

Set 3. 13.02.2015. Problems 4.5, 4.19, 4.20, 4.24, 4.25

February 14, 2015

4. Basic principles of statistical mechanics

Problem 4.5 Model for rubber elasticity.

The rubber is assumed to consist of a polymer chain of N rod-like monomers, each of length a and is subjected to a force F in the $+X$ direction. Each monomer can point independently along any of X, Y, Z axes, in either the $+$ or $-$ direction. The energy is only X -dependent; $\epsilon = aF$ for the monomer pointing along $-X$, $\epsilon = -aF$ for the monomer pointing along $+X$, $\epsilon = 0$ for the monomer along $\pm Y$ and $\pm Z$.

- Calculate the partition function for the N -monomer chain.
- Show that the linear thermal expansivity is negative, as for the real rubber. Interpret the result physically.

Solution to Problem 4.5

- Each monomer has the partition function

$$Z_1 = 2 + 2 + e^{-\beta Fa} + e^{\beta Fa} = 4 + 2 \cosh(\beta Fa)$$

The first terms are from $e^{0y} + e^{-0y}$ and $e^{0z} + e^{-0z}$: the total partition function being

$$Z = Z_1^N = 2^N [2 + \cosh(\beta Fa)]^N.$$

- If $N\xi_+$ states point on the average to $+X$, $N\xi_-$ states point to $-X$, etc., then

$$\langle L_X \rangle = Na(\xi_+ - \xi_-), \quad \langle L_Y \rangle = Na(\eta_+ - \eta_-), \quad \langle L_Z \rangle = Na(\zeta_+ - \zeta_-),$$

We immediately obtain that $\langle L_Y \rangle = \langle L_Z \rangle = 0$. Furthermore,

$$\xi_{\pm} = e^{\pm\beta aF} / Z_1, \quad \rightarrow \quad \langle L_X \rangle = Na \frac{\sinh \beta aF}{2 + \cosh \beta aF}.$$

We immediately get $\partial \langle L_X \rangle / \partial \beta > 0$. Consequently, $\partial \langle L_X \rangle / \partial T < 0$. Rubber contracts upon heating.

TD Theory of the rods

Consider the rod of length l stretching in longitudinal direction with force f . The work done at stretching of the rod on the length dl is

$$dW = -f dl$$

Let us compare the rod with the ideal gas:

$$dW = PdV$$

All formulas used for ideal gas is valid for rod with substitution of $P \rightarrow -f$ and $V \rightarrow l$. So the generalized force in our problem is $-f$ and generalized coordinate is l . Then

$$dU(S, l) = T dS = f dl$$

Maxwell rule will look like

$$\frac{\partial(T, S)}{\partial(f, l)} = -1$$

In the TD of rod the EoS will be $f = f(l, T)$ instead of $P = P(V, T)$ for gases and will have a linear dependence on T in a range of the small elastic deformations:

$$l(T, 0) = l(T_0, 0) [1 - \alpha(T - T_0)]$$

where $T_0 = 273.25K^o$, α is the coefficient of linear expansion, defined only experimentally.

Hook's law tells

$$\frac{l(T, 0) - l(T_0, 0)}{l(T, 0)} = \frac{1}{E\sigma} f$$

where E is Young module, does not depend on T , σ is the rod area in the transverse plane. Two last equations gives

$$f = E\sigma \left\{ \frac{l}{l_0(1 + \alpha(T - T_0))} - 1 \right\} \text{ where } l_0 = l(T_0, 0)$$

Let us consider E and σ constants, $\alpha (\approx 10^{-5} \text{ grad}^{-1})$ small, then we will obtain the EOS for rod:

$$f = E\sigma \left\{ \frac{l}{l_0} (1 - \alpha(T - T_0)) - 1 \right\}$$

Let us find entropy of rod:

$$dS = \left(\frac{\partial S}{\partial T} \right)_l dT + \left(\frac{\partial S}{\partial l} \right)_T dl = \frac{C_l}{T} dT - \left(\frac{\partial f}{\partial T} \right)_l dl$$

From EOS which gives

$$\left(\frac{\partial f}{\partial T} \right)_l = -\frac{\alpha E \sigma l}{l_0}$$

$$dS = \frac{C_l}{T}dT + \frac{\alpha E \sigma l}{l_0}dl$$

To obtain S we need to know $C_l(T, l)$. There are similarities between ideal gases, real gases and perfect rods: in all three cases the generalized force (P for gases and f for rods) is linear function of temperature, it means C_l does not depend on l as C_V does not depend on V for gases:

$$\left(\frac{\partial C_l}{\partial l}\right)_T = \left(\frac{\partial^2 f}{\partial T^2}\right)_l = 0$$

From here for the case $C_l = \text{const}$

$$S = \int \frac{C_l(T)}{T}dT + \frac{\alpha E \sigma l^2}{2l_0} + \text{const}$$

$$S = C_l \log T + \frac{\alpha E \sigma l^2}{2l_0} + \text{const}$$

The internal energy of ideal rod is

$$dU = TdS + fdl = C_l dT + \left(\alpha E \sigma \frac{l}{l_0} + f\right) dl \approx C_l dT + E \sigma \frac{l - l_0}{l_0} dl$$

$$U = C_l T + \frac{E \sigma (l - l_0)^2}{2l_0} + \text{const}$$

In contrast to ideal gases which energy does not depend on volume, internal energy of ideal rods is a square of its deformations.

Subproblem on Rubber Elasticity

As a simple model of an elastic string like, e.g., a rubber band, we consider a linear chain of N building blocks. Each building block can be in two different states a or b . In these states the building blocks have length l_a and l_b and energies ϵ_a and ϵ_b , respectively. The total length of the chain is $L = N_a l_a + N_b l_b$ and the total energy of the string by itself is $E_0 = N_a \epsilon_a + N_b \epsilon_b$ where $N_a = N - N_b$ is the number of building blocks in state a . The string is stretched by an external force f which turns the total energy of a state into $E = E_0 - Lf$.

a) Calculate the partition function of this string as a function of temperature T , the number of building blocks N , and the external force f . Introduce variables $n_i \in \{a, b\}$ that describe in which state building block i is and write the partition function as a sum over these variables n_i .

Solution a)

$$\begin{aligned} Z(T) &= \sum_{n_i} e^{-\beta(E_0 - Lf)} = \sum_{n_i \in \{a, b\}} \dots \sum_{n_N \in \{a, b\}} e^{-\beta(\sum_{i=1}^N \epsilon_{n_i})} e^{\beta(f \sum_{i=1}^N l_{n_i})} \\ &= \left(\sum_{n \in \{a, b\}} e^{-\beta(\epsilon_n + f l_n)} \right)^N = \left(e^{-\beta \epsilon_a + \beta f l_a} + e^{-\beta \epsilon_b + \beta f l_b} \right)^N \end{aligned}$$

b) Calculate the average internal energy U of this string as a function of temperature T , the number of building blocks N , and the external force f .

Solution b)

$$U = - \left(\frac{\partial \ln Z(T)}{\partial \beta} \right) = N \frac{(\epsilon_a - fl_a)e^{-\beta\epsilon_a + \beta fl_a} + (\epsilon_b - fl_b)e^{-\beta\epsilon_b + \beta fl_b}}{e^{-\beta\epsilon_a + \beta fl_a} + e^{-\beta\epsilon_b + \beta fl_b}} \quad (1)$$

c) Calculate the expected length $\langle L \rangle$ of this string as a function of temperature T , the number of building blocks N , and the external force f . (Hint: The expected length is a similar quantity as the expected energy. Find an expression for the expected length through a derivative similar to the derivative which we use to calculate the average internal energy.) What is the expected length at zero force in the case $\epsilon_a = \epsilon_b$? Why?

Solution c)

$$\begin{aligned} \langle L \rangle &= \left\langle \sum_{i=1}^N l_{n_i} \right\rangle = \frac{1}{\beta} \left(\frac{\partial \ln Z(T)}{\partial f} \right) \Big|_{\beta, N} = \\ &= N \frac{l_a e^{-\beta\epsilon_a + \beta fl_a} + l_b e^{-\beta\epsilon_b + \beta fl_b}}{e^{-\beta\epsilon_a + \beta fl_a} + e^{-\beta\epsilon_b + \beta fl_b}} \end{aligned}$$

At $\epsilon_a = \epsilon_b$ and $f = 0$:

$$\langle L \rangle = N \frac{l_a e^{-\beta\epsilon_a} + l_b e^{-\beta\epsilon_a}}{e^{-\beta\epsilon_a} + e^{-\beta\epsilon_a}} = N \frac{l_a + l_b}{2}$$

If (roughly) half of the building blocks are in state a and half in state b the entropy is maximal and it is the most preferable state.

Problem 4.19 Suppose the expression $S = -k_B \sum_r P_r \ln P_r$ is accepted as a definition of the entropy. Imagine that a system A_1 has probability $P_r^{(1)}$ of being in a state r and a system A_2 has probability $P_s^{(2)}$ of being in a state s . Then

$$S_1 = -k_B \sum_r P_r^{(1)} \ln P_r^{(1)}, \quad S_2 = -k_B \sum_s P_s^{(2)} \ln P_s^{(2)}.$$

Each state of a composite system A consisting of A_1 and A_2 can then be labeled by the pair of numbers, r, s . Let the probability of A being found in the state r, s be denoted by P_{rs} , and the corresponding entropy is $-k_B \sum_{r,s} P_{rs} \ln P_{rs}$.

(a) If A_1 and A_2 are weakly interacting so they are statistically independent, then $P_{rs} = P_r^{(1)} P_s^{(2)}$. Show that under such circumstances the entropy is simply additive, i. e. $S = S_1 + S_2$.

(b) Suppose that A_1 and A_2 are *not* weakly so that $P_{rs} \neq P_r^{(1)} P_s^{(2)}$. One has, of course, the general, relations $\sum_s P_{rs} = P_r^{(1)}$, $\sum_r P_{rs} = P_s^{(2)}$, and $\sum_{r,s} P_{rs} = 1$. Show that

$$S - (S_1 + S_2) = k_B \sum_{rs} P_{rs} \ln \frac{P_r^{(1)} P_s^{(2)}}{P_{rs}}.$$

Moreover, by using the inequality

$$-\ln x \geq 1 - x,$$

show that $S \leq S_1 + S_2$, where the equality holds only if $P_{rs} = P_r^{(1)}P_s^{(2)}$ for all r and s . This means that the existence of correlation between the systems leads to a situation less random than where the systems are completely independent of each other.

Solution to Problem 4.19 Let us start from the part (b), and the 1st part will be a limiting case. We have

$$\begin{aligned} -(S_1 + S_2)k_B &= \sum_r P_r^{(1)} \ln P_r^{(1)} + \sum_s P_s^{(2)} \ln P_s^{(2)} \\ &= \sum_{r,s} P_{rs} \ln(P_r^{(1)}) + \sum_{s,r} P_{rs} \ln(P_s^{(2)}) \\ &= \sum_{r,s} P_{rs} \ln(P_r^{(1)} P_s^{(2)}). \end{aligned}$$

If $P_{rs} = P_r^{(1)}P_s^{(2)}$ then $S = S_1 + S_2$. Now

$$\begin{aligned} S - (S_1 + S_2) &= k_B \sum_{r,s} P_{rs} \ln \frac{P_r^{(1)} P_s^{(2)}}{P_{rs}} \\ &\leq k_B \sum_{r,s} P_{rs} \left[\frac{P_r^{(1)} P_s^{(2)}}{P_{rs}} - 1 \right] \\ &= k_B \sum_{r,s} [P_r^{(1)} P_s^{(2)} - P_{rs}] = 0. \end{aligned}$$

Problem 4.20 0.1. Consider a system distributed over its accessible states r in accordance with a probability distribution P_r , and let its entropy be defined by the relations

$$S = -k_B \sum_r P_r \ln P_r, \quad \sum_r P_r = 1.$$

Compare this distribution with the canonical distribution

$$P_r^{(0)} = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}$$

corresponding to the same mean energy $\langle E \rangle$, i. e.

$$\sum_r P_r E_r = \sum_r P_r^{(0)} E_r = \langle E \rangle.$$

The entropy of the canonical distribution is

$$S_0 = -k_B \sum_r P_r^{(0)} \ln P_r^{(0)}.$$

(a) Show that

$$S - S_0 = k_B \sum_r P_r \ln \frac{P_r^{(0)}}{P_r}.$$

(b) Using the inequality $\ln x \leq x - 1$ show that $S_0 \geq S$; the equality sign holds only if $P_r = P_r^{(0)}$ for all states r . This shows that, for a specific value of mean energy, the entropy S is a maximum for the canonical distribution.

Solution to Problem 4.20

Solution 0.2:

(a)

$$\begin{aligned} (S - S_0)/k_B &= - \sum_r \left[P_r \ln P_r - P_r^{(0)} \ln P_r^{(0)} \right] \\ &= - \sum_r \left[P_r \ln P_r - P_r^{(0)} (-\beta E_r - \ln \mathcal{N}) \right] \\ &= - \ln \mathcal{N} - \beta \langle E \rangle - \sum_r P_r \ln P_r \\ &= \sum_r P_r \ln \frac{P_r^{(0)}}{P_r}. \end{aligned}$$

(b) We have

$$\sum_r P_r \ln \frac{P_r^{(0)}}{P_r} \leq \sum_r P_r \left(\frac{P_r^{(0)}}{P_r} - 1 \right) = \sum_r \left[P_r^{(0)} - P_r \right] = 0.$$

Problem 4.24 Consider non-interacting particles subjected to a harmonic potential. Calculate the canonical partition function

- (a) for a single particle
- (b) for two distinguishable particles
- (c) for two spinless fermions
- (d) for two spin-zero bosons
- (e) for two spin-1/2 fermions.

Compare the internal energies and entropies in these various cases. Study the limit $T \rightarrow 0$, $T \rightarrow \infty$, and $\hbar = 0$ and interpret the results physically.

Solution to Problem 4.24 Quantum states for a particle in a harmonic potential are specified by the quantum number n and the energies are $\varepsilon_n = \hbar\omega(n + 1/2)$. Thus we have:

(a)

$$\begin{aligned}Z_1 &= e^{-\beta\hbar\omega/2} \sum_{n=0}^{\infty} e^{-\beta\hbar\omega n} = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}} = \frac{1}{2 \sinh(\beta\hbar\omega/2)} \\F_1 &= -\beta^{-1} \ln Z = \frac{1}{\beta} \ln \left[2 \sinh \left(\frac{\beta\hbar\omega}{2} \right) \right] \\E_1 &= -\frac{\partial \ln Z}{\partial \beta} = \frac{\hbar\omega}{2} \coth(\beta\hbar\omega/2) = \frac{\hbar\omega}{2} + \hbar\omega N(\omega), \quad N(\omega) = \frac{1}{e^{\beta\hbar\omega} - 1}, \\S_1/k_B &= -\frac{\partial F}{\partial k_B T} = \frac{\beta\hbar\omega}{2} \coth \left(\frac{\beta\hbar\omega}{2} \right) - \ln \left[2 \sinh \left(\frac{\beta\hbar\omega}{2} \right) \right]\end{aligned}$$

Limiting cases

- $T \rightarrow \infty$ or $\beta \rightarrow 0$

$$Z_1 \approx k_B T / \hbar\omega, \quad F_1 \approx -k_B T \ln(k_B T / \hbar\omega), \quad E_1 \approx k_B T, \quad S_1/k_B \approx 1 + \ln(k_B T / \hbar\omega).$$

- $T \rightarrow 0$ or $\beta \rightarrow \infty$

$$Z_1 \approx e^{-\beta\hbar\omega/2}, \quad F_1 = \hbar\omega/2, \quad E_1 = \hbar\omega/2, \quad S_1 = 0.$$

(b)

$$\begin{aligned}Z_2 &= Z_1^2 = e^{-\beta\hbar\omega} \left(\sum_{n=0}^{\infty} e^{-\beta\hbar\omega n} \right)^2 = \frac{e^{-\beta\hbar\omega}}{[1 - e^{-\beta\hbar\omega}]^2} = \frac{1}{4 \sinh^2(\beta\hbar\omega/2)} \\F_2 &= -2k_B T \ln[2 \sinh(\beta\hbar\omega/2)] \\E_2 &= 2\hbar\omega [1/2 + N(\omega)] \\S_2/k_B &= 2S_1/k_B.\end{aligned}$$

(c) Consider first two identical classical particles. In the product Z_1^2 there are two identical terms in which one of the particles occupy a state a while the second one occupies the state b . In the particles are non-distinguishable then we have to divide the product by $2! = 2$ to get

$$Z_2^{\text{cl}} = Z_1^2 / 2 = \frac{1}{2} \frac{\eta}{(1 - \eta)^2}, \quad \eta \equiv e^{-\beta\hbar\omega}.$$

Then the configuration in which both particles occupy *the same state* get the weight $1/2$. Fermions are not allowed to occupy this state, thus we have to extract this configuration. In this way we get

$$Z_2^{\text{FD}} = Z_2^{\text{cl}} - D/2, \quad D = e^{-\beta\hbar\omega} \sum_{n=0}^{\infty} e^{-2n\beta\hbar\omega} = \frac{\eta}{1 - \eta^2}.$$

Thus

$$Z_2^{\text{FD}} = \frac{\eta^2}{(1 - \eta)(1 - \eta^2)}.$$

(d) In a similar way,

$$Z_2^{\text{BE}} = Z_2^{\text{cl}} + D/2 = \frac{\eta}{(1-\eta)(1-\eta^2)}.$$

There is no difference between classical and quantum statistics at high temperatures when $\eta \ll 1$.

(d) In the case of spin-1/2 fermions each state is doubly degenerate. Thus the proper partition function is

$$(2Z_1)^2/2! - 2D/2 = 2Z_1^2 - D = \eta \left(\frac{1}{(1-\eta)^2} - \frac{1}{1-\eta^2} \right) = \frac{2\eta^2}{(1-\eta)(1-\eta^2)}.$$

The calculation of all thermodynamic quantities is straightforward.

Problem 4.25 Let f_n be the average occupation of the n -th single-particle level in an ideal Fermi gas. Consider the binary scattering process where two fermions in states 1 and 2 get scattered into states 3 and 4. then , rate of forward scattering is

$$f_1 f_2 (1 - f_3)(1 - f_4) R$$

whereas the rate of reverse scattering is

$$f_3 f_4 (1 - f_1)(1 - f_2) R'$$

where $R = |M|^2$ is the square of the matrix element M of the scattering operator the states 1 and 2 and $R = |M^*|^2$. The principle of detailed balance states that. in equilibrium,

$$f_1 f_2 (1 - f_3)(1 - f_4) = f_3 f_4 (1 - f_1)(1 - f_2).$$

Show that the Fermi-Dirac distribution is the non-trivial solution of this equation. (This derivation shows how Pauli exclusion principle leads to the FD distribution).

Solution to Problem 4.25 Since $f_i = \left[e^{\beta(\epsilon_i - \mu)} + 1 \right]^{-1}$ we have

$$1 - f_i = \frac{e^{\beta(\epsilon_i - \mu)}}{e^{\beta(\epsilon_i - \mu)} + 1} = e^{\beta(\epsilon_i - \mu)} f_i.$$

Thus,

$$f_1 f_2 (1 - f_3)(1 - f_4) = e^{\beta(\epsilon_3 + \epsilon_4 - 2\mu)} f_1 f_2 f_3 f_4, \quad f_3 f_4 (1 - f_1)(1 - f_2) = e^{\beta(\epsilon_1 + \epsilon_2 - 2\mu)} f_1 f_2 f_3 f_4.$$

Because of the energy conservation law,

$$\epsilon_1 + \epsilon_2 = \epsilon_3 + \epsilon_4.$$