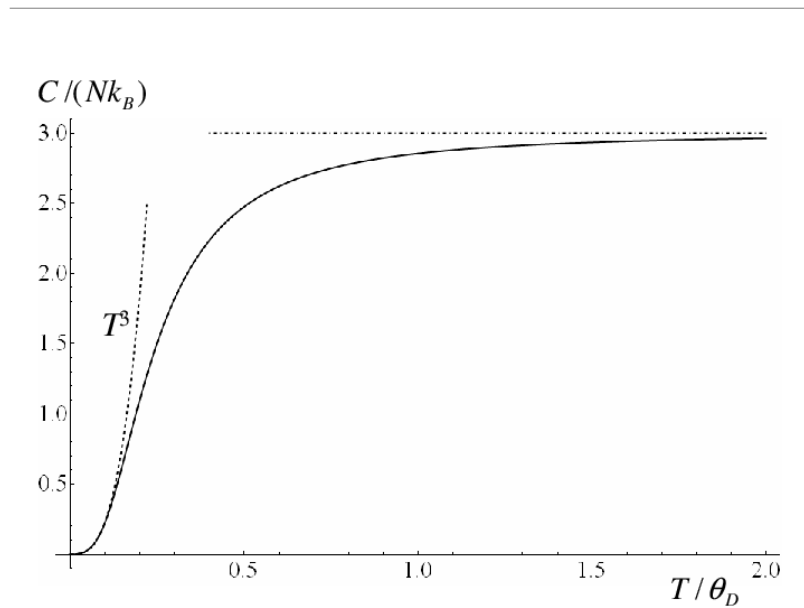


FIG. 4: Temperature dependence of the phonon heat capacity. The low-temperature result $C \propto T^3$ (dashed line) holds only for temperatures much smaller than the Debye temperature θ_D .

For $k_B T \gg \hbar \omega_D$, the exponential in Eq. (131) can be expanded for $\beta \hbar \omega \ll 1$. It is, however, convenient to step back and to do the same in Eq. (129). With the help of Eq. (120) one obtains

$$U = U_0 + 3 \sum_{\mathbf{k}} \frac{\hbar \omega_{\mathbf{k}}}{\beta \hbar \omega_{\mathbf{k}}} = U_0 + 3k_B T \sum_{\mathbf{k}} 1 = U_0 + 3Nk_B T. \quad (136)$$

For the heat capacity one then obtains

$$C_V = 3Nk_B, \quad (137)$$

k_B per each of approximately $3N$ vibrational modes. One can see that Eqs. (136) and (137) are accurate because they do not use the Debye model. The assumption of the Debye model is really essential at intermediate temperatures, where Eq. (131) is approximate.

The temperature dependence of the phonon heat capacity, following from Eq. (131), is shown in Fig. 4 together with its low-temperature asymptote, Eq. (135), and the high-temperature asymptote, Eq. (137). Because of the large numerical coefficient in Eq. (135), the law $C_V \propto T^3$ in fact holds only for the temperatures much smaller than the Debye temperature.

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 the quantum-mechanical eigenvalue of the square of the electron's angular momentum (in the units of \hbar) is

$$\hat{\mathbf{s}}^2 = s(s+1) = 3/4 \quad (138)$$

c.f. Eq. (97). Eigenvalues of \hat{s}_z , projection of a free spin on any direction z , are given by

$$\hat{s}_z = m, \quad m = \pm 1/2 \quad (139)$$

c.f. Eq. (98). 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

$$\hat{\boldsymbol{\mu}} = g\mu_B \hat{\mathbf{s}}, \quad (140)$$

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 \mathbf{B} has the form

$$\hat{H} = -g\mu_B \hat{\mathbf{S}} \cdot \mathbf{B}, \quad (141)$$

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

$$\hat{H} = -g\mu_B \hat{S}_z B. \quad (142)$$

Thus the energy eigenvalues of the electronic spin in a magnetic field with the help of Eq. (139) become

$$\varepsilon_m = -g\mu_B m B, \quad (143)$$

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

In an atom, spins of all electrons usually combine into a collective spin S that can be greater than $1/2$. Thus instead of Eq. (141) one has

$$\hat{H} = -g\mu_B \hat{\mathbf{S}} \cdot \mathbf{B}. \quad (144)$$

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

$$m = -S, -S+1, \dots, S-1, S, \quad (145)$$

all together $2S+1$ different values, c.f. Eq. (97). The $2S+1$ different energy levels of the spin are given by Eq. (143).

Physical quantities of the spin are determined by the partition function

$$Z_S = \sum_{m=-S}^S e^{-\beta \varepsilon_m} = \sum_{m=-S}^S e^{my}, \quad (146)$$

where ε_m is given by Eq. (143) and

$$y \equiv \beta g \mu_B B = \frac{g \mu_B B}{k_B T}. \quad (147)$$

Eq. (146) can be reduced to a finite geometrical progression

$$Z_S = e^{-Sy} \sum_{k=0}^{2S} (e^y)^k = e^{-Sy} \frac{e^{(2S+1)y} - 1}{e^y - 1} = \frac{e^{(S+1/2)y} - e^{-(S+1/2)y}}{e^{y/2} - e^{-y/2}} = \frac{\sinh[(S+1/2)y]}{\sinh(y/2)}. \quad (148)$$

For $S = 1/2$ with the help of $\sinh(2x) = 2 \sinh(x) \cosh(x)$ one can transform Eq. (148) to

$$Z_{1/2} = 2 \cosh(y/2). \quad (149)$$

The partition function being found, one can easily obtain thermodynamic quantities.. For instance, the free energy F is given by Eq. (37),

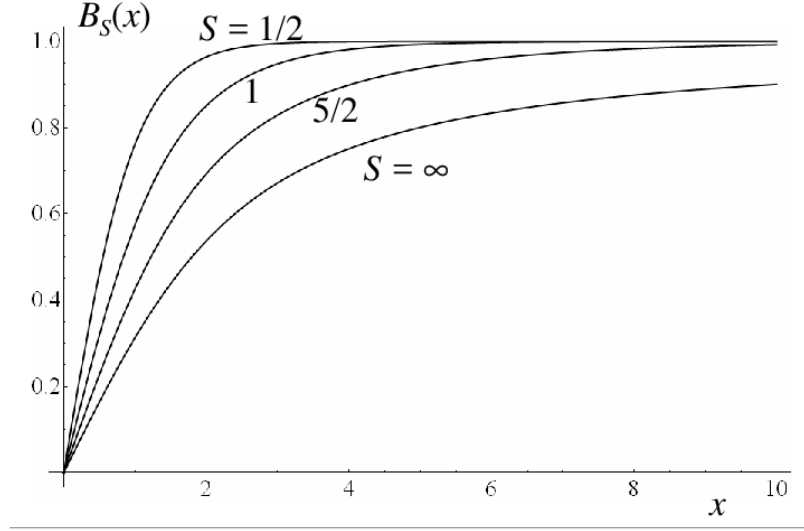
$$F = -Nk_B T \ln Z_S = -Nk_B T \ln \frac{\sinh[(S+1/2)y]}{\sinh(y/2)}. \quad (150)$$

The average spin polarization is defined by

$$\langle S_z \rangle = \langle m \rangle = \frac{1}{Z} \sum_{m=-S}^S m e^{-\beta \varepsilon_m}. \quad (151)$$

With the help of Eq. (146) one obtains

$$\langle S_z \rangle = \frac{1}{Z} \frac{\partial Z}{\partial y} = \frac{\partial \ln Z}{\partial y}. \quad (152)$$

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

With the use of Eq. (148) and the derivatives

$$\sinh(x)' = \cosh(x), \quad \cosh(x)' = \sinh(x) \quad (153)$$

one obtains

$$\langle S_z \rangle = b_S(y), \quad (154)$$

where

$$b_S(y) = \left(S + \frac{1}{2}\right) \coth \left[\left(S + \frac{1}{2}\right) y \right] - \frac{1}{2} \coth \left[\frac{1}{2} y \right]. \quad (155)$$

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

$$B_S(x) = \left(1 + \frac{1}{2S}\right) \coth \left[\left(1 + \frac{1}{2S}\right) x \right] - \frac{1}{2S} \coth \left[\frac{1}{2S} x \right]. \quad (156)$$

For $S = 1/2$ from Eq. (149) one obtains

$$\langle S_z \rangle = b_{1/2}(y) = \frac{1}{2} \tanh \frac{y}{2} \quad (157)$$

and $B_{1/2}(x) = \tanh x$. One can see that $b_S(\pm\infty) = \pm S$ and $B_S(\pm\infty) = \pm 1$. At zero magnetic field, $y = 0$, the spin polarization should vanish. It is immediately seen in Eq. (157) but not in Eq. (154). To clarify the behavior of $b_S(y)$ at small y , one can use $\coth x \cong 1/x + x/3$ that yields

$$\begin{aligned} b_S(y) &\cong \left(S + \frac{1}{2}\right) \left[\frac{1}{\left(S + \frac{1}{2}\right) y} + \left(S + \frac{1}{2}\right) \frac{y}{3} \right] - \frac{1}{2} \left[\frac{1}{\frac{1}{2} y} + \frac{1}{2} \frac{y}{3} \right] \\ &= \frac{y}{3} \left[\left(S + \frac{1}{2}\right)^2 - \left(\frac{1}{2}\right)^2 \right] = \frac{S(S+1)}{3} y. \end{aligned} \quad (158)$$

In physical units, this means

$$\langle S_z \rangle \cong \frac{S(S+1)}{3} \frac{g\mu_B B}{k_B T}, \quad g\mu_B B \ll k_B T. \quad (159)$$

The average magnetic moment of the spin can be obtained from Eq. (140)

$$\langle \mu_z \rangle = g\mu_B \langle S_z \rangle. \quad (160)$$

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

$$M = \frac{\langle \mu_z \rangle}{v_0} = \frac{g\mu_B}{v_0} \langle S_z \rangle, \quad (161)$$

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. (30). The calculation can be, however, avoided since from Eq. (143) simply follows

$$U = N \langle \varepsilon_m \rangle = -Ng\mu_B B \langle m \rangle = -Ng\mu_B B \langle S_z \rangle = -Ng\mu_B B b_S(y) = -Nk_B T y b_S(y). \quad (162)$$

In particular, at low magnetic fields (or high temperatures) one has

$$U \cong -N \frac{S(S+1)}{3} \frac{(g\mu_B B)^2}{k_B T}. \quad (163)$$

The magnetic susceptibility per spin is defined by

$$\chi = \frac{\partial \langle \mu_z \rangle}{\partial B}. \quad (164)$$

From Eqs. (160) and (154) one obtains

$$\chi = \frac{(g\mu_B)^2}{k_B T} b'_S(y), \quad (165)$$

where

$$b'_S(y) \equiv \frac{db_S(y)}{dy} = - \left(\frac{S+1/2}{\sinh[(S+1/2)y]} \right)^2 + \left(\frac{1/2}{\sinh[y/2]} \right)^2. \quad (166)$$

For $S = 1/2$ from Eq. (157) one obtains

$$b'_{1/2}(y) = \frac{1}{4 \cosh^2(y/2)}. \quad (167)$$

From Eq. (158) follows $b'_S(0) = S(S+1)/3$, thus one obtains the high-temperature limit

$$\chi = \frac{S(S+1)}{3} \frac{(g\mu_B)^2}{k_B T}, \quad k_B T \gg g\mu_B B. \quad (168)$$

In the opposite limit $y \gg 1$ the function $b'_S(y)$ and thus the susceptibility 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. (162) as

$$C = \frac{\partial U}{\partial T} = -Ng\mu_B B b'_S(y) \frac{\partial y}{\partial T} = Nk_B b'_S(y) y^2. \quad (169)$$

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

$$C \cong Nk_B \frac{S(S+1)}{3} \left(\frac{g\mu_B B}{k_B T} \right)^2, \quad (170)$$

and at low temperatures C becomes exponentially small, except for the case $S = \infty$ (see Fig. 6). Finally, Eqs. (165) and (169) imply a simple relation between χ and C

$$\frac{N\chi}{C} = \frac{T}{B^2} \quad (171)$$

that does not depend on the spin value S .

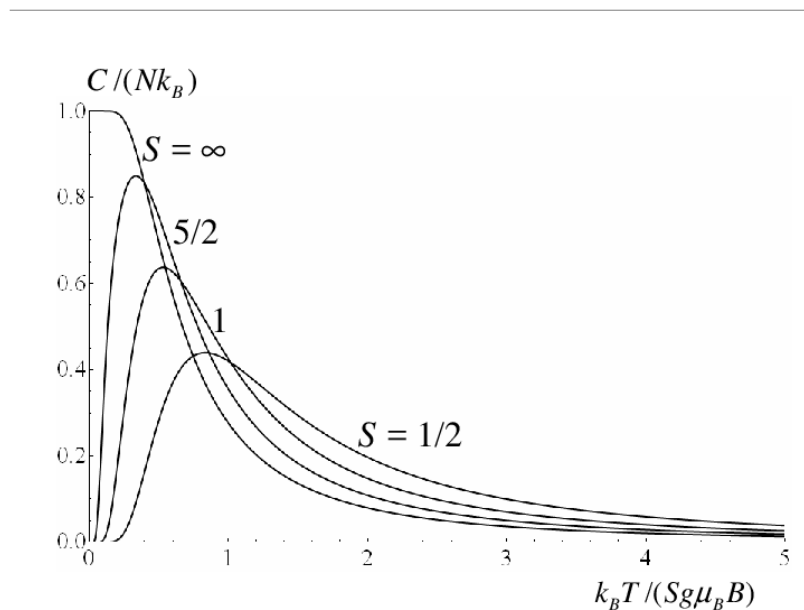


FIG. 6: Temperature dependence of the heat capacity of spins in a magnetic fields with different values of S .

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 transitions are 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. XV. 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, $|\langle \hat{\mathbf{S}}_i \rangle| \rightarrow S$. With increasing

temperature, excited levels of the system become populated and the average spin value decreases, $|\langle \hat{\mathbf{S}}_i \rangle| < S$. 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 are 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 $|\langle \hat{\mathbf{S}}_i \rangle|$ as the temperature is lowered.

Although the scenario outlined above looks persuasive, there are subtle effects that may preclude ordering and ensure $|\langle \hat{\mathbf{S}}_i \rangle| = 0$ 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. (144). 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: (144) and has the form

$$\hat{H} = -\hat{\mathbf{S}} \cdot (g\mu_B \mathbf{B} + Jz \langle \hat{\mathbf{S}} \rangle) + \frac{1}{2}Jz \langle \hat{\mathbf{S}} \rangle^2, \quad (172)$$

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. (172) to

$$\hat{H} = -\left(g\mu_B B + Jz \langle \hat{S}_z \rangle\right) \hat{S}_z + \frac{1}{2}Jz \langle \hat{S}_z \rangle^2. \quad (173)$$

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. (173) are

$$\varepsilon_m = -\left(g\mu_B B + Jz \langle \hat{S}_z \rangle\right) m + \frac{1}{2}Jz \langle \hat{S}_z \rangle^2, \quad m = -S, -S+1, \dots, S-1, S. \quad (174)$$

Now, after calculation of the partition function Z , Eq. (146), one arrives at the free energy per spin

$$F = -k_B T \ln Z = \frac{1}{2}Jz \langle \hat{S}_z \rangle^2 - k_B T \ln \frac{\sinh[(S+1/2)y]}{\sinh(y/2)}, \quad (175)$$

where

$$y \equiv \frac{g\mu_B B + Jz \langle \hat{S}_z \rangle}{k_B T}. \quad (176)$$

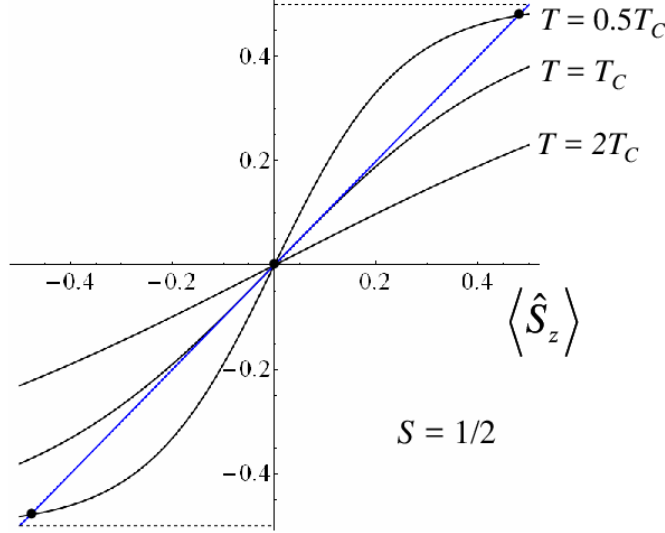


FIG. 7: Graphic solution of the Curie-Weiss equation.

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

$$0 = \frac{\partial F}{\partial \langle \hat{S}_z \rangle} = Jz \langle \hat{S}_z \rangle - Jz b_S(y), \quad (177)$$

where $b_S(y)$ is defined by Eq. (155). Rearranging terms one arrives at the transcendental Curie-Weiss equation

$$\langle \hat{S}_z \rangle = b_S \left(\frac{g\mu_B B + Jz \langle \hat{S}_z \rangle}{k_B T} \right) \quad (178)$$

that defines $\langle \hat{S}_z \rangle$. In fact, this equation could be obtained in a shorter way by using the modified argument, Eq. (176), in Eq. (154).

For $B = 0$, Eq. (178) 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. (158), one obtains that the only solution $\langle \hat{S}_z \rangle = 0$ is realized for $T \geq T_C$, where

$$T_C = \frac{S(S+1)}{3} \frac{Jz}{k_B} \quad (179)$$

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,

$$b_{1/2}(y) = \frac{1}{2} \tanh \frac{y}{2} \cong \frac{1}{4} y - \frac{1}{48} y^3. \quad (180)$$

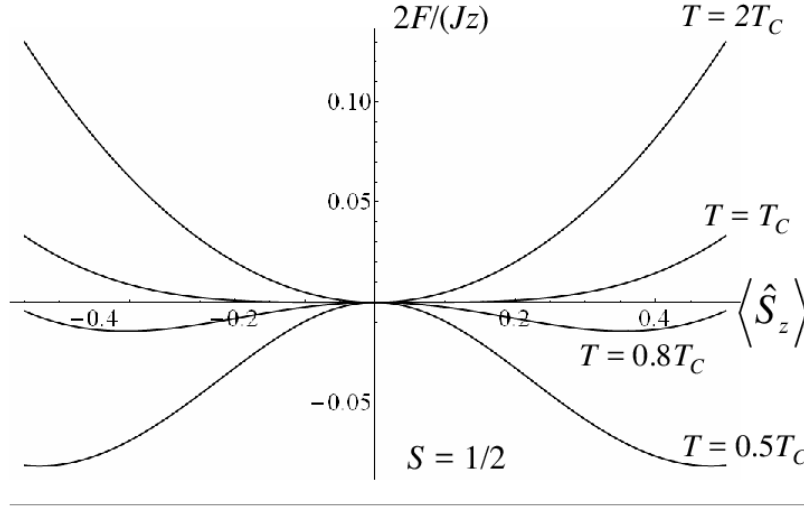


FIG. 8: Free energy of a ferromagnet vs $\langle \hat{S}_z \rangle$ within the MFA. (Arbitrary vertical shift.)

Using $T_C = (1/4)Jz/k_B$ and thus $Jz = 4k_BT_C$ for $S = 1/2$, one can rewrite Eq. (178) with $B = 0$ in the form

$$\langle \hat{S}_z \rangle = \frac{T_C}{T} \langle \hat{S}_z \rangle - \frac{4}{3} \left(\frac{T_C}{T} \right)^3 \langle \hat{S}_z \rangle^3. \quad (181)$$

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

$$\frac{\langle \hat{S}_z \rangle}{S} = \pm \sqrt{3 \left(1 - \frac{T}{T_C} \right)}, \quad S = \frac{1}{2}, \quad (182)$$

where the factor T/T_C was replaced by 1 near T_C . 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 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. (161).

Let us now consider the magnetic susceptibility per spin χ defined by Eq. (164) above T_C . Linearizing Eq. (178) with the use of Eq. (158), one obtains

$$\langle \hat{S}_z \rangle = \frac{S(S+1)}{3} \frac{g\mu_B B + Jz \langle \hat{S}_z \rangle}{k_B T} = \frac{S(S+1)}{3} \frac{g\mu_B B}{k_B T} + \frac{T_C}{T} \langle \hat{S}_z \rangle. \quad (183)$$

Here from one obtains

$$\chi = \frac{\partial \langle \mu_z \rangle}{\partial B} = g\mu_B \frac{\partial \langle \hat{S}_z \rangle}{\partial B} = \frac{S(S+1)}{3} \frac{(g\mu_B)^2}{k_B (T - T_C)}. \quad (184)$$

In contrast to non-interacting spins, Eq. (168), 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 $\chi \propto (T - T_C)^{-\gamma}$. One can see that $\gamma = 1$ within the MFA.

More precise methods than the MFA yield smaller values of β and larger values of γ that depend 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. On the other hand, 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.

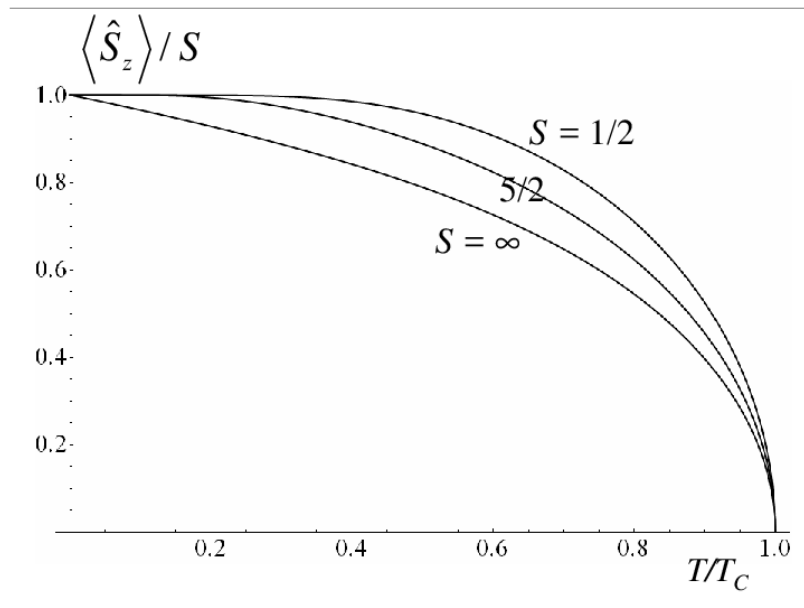


FIG. 9: Temperature dependences of normalized spin averages $\langle \hat{S}_z \rangle / S$ for $S = 1/2, 5/2, \infty$ obtained from the numerical solution of the Curie-Weiss equation.

XV. 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. (18), 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. (11), 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 an ensemble of \mathcal{N} systems. Quantum states of the systems are labeled by ξ , so that

$$\mathcal{N} = \sum_{\xi} \mathcal{N}_{\xi}. \quad (185)$$

The number of particles in the system 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:

$$N = \frac{1}{\mathcal{N}} \sum_{\xi} \mathcal{N}_{\xi} N_{\xi}, \quad U = \frac{1}{\mathcal{N}} \sum_{\xi} \mathcal{N}_{\xi} E_{\xi}. \quad (186)$$

Do not confuse \mathcal{N}_ξ with N_ξ . The number of ways W in which the state ξ can be realized (i.e., the number of microstates) 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

$$\mathcal{W} = \frac{\mathcal{N}!}{\prod_\xi \mathcal{N}_\xi!}. \quad (187)$$

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. (186). Within the method of Lagrange multipliers, one has to maximize the target function

$$\Phi(\mathcal{N}_1, \mathcal{N}_2, \dots) = \ln \mathcal{W} + \alpha \sum_\xi \mathcal{N}_\xi N_\xi - \beta \sum_\xi \mathcal{N}_\xi E_\xi \quad (188)$$

[c.f. Eq. (20) and below]. Using the Stirling formula, Eq. (11), one obtains

$$\Phi \cong \ln \mathcal{N}! - \sum_\xi \mathcal{N}_\xi \ln \mathcal{N}_\xi + \sum_\xi \mathcal{N}_\xi + \alpha \sum_\xi \mathcal{N}_\xi N_\xi - \beta \sum_\xi \mathcal{N}_\xi E_\xi. \quad (189)$$

Note that we do not require N_i to be large. In particular, for fermions one has $N_i = 0, 1$. Minimizing, one obtains the equations

$$\frac{\partial \Phi}{\partial \mathcal{N}_\xi} = -\ln \mathcal{N}_\xi + \alpha N_\xi - \beta E_\xi = 0 \quad (190)$$

that yield

$$\mathcal{N}_\xi = e^{\alpha N_\xi - \beta E_\xi}, \quad (191)$$

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

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

$$\mathcal{N} = \sum_\xi \mathcal{N}_\xi = \sum_\xi e^{\alpha N_\xi - \beta E_\xi} = \mathcal{Z}, \quad (192)$$

where \mathcal{Z} is the partition function of the grand canonical ensemble. Thus the ensemble average of the internal energy, Eq. (186), becomes

$$U = \frac{1}{\mathcal{Z}} \sum_\xi e^{\alpha N_\xi - \beta E_\xi} E_\xi = -\frac{\partial \ln \mathcal{Z}}{\partial \beta}. \quad (193)$$

In contrast to Eq. (30), this formula does not contain N explicitly since the average number of particles in a system is encapsulated in \mathcal{Z} . As before, the parameter β can be associated with temperature, $\beta = 1/(k_B T)$. Thus Eq. (193) can be rewritten as

$$U = -\frac{\partial \ln \mathcal{Z}}{\partial T} \frac{\partial T}{\partial \beta} = k_B T^2 \frac{\partial \ln \mathcal{Z}}{\partial T}. \quad (194)$$

Now the entropy S can be found thermodynamically as

$$S = \int_0^T dT' \frac{C_V}{T'} = \int_0^T dT' \frac{1}{T'} \frac{\partial U}{\partial T'}. \quad (195)$$

Integrating by parts and using Eq. (194), one obtains

$$S = \frac{U}{T} + \int_0^T dT' \frac{1}{T'^2} U = \frac{U}{T} + \int_0^T dT' k_B \frac{\partial \ln \mathcal{Z}}{\partial T'} = \frac{U}{T} + k_B \ln \mathcal{Z}. \quad (196)$$

This yields the free energy

$$F = U - TS = -k_B T \ln \mathcal{Z}. \quad (197)$$

XVI. STATISTICAL DISTRIBUTIONS OF INDISTINGUISHABLE PARTICLES

The Gibbs distribution looks similar to the Boltzmann distribution, Eq. (25). 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

$$N_\xi = \sum_i N_i, \quad E_\xi = \sum_i \varepsilon_i N_i. \quad (198)$$

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

$$\bar{N}_i = \frac{1}{\mathcal{Z}} \sum_\xi N_i \mathcal{N}_\xi = \frac{1}{\mathcal{Z}} \sum_\xi N_i e^{\alpha N_\xi - \beta E_\xi}, \quad (199)$$

where \mathcal{Z} is defined by Eq. (192). As both N_ξ and E_ξ are additive in N_i , see Eqs. (198), the summand of Eq. (192) is multiplicative:

$$\mathcal{Z} = \sum_{N_1} e^{(\alpha - \beta \varepsilon_1) N_1} \times \sum_{N_2} e^{(\alpha - \beta \varepsilon_2) N_2} \times \dots = \prod_j \mathcal{Z}_j. \quad (200)$$

As similar factorization occurs in Eq. (199), all factors except the factor containing N_i cancel each other leading to

$$\bar{N}_i = \frac{1}{\mathcal{Z}_i} \sum_{N_i} N_i e^{(\alpha - \beta \varepsilon_i) N_i} = \frac{\partial \ln \mathcal{Z}_i}{\partial \alpha}. \quad (201)$$

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

$$\mathcal{Z}_i = 1 + e^{\alpha - \beta \varepsilon_i}. \quad (202)$$

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

$$\mathcal{Z}_i = \sum_{N_i=0}^{\infty} e^{(\alpha - \beta \varepsilon_i) N_i} = \frac{1}{1 - e^{\alpha - \beta \varepsilon_i}}. \quad (203)$$

Now \bar{N}_i can be calculated from Eq. (201). Discarding the bar over N_i , one obtains

$$N_i = \frac{1}{e^{\beta \varepsilon_i - \alpha} \pm 1}, \quad (204)$$

where (+) corresponds to fermions and (-) corresponds to bosons. In the first case the distribution is called Fermi-Dirac distribution and in the second case the Bose-Einstein distribution. Eq. (204) should be compared with the Boltzmann distribution, Eq. (25). Whereas $\beta = 1/(k_B T)$, the parameter α is defined by the normalization condition

$$N = \sum_i N_i = \sum_i \frac{1}{e^{\beta \varepsilon_i - \alpha} \pm 1}. \quad (205)$$

It can be shown that the parameter α is related to the chemical potential μ as $\alpha = \beta \mu = \mu/(k_B T)$. Thus Eq. (204) can be written as

$$N_i = f(\varepsilon_i), \quad f(\varepsilon) = \frac{1}{e^{\beta(\varepsilon - \mu)} \pm 1}. \quad (206)$$

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

$$N = e^{\beta \mu} \int_0^\infty d\varepsilon \rho(\varepsilon) e^{-\beta \varepsilon} = e^{\beta \mu} Z. \quad (207)$$

Using Eqs. (59) and (222) yields

$$e^{-\beta \mu} = \frac{Z}{N} = \frac{1}{n} \left(\frac{m k_B T}{2\pi \hbar^2} \right)^{3/2} \gg 1 \quad (208)$$

and our calculations are self-consistent. At low temperatures ± 1 in the denominator of Eq. (206) cannot be neglected, and the system is called *degenerate*.

XVII. 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. (205) can be replaced by integration. However, it turns out that 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. (206) one obtains

$$N_0 = \frac{1}{e^{-\beta\mu} - 1}. \quad (209)$$

Resolving this for μ , one obtains

$$\mu = -k_B T \ln \left(1 + \frac{1}{N_0} \right) \cong -\frac{k_B T}{N_0}. \quad (210)$$

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

$$N_{\text{ex}} = \int_0^\infty d\varepsilon \frac{\rho(\varepsilon)}{e^{\beta\varepsilon} - 1}. \quad (211)$$

The total number of particles is then

$$N = N_0 + N_{\text{ex}}. \quad (212)$$

In three dimensions, using the density of states $\rho(\varepsilon)$ given by Eq. (55), one obtains

$$N_{\text{ex}} = \frac{V}{(2\pi)^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty d\varepsilon \frac{\sqrt{\varepsilon}}{e^{\beta\varepsilon} - 1} = \frac{V}{(2\pi)^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \frac{1}{\beta^{3/2}} \int_0^\infty dx \frac{\sqrt{x}}{e^x - 1}. \quad (213)$$

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

$$\int_0^\infty dx \frac{x^{s-1}}{e^x - 1} = \Gamma(s)\zeta(s), \quad (214)$$

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

$$\Gamma(n+1) = n\Gamma(n) = n! \quad (215)$$

$$\Gamma(1/2) = \sqrt{\pi}, \quad \Gamma(3/2) = \sqrt{\pi}/2 \quad (216)$$

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

$$\zeta(s) = \sum_{k=1}^{\infty} k^{-s} \quad (217)$$

$$\zeta(1) = \infty, \quad \zeta(3/2) = 2.612, \quad \zeta(5/2) = 1.341 \quad (218)$$

$$\frac{\zeta(5/2)}{\zeta(3/2)} = 0.5134. \quad (219)$$

Thus Eq. (213) yields

$$N_{\text{ex}} = \frac{V}{(2\pi)^2} \left(\frac{2mk_B T}{\hbar^2} \right)^{3/2} \Gamma(3/2)\zeta(3/2) \quad (220)$$

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

$$N = \frac{V}{(2\pi)^2} \left(\frac{2mk_B T_B}{\hbar^2} \right)^{3/2} \Gamma(3/2)\zeta(3/2), \quad (221)$$

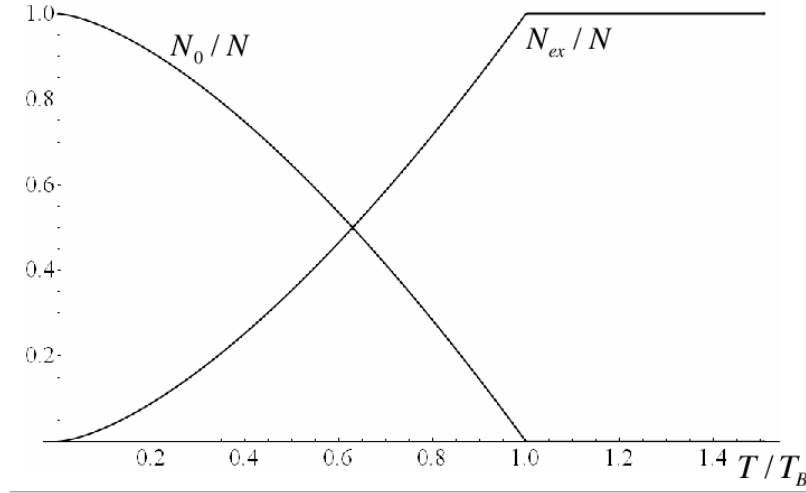


FIG. 10: Condensate fraction $N_0(T)/N$ and the fraction of excited particles $N_{ex}(T)/N$ for the ideal Bose-Einstein gas.

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

$$k_B T_B = \frac{\hbar^2}{2m} \left(\frac{(2\pi)^2 n}{\Gamma(3/2)\zeta(3/2)} \right)^{2/3}, \quad n = \frac{N}{V}, \quad (222)$$

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. (220) can be rewritten as

$$\frac{N_{ex}}{N} = \left(\frac{T}{T_B} \right)^{3/2}, \quad T \leq T_B \quad (223)$$

The temperature dependence of the Bose-condensate is given by

$$\frac{N_0}{N} = 1 - \frac{N_{ex}}{N} = 1 - \left(\frac{T}{T_B} \right)^{3/2}, \quad T \leq T_B. \quad (224)$$

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.

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

$$N = \int_0^\infty d\varepsilon \frac{\rho(\varepsilon)}{e^{\beta(\varepsilon-\mu)} - 1}. \quad (225)$$

This is a nonlinear equation that has no general analytical solution. At high temperatures the Bose-Einstein (and also Fermi-Dirac) distribution simplifies to the Boltzmann distribution and μ can be easily found. Equation (208) with the help of Eq. (222) can be rewritten in the form

$$e^{-\beta\mu} = \frac{1}{\zeta(3/2)} \left(\frac{T}{T_B} \right)^{3/2} \gg 1, \quad (226)$$

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

$$U = \int_0^\infty d\varepsilon \frac{\varepsilon \rho(\varepsilon)}{e^{\beta(\varepsilon-\mu)} - 1} \quad (227)$$

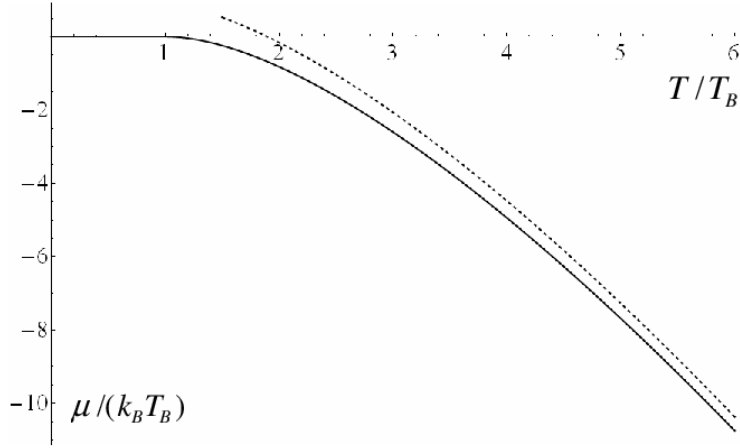


FIG. 11: Chemical potential $\mu(T)$ of the ideal Bose-Einstein gas. Dashed line: High-temperature asymptote corresponding to the Boltzmann statistics.

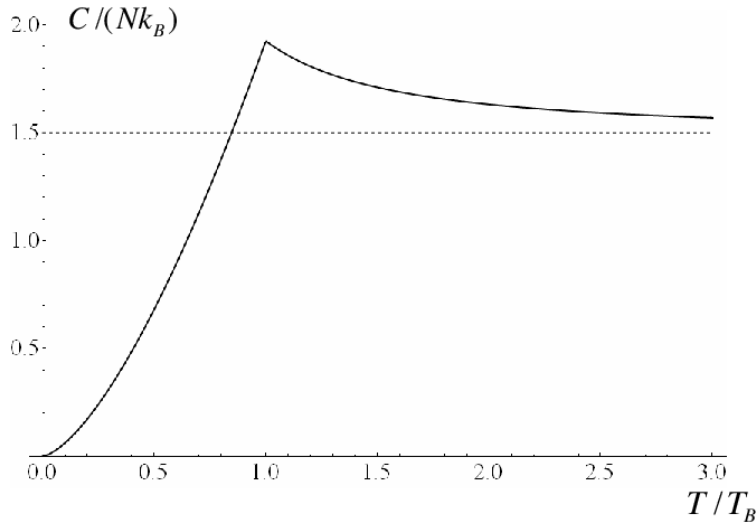


FIG. 12: Heat capacity $C(T)$ of the ideal Bose-Einstein gas.

in the whole temperature range. At high temperatures, $T \gg T_B$, the Boltzmann distribution applies, so that U is given by Eq. (64) and the heat capacity is a constant, $C = (3/2) Nk_B$. For $T < T_B$ one has $\mu = 0$, thus

$$U = \int_0^\infty d\varepsilon \frac{\varepsilon \rho(\varepsilon)}{e^{\beta\varepsilon} - 1} \quad (228)$$

that in three dimensions becomes

$$U = \frac{V}{(2\pi)^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty d\varepsilon \frac{\varepsilon^{3/2}}{e^{\beta\varepsilon} - 1} = \frac{V}{(2\pi)^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \Gamma(5/2) \zeta(5/2) (k_B T)^{5/2}. \quad (229)$$

With the help of Eq. (221) this can be expressed in the form

$$U = Nk_B T \left(\frac{T}{T_B} \right)^{3/2} \frac{\Gamma(5/2)\zeta(5/2)}{\Gamma(3/2)\zeta(3/2)} = Nk_B T \left(\frac{T}{T_B} \right)^{3/2} \frac{3}{2} \frac{\zeta(5/2)}{\zeta(3/2)}, \quad T \leq T_B. \quad (230)$$

The corresponding heat capacity is

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = Nk_B \left(\frac{T}{T_B} \right)^{3/2} \frac{15}{4} \frac{\zeta(5/2)}{\zeta(3/2)}, \quad T \leq T_B. \quad (231)$$

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

$$S = \int_0^T dT' \frac{C_V(T')}{T'} = \frac{2}{3} C_V = Nk_B \left(\frac{T}{T_B} \right)^{3/2} \frac{5}{2} \frac{\zeta(5/2)}{\zeta(3/2)}, \quad T \leq T_B. \quad (232)$$

Differentiating the free energy

$$F = U - TS = -Nk_B T \left(\frac{T}{T_B} \right)^{3/2} \frac{\zeta(5/2)}{\zeta(3/2)}, \quad T \leq T_B \quad (233)$$

one obtains the pressure

$$P = - \left(\frac{\partial F}{\partial V} \right)_T = - \left(\frac{\partial F}{\partial T_B} \right)_T \left(\frac{\partial T_B}{\partial V} \right)_T = - \left(-\frac{3}{2} \frac{F}{T_B} \right) \left(-\frac{2}{3} \frac{T_B}{V} \right) = -\frac{F}{V}, \quad (234)$$

i.e. the equation of state

$$PV = Nk_B T \left(\frac{T}{T_B} \right)^{3/2} \frac{\zeta(5/2)}{\zeta(3/2)}, \quad T \leq T_B, \quad (235)$$

compared to $PV = Nk_B T$ at high temperatures. One can see that the pressure of the ideal bose gas with the condensate contains an additional factor $(T/T_B)^{3/2} < 1$. This is because the particles in the condensate are not thermally agitated and thus they do not contribute into the pressure.

XVIII. FERMI-DIRAC GAS

Properties of the Fermi gas [plus sign in Eq. (206)] 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, and for a macroscopic system the chemical potential can be found from the equation

$$N = \int_0^\infty d\varepsilon \rho(\varepsilon) f(\varepsilon) = \int_0^\infty d\varepsilon \frac{\rho(\varepsilon)}{e^{\beta(\varepsilon-\mu)} + 1} \quad (236)$$

at all temperatures. This is a nonlinear equation for μ that in general can be solved only numerically.

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. (236) becomes

$$f(\varepsilon) = \begin{cases} 1, & \varepsilon < \mu \\ 0, & \varepsilon > \mu. \end{cases} \quad (237)$$

Then the zero-temperature value μ_0 of μ is defined by the equation

$$N = \int_0^{\mu_0} d\varepsilon \rho(\varepsilon). \quad (238)$$

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. (55) with an additional factor 2 for the degeneracy one obtains

$$N = \frac{2V}{(2\pi)^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^{\mu_0} d\varepsilon \sqrt{\varepsilon} = \frac{2V}{(2\pi)^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \frac{2}{3} \mu_0^{3/2}. \quad (239)$$

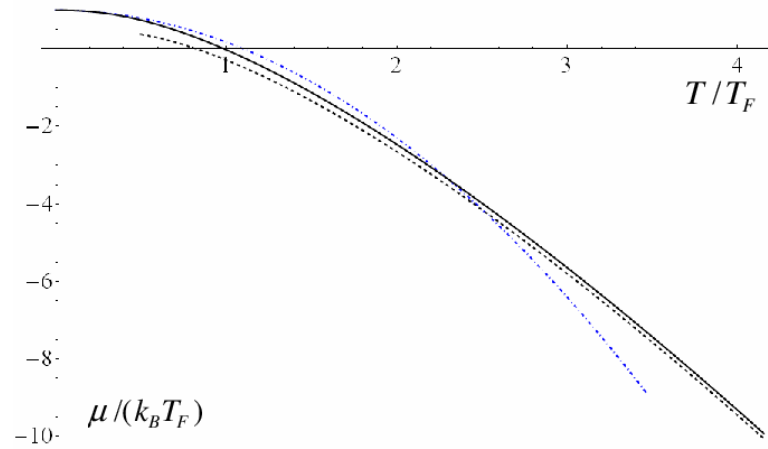


FIG. 13: Chemical potential $\mu(T)$ of the ideal Fermi-Dirac gas. Dashed line: High-temperature asymptote corresponding to the Boltzmann statistics. Dashed-dotted line: Low-temperature asymptote.

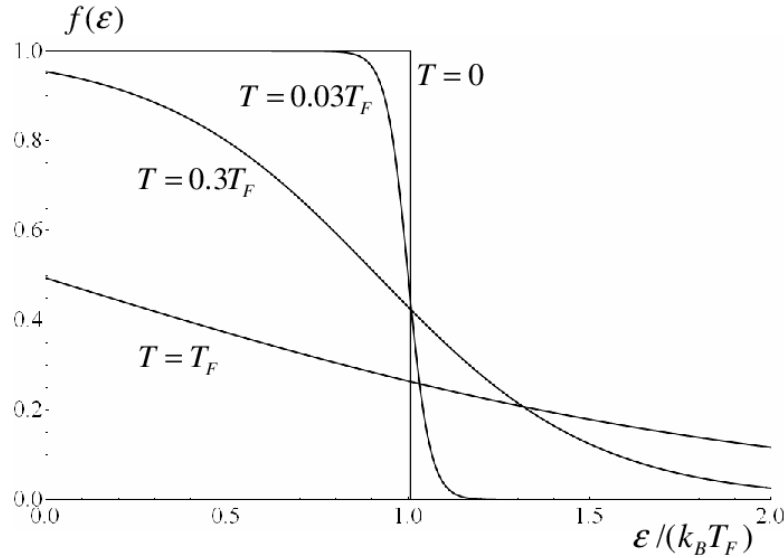


FIG. 14: Fermi-Dirac distribution function at different temperatures.

From here one obtains

$$\mu_0 = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3} = \varepsilon_F, \quad (240)$$

where we have introduced the Fermi energy ε_F that coincides with μ_0 . It is convenient also to introduce the Fermi temperature as

$$k_B T_F = \varepsilon_F. \quad (241)$$

One can see that T_F has the same structure as T_B defined by Eq. (222). 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

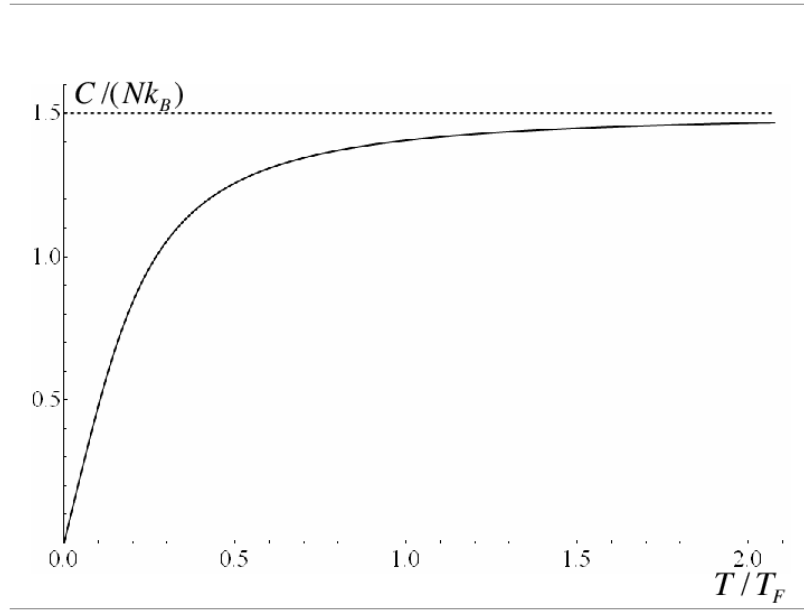


FIG. 15: Heat capacity $C(T)$ of the ideal Fermi-Dirac gas.

three dimensions, Eq. (55), in terms of ε_F :

$$\rho(\varepsilon) = \frac{3}{2} N \frac{\sqrt{\varepsilon}}{\varepsilon_F^{3/2}}. \quad (242)$$

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

$$U = \int_0^{\mu_0} d\varepsilon \rho(\varepsilon) \varepsilon = \frac{3}{2} \frac{N}{\varepsilon_F^{3/2}} \int_0^{\varepsilon_F} d\varepsilon \varepsilon^{3/2} = \frac{3}{2} \frac{N}{\varepsilon_F^{3/2}} \frac{2}{5} \varepsilon_F^{5/2} = \frac{3}{5} N \varepsilon_F. \quad (243)$$

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

$$P = - \left(\frac{\partial F}{\partial V} \right)_{T=0} \cong - \left(\frac{\partial U}{\partial V} \right)_{T=0} = - \frac{3}{5} N \frac{\partial \varepsilon_F}{\partial V} = - \frac{3}{5} N \left(- \frac{2}{3} \frac{\varepsilon_F}{V} \right) = \frac{2}{5} n \varepsilon_F = \frac{\hbar^2}{2m} \frac{2}{5} (3\pi^2)^{2/3} n^{5/3}. \quad (244)$$

To calculate the heat capacity at low temperatures, one has to find temperature-dependent corrections to Eq. (243). We will need the integral of a general type

$$M_\eta = \int_0^\infty d\varepsilon \varepsilon^\eta f(\varepsilon) = \int_0^\infty d\varepsilon \frac{\varepsilon^\eta}{e^{(\varepsilon - \mu)/(k_B T)} + 1} \quad (245)$$

that enters Eq. (236) for N and the similar equation for U . With the use of Eq. (242) one can write

$$N = \frac{3}{2} \frac{N}{\varepsilon_F^{3/2}} M_{1/2}, \quad (246)$$

$$U = \frac{3}{2} \frac{N}{\varepsilon_F^{3/2}} M_{3/2} \quad (247)$$

If can be shown that for $k_B T \ll \mu$ the expansion of M_η up to quadratic terms has the form

$$M_\eta = \frac{\mu^{\eta+1}}{\eta+1} \left[1 + \frac{\pi^2 \eta (\eta+1)}{6} \left(\frac{k_B T}{\mu} \right)^2 \right]. \quad (248)$$

Now Eq. (246) takes the form

$$\varepsilon_F^{3/2} = \mu^{3/2} \left[1 + \frac{\pi^2}{8} \left(\frac{k_B T}{\mu} \right)^2 \right] \quad (249)$$

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

$$\mu = \varepsilon_F \left[1 + \frac{\pi^2}{8} \left(\frac{k_B T}{\mu} \right)^2 \right]^{-2/3} \cong \varepsilon_F \left[1 - \frac{\pi^2}{12} \left(\frac{k_B T}{\mu} \right)^2 \right] \cong \varepsilon_F \left[1 - \frac{\pi^2}{12} \left(\frac{k_B T}{\varepsilon_F} \right)^2 \right] \quad (250)$$

or, with the help of Eq. (241),

$$\mu = \varepsilon_F \left[1 - \frac{\pi^2}{12} \left(\frac{T}{T_F} \right)^2 \right]. \quad (251)$$

It is not surprising that the chemical potential decreases with temperature because at high temperatures it takes large negative values, see Eq. (208). Equation (247) becomes

$$U = \frac{3}{2} \frac{N}{\varepsilon_F^{3/2}} \frac{\mu^{5/2}}{(5/2)} \left[1 + \frac{5\pi^2}{8} \left(\frac{k_B T}{\mu} \right)^2 \right] \cong \frac{3}{5} N \frac{\mu^{5/2}}{\varepsilon_F^{3/2}} \left[1 + \frac{5\pi^2}{8} \left(\frac{k_B T}{\varepsilon_F} \right)^2 \right]. \quad (252)$$

Using Eq. (251), one obtains

$$\begin{aligned} U &= \frac{3}{5} N \varepsilon_F \left[1 - \frac{\pi^2}{12} \left(\frac{T}{T_F} \right)^2 \right]^{5/2} \left[1 + \frac{5\pi^2}{8} \left(\frac{T}{T_F} \right)^2 \right] \\ &\cong \frac{3}{5} N \varepsilon_F \left[1 - \frac{5\pi^2}{24} \left(\frac{T}{T_F} \right)^2 \right] \left[1 + \frac{5\pi^2}{8} \left(\frac{T}{T_F} \right)^2 \right] \end{aligned} \quad (253)$$

that yields

$$U = \frac{3}{5} N \varepsilon_F \left[1 + \frac{5\pi^2}{12} \left(\frac{T}{T_F} \right)^2 \right]. \quad (254)$$

At $T = 0$ this formula reduces to Eq. (243). Now one obtains

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = N k_B \frac{\pi^2}{2} \frac{T}{T_F} \quad (255)$$

that is small at $T \ll T_F$.

Let us now derive Eq. (248). Integrating Eq. (245) by parts, one obtains

$$M_\eta = \frac{\varepsilon^{\eta+1}}{\eta+1} f(\varepsilon) \Big|_0^\infty - \int_0^\infty d\varepsilon \frac{\varepsilon^{\eta+1}}{\eta+1} \frac{\partial f(\varepsilon)}{\partial \varepsilon}. \quad (256)$$

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

$$\frac{\partial f(\varepsilon)}{\partial \varepsilon} = \frac{\partial}{\partial \varepsilon} \frac{1}{e^{\beta(\varepsilon-\mu)} + 1} = - \frac{\beta e^{\beta(\varepsilon-\mu)}}{[e^{\beta(\varepsilon-\mu)} + 1]^2} = - \frac{\beta}{4 \cosh^2 [\beta(\varepsilon - \mu)/2]} \quad (257)$$

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

$$\begin{aligned} \varepsilon^{\eta+1} &= \mu^{\eta+1} + \frac{\partial \varepsilon^{\eta+1}}{\partial \varepsilon} \Big|_{\varepsilon=\mu} (\varepsilon - \mu) + \frac{1}{2} \frac{\partial^2 \varepsilon^{\eta+1}}{\partial \varepsilon^2} \Big|_{\varepsilon=\mu} (\varepsilon - \mu)^2 \\ &= \mu^{\eta+1} + (\eta+1) \mu^\eta (\varepsilon - \mu) + \frac{1}{2} \eta(\eta+1) \mu^{\eta-1} (\varepsilon - \mu)^2. \end{aligned} \quad (258)$$

Introducing $x \equiv \beta (\varepsilon - \mu) / 2$ and formally extending integration in Eq. (256) from $-\infty$ to ∞ , one obtains

$$M_\eta = \frac{\mu^{\eta+1}}{\eta+1} \int_{-\infty}^{\infty} dx \left[\frac{1}{2} + \frac{\eta+1}{\beta\mu} x + \frac{\eta(\eta+1)}{\beta^2\mu^2} x^2 \right] \frac{1}{\cosh^2(x)}. \quad (259)$$

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

$$\int_{-\infty}^{\infty} dx \frac{1}{\cosh^2(x)} = 2, \quad \int_{-\infty}^{\infty} dx \frac{x^2}{\cosh^2(x)} = \frac{\pi^2}{6}, \quad (260)$$

one arrives at Eq. (248).