Weekly exercise W43: FYS2160, Thermodynamics and statistical physics

1 Problems from Schroeder

1.1 Schroeder 6.2

Solution:
For an energy level with energy E and n degenerate states, the probability of finding an atom at that energy level is
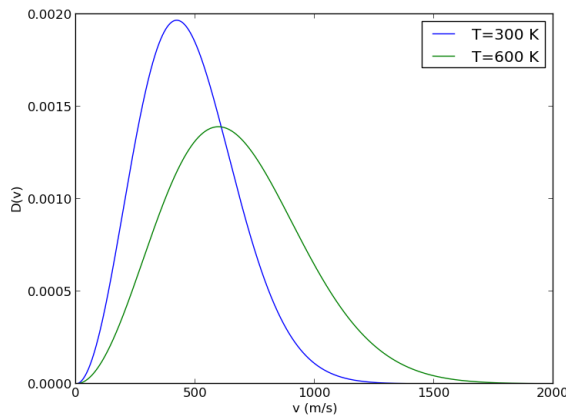
$$P(E) = nP(s) = \frac{n}{Z}e^{-E/kT},$$

where s is any one of the degenerate states. From the definition of Helmholtz free energy we know that $E = F + TS$. Using this together with the entropy, $S = k\ln(n)$, we get

$$P(E) = \frac{n}{Z}e^{-(F+TS)/kT} = \frac{n}{Z}e^{-F/kT}e^{-\ln(n)} = \frac{1}{Z}e^{-F/kT}.$$

1.2 Schroeder 6.34
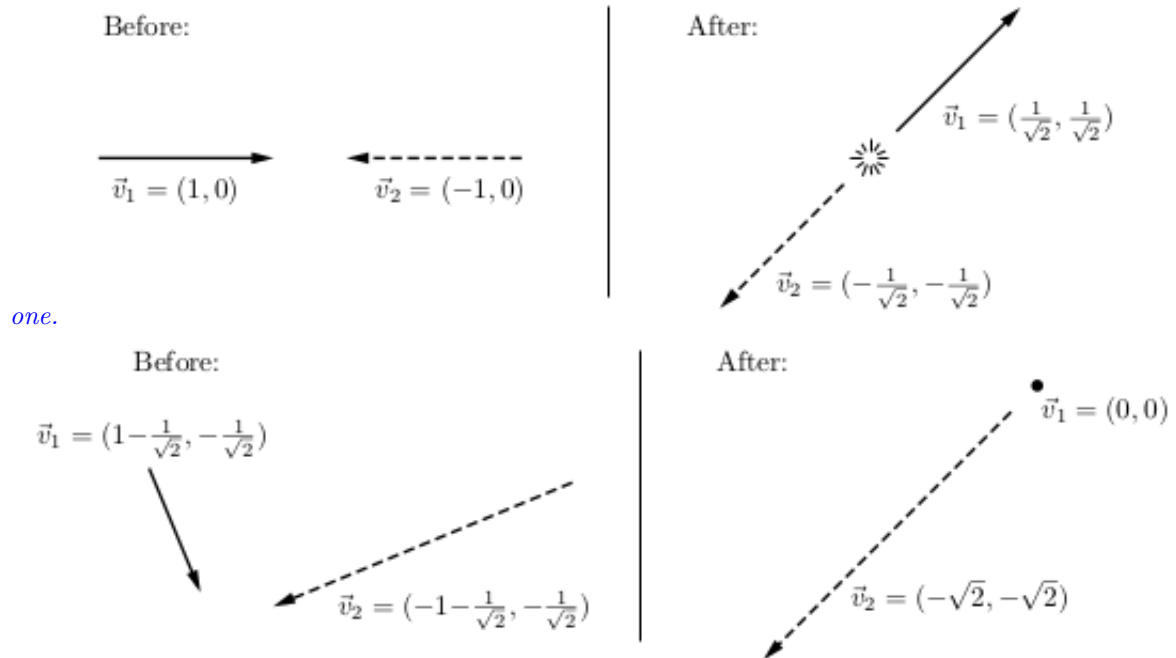
Solution:
See Figure

Maxwell speed distribution for nitrogen molecules at 300 K and 600 K.

1.3 Schroeder 6.40

Solution:
Assume that the two colliding balls have equal masses. The easiest approach is then two first consider the system in the centre-of-mass (CM) frame (to ensure conservation of momentum and energy), and then transform to a different reference frame. An example of a collision in the CM frame is

given in Figure ??. The velocities are chosen such that $|\vec{v}| = 1$ (in some arbitrary unit). Now transform the system to the frame where the first ball is at rest after the collision. This means subtracting $(\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}})$ from all vectors in Figure ??. We are now left with the scenario illustrated in Figure ??, where we see that the ball initially moving faster actually "steals" energy from the slower moving

Before:

After:

$\vec{v}_1 = (1, 0)$ $\vec{v}_2 = (-1, 0)$

$\vec{v}_1 = (\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}})$

$\vec{v}_2 = (-\frac{1}{\sqrt{2}}, -\frac{1}{\sqrt{2}})$

one.

Before:

After:

$\vec{v}_1 = (1 - \frac{1}{\sqrt{2}}, -\frac{1}{\sqrt{2}})$

$\vec{v}_2 = (-1 - \frac{1}{\sqrt{2}}, -\frac{1}{\sqrt{2}})$

$\vec{v}_1 = (0, 0)$

$\vec{v}_2 = (-\sqrt{2}, -\sqrt{2})$

1.4   Schroeder 6.44

Solution:
For a system of N indistinguishable, non-interacting particles, the partition function is given by

$$Z = \frac{1}{N!} Z_1^N,$$

where Z_1 is the one-particle partition function. Using the expression $F = -kT \ln Z$ for Helmholtz free energy we get

$$
\begin{aligned}
F &= -kT \ln \left(\frac{1}{N!} Z_1^N \right) \\
&= kT \left[\ln N! - N \ln Z_1 \right] \\
&\approx kT \left[N \ln N - N - N \ln Z_1 \right] \\
&= -NkT \left[1 + \ln \left(\frac{Z_1}{N} \right) \right],
\end{aligned}
$$

where we have used the Stirling approximation in the third line. Further, the chemical potential, μ, is given in terms of Helmholtz free energy as

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T,V}$$

$$= -kT \frac{\partial}{\partial N} \left[N + N \ln \left(\frac{Z_1}{N} \right) \right]$$

$$= -kT \ln \left(\frac{Z_1}{N} \right).$$

1.5 Schroeder 6.45

Solution:
The Helmholtz free energy is given by

$$F = -NkT \left[\ln V + \ln Z_{int} - \ln N - \ln v_Q + 1 \right],$$

where

$$v_Q = \left(\frac{h}{\sqrt{2\pi mkT}} \right)^3.$$

In order to make our lives slightly easier in the further calculation, we can rewrite $\ln v_Q$ as

$$\ln v_Q = \ln C - \frac{3}{2} \ln T, \quad \text{where} \quad C = \ln \left(\frac{h}{\sqrt{2\pi mk}} \right)^3.$$

The entropy, S, is then given by

$$S = -\left(\frac{\partial F}{\partial T} \right)_{V,N}$$

$$= Nk \frac{\partial}{\partial T} \left[T \ln V + T \ln Z_{int} - T \ln N - T \ln C + \frac{3}{2} T \ln T + T \right]$$

$$= Nk \left[\ln V - \ln N - \ln C + \frac{3}{2} \ln T + \frac{3}{2} + 1 \right] - \frac{\partial F_{int}}{\partial T}$$

$$= Nk \left[\ln \left(\frac{V}{Nv_Q} \right) + \frac{5}{2} \right] - \frac{\partial F_{int}}{\partial T}.$$

The chemical potential, μ, is calculated in a similar way, taking the derivative of F w.r.t. N. Notice however that neither v_Q nor Z_{int} depend on N, which makes the calculation slightly easier:

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T,V}$$

$$= -kT \frac{\partial}{\partial N} \left[N \ln V + N \ln Z_{int} - N \ln N - N \ln v_Q + N \right]$$

$$= -kT \left[\ln V + \ln Z_{int} - \ln N - 1 - \ln v_Q + 1 \right]$$

$$= -kT \ln \left(\frac{V Z_{int}}{Nv_Q} \right).$$

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2   Thermodynamic potentials

In this assignment we will have a closer look at the thermodynamic potentials, and how they are related.

(a) Write down the expressions for U, H, F and G as functions of S,T,P, V, N and μ. What are these quantities called? Give a physical interpretation of each quantity.

Solution:

- *$U = TS$ - PV + μN: Internal energy*

- *$H = U$ + PV: Enthalpy*

- *$F = U$ - TS: Helmholtz free energy*

- *$G = U$ - TS - PV: Gibbs free energy*

These quantities are called thermodynamic potentials. For physical interpretations of them, read page 149-151 in the textbook.

(b) Write down the thermodynamic identity for U (dU).

Solution:

$$dU = T\,dS + P\,dV + \mu\,dN \tag{1}$$

(c) Derive the Gibbs-Duhem equation:

$$S\mathrm{d}T - V\mathrm{d}P + N\mathrm{d}\mu = 0. \tag{2}$$

Solution:
Differentiate U

$$dU = T\,dS + S\,dT + P\,dV + V\,dP + \mu\,dN + N\,d\mu \tag{3}$$

and compare to the thermodynamic identity for U. This gives

$$S\,dT - V\,dP + N\,d\mu = 0. \tag{4}$$

(d) Find the thermodynamic identities dH, dF and dG. List the independent variables of U,H,F and G, and explain how the relations between the thermodynamical identities changes the independent variables. What is this transformation between different independent variables called?

Solution:

$$dH = T\,dS + V\,dP + \mu\,dN \tag{5}$$

$$dF = -S\,dT - P\,dV + \mu\,dN \tag{6}$$

$$dG = -S\,dT + V\,dP + \mu\,dN \tag{7}$$

The independent (or natural) variables are $U = U(S,V,N)$, $H = H(S,P,N)$, $F = F(T,V,N)$, $G = G(T,P,N)$. The transformations are called Legendre-transformations.

(e) Show that

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,N}, \tag{8}$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}, \tag{9}$$

$$P = -\left(\frac{\partial U}{\partial V}\right)_{S,N}, \tag{10}$$

$$T = \left(\frac{\partial H}{\partial S}\right)_{P,N} \tag{11}$$

and

$$V = \left(\frac{\partial G}{\partial P}\right)_{T,N}. \tag{12}$$

Solution:
We can write a change in G, dG as infinitesimal changes in the independent variables

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,N} dT + \left(\frac{\partial G}{\partial P}\right)_{T,N} dT + \left(\frac{\partial G}{\partial N}\right)_{T,P} dT \tag{13}$$

We also have that

$$dG = -S\,dT + V\,dP + \mu\,dN \tag{14}$$

Comparing the two gives us a formula for the entropy as a partial derivative of G with respect to T:

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,N}, \tag{15}$$

The other formulas are found in the same way.

(f) (This was given on a recent exam) Use the thermodynamic identities to derive the following relation

$$\left(\frac{\partial \mu}{\partial T}\right)_{V,N} = -\left(\frac{\partial S}{\partial N}\right)_{T,V} \tag{16}$$

What is this type of relation called?

Solution:

We recognize the constants in the partial derivatives to be the independent variables of F. We have that

$$\left(\frac{\partial}{\partial T}\right)_{V,N}\left(\frac{\partial F}{\partial N}\right)_{T,V} = \left(\frac{\partial}{\partial N}\right)_{T,V}\left(\frac{\partial F}{\partial T}\right)_{V,N} \tag{17}$$

since we can choose the order of which we take the derivative. We have that

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}, \tag{18}$$

and

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}. \tag{19}$$

Inserting for S and μ, we find

$$\left(\frac{\partial \mu}{\partial T}\right)_{V,N} = -\left(\frac{\partial S}{\partial N}\right)_{T,V}. \tag{20}$$

This type of relation is called a Maxwell relation, and is a non-trivial relation between the second derivatives of thermodynamic potentials.

(g) Assume $U = U(T)$. Use the thermodynamic identity to derive

$$S(T) = \int_0^T \frac{C_V}{T'}\,\mathrm{d}T' \tag{21}$$

Solution:

Differentiate $U = U(T)$:

$$dU = \frac{\partial U}{\partial T}dT \tag{22}$$

Thermodynamic identity with $dV = 0$

$$dS = \frac{1}{T}dU = \frac{C_V}{T}dT \tag{23}$$

(h) We will now look at the relation between the canonical partition function and the thermodynamic potentials. Use that $U = \langle \epsilon \rangle$ and show that

$$U = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} \tag{24}$$

Solution:

The canonical partition function is

$$Z = \sum_n e^{-\beta \epsilon_n}. \tag{25}$$

The expected value of ϵ is

$$\langle \epsilon \rangle = U = \frac{1}{Z}\sum_n \epsilon_n e^{-\beta \epsilon_n} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} \tag{26}$$

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(i) The probability for a state n, P_n, is related to the canonical partition function through $P_n = \frac{e^{-\beta\epsilon_n}}{Z}$ Starting with the Gibbs formula for entropy (which you do not have to prove)

$$S = k \ln \Omega = -k \left(\sum_n P_n \ln P_n \right),\tag{27}$$

show that

$$F = U - TS = -kT \ln Z\tag{28}$$

Solution:
We insert for the probability $\ln(P_n)$ *in Gibbs formula for entropy*

$$S = -k \sum_n (P_n \ln \frac{e^{-\beta\epsilon_n}}{Z}) = -k \sum_n (P_n(-\beta\epsilon_n - \ln Z)\tag{29}$$

$$S = \beta k \sum_n (P_n \epsilon_n) + k \sum_n (P_n \ln Z) = \frac{1}{T}\langle\epsilon\rangle + k \ln Z.\tag{30}$$

We insert this into $F = U\text{-}TS$

$$F = U - T(\frac{1}{T}\langle\epsilon\rangle + k \ln Z) = -kT \ln Z.\tag{31}$$

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