Qualifying Exam 2018 Statistical Mechanics

Problem 1

The probability distribution of a particle's velocity in an ideal gas is given by

$$f(\vec{v}) = A \exp\left(-\frac{m\vec{v}^2}{2k_B T}\right)$$

a) Compute the normalization constant A in $D = 3$ dimensions.

Solution:

Normalization requires

$$\begin{aligned} \int d^3v\, f(\vec{v}) &= 1 \\ 4\pi \int_0^\infty dv\, v^2 A \exp\left(-\frac{mv^2}{2k_B T}\right) &= 1 \\ A 4\pi \left(\frac{2k_B T}{m}\right)^{3/2} \int_0^\infty dx\, x^2 \exp\left(-x^2\right) &= 1 \end{aligned}$$

where I used

$$x = \sqrt{\frac{m}{2k_B T}} v$$

This yields

$$\begin{aligned} A 4\pi \left(\frac{2k_B T}{m}\right)^{3/2} \frac{\sqrt{\pi}}{4} &= 1 \\ A \left(\frac{2\pi k_B T}{m}\right)^{3/2} &= \left(\frac{m}{2\pi k_B T}\right)^{3/2} \end{aligned}$$

where I used

$$\int_0^\infty dx\, x^2 \exp\left(-x^2\right) = \frac{\sqrt{\pi}}{4}$$

b) Compute the most probable speed of a particle of the ideal gas

Solution:

The most probable speed is given by

$$\begin{aligned} \frac{d}{dv}\left[v^2 \exp\left(-\frac{mv^2}{2k_B T}\right)\right] &= 0 \\ \left[2v - v^2 \frac{2mv}{2k_B T}\right] \exp\left(-\frac{mv^2}{2k_B T}\right) &= 0 \\ v_{mp} &= \left(\frac{2k_B T}{m}\right)^{1/2} \end{aligned}$$

c) Compute the probability distribution $P(E)$ of a particle's energy in an ideal gas.

Solution:

The energy distribution function is derived via

$$d^3v\, f(\vec{v}) = dE\, P(E)$$

where

$$E = \frac{mv^2}{2}$$

We rewrite

$$d^3v\, f(\vec{v}) = 4\pi dv\, v^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{mv^2}{2k_B T}\right)$$

and perform a variable transformation

$$\begin{aligned} v &= \left(\frac{2E}{m}\right)^{1/2} \\ \frac{dv}{dE} &= \frac{1}{2}\left(\frac{2}{m}\right)^{1/2} E^{-1/2} \end{aligned}$$

which yields

$$\begin{aligned} d^3v\, f(\vec{v}) &= 4\pi dE \frac{1}{2}\left(\frac{2}{m}\right)^{1/2} E^{-1/2}\frac{2E}{m}\left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{E}{k_B T}\right) \\ &= dE\, 2\pi E^{1/2}\left(\frac{1}{\pi k_B T}\right)^{3/2} \exp\left(-\frac{E}{k_B T}\right) \end{aligned}$$

and hence

$$P(E) = 2\pi E^{1/2}\left(\frac{1}{\pi k_B T}\right)^{3/2} \exp\left(-\frac{E}{k_B T}\right)$$

d) Compute the fraction of particles that exceed a certain speed v_g.

Solution:

The fraction of particles n_g that exceed a certain velocity v_g is given by

$$\begin{aligned} n_g &= \int_{v>v_g} d^3v\, f(\vec{v}) \\ &= 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} \int_{v_g}^{\infty} dv\, v^2 \exp\left(-\frac{mv^2}{2k_B T}\right) \end{aligned}$$

Using next

$$x = \sqrt{\frac{m}{2k_BT}}v$$

I get

$$\begin{aligned}
n_g &= 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} \left(\frac{2k_BT}{m}\right)^{3/2} \int_{x_g}^{\infty} dx\, x^2 \exp\left(-x^2\right) \\
&= 4 \left(\frac{1}{\pi}\right)^{1/2} \frac{1}{4} \left[2x_g e^{-x_g^2} + \sqrt{\pi}\,\mathrm{Erf}\left(x_g\right)\right] \\
&= \left[2\sqrt{\frac{m}{2\pi k_B T}} v_g \exp\left(-\frac{m v_g^2}{2k_BT}\right) + \mathrm{Erf}\left(\sqrt{\frac{m}{2k_BT}} v_g\right)\right]
\end{aligned}$$

where I used

$$\int_{x_g}^{\infty} dx\, x^2 \exp\left(-x^2\right) = \frac{1}{4}\left[2x_g e^{-x_g^2} + \sqrt{\pi}\,\mathrm{Erf}\left(x_g\right)\right]$$

Problem 2

A model of a rubber band consists of a one-dimensional chain containing a large number N of linked rigid segments as shown in figure 1. Each segment is independent of the others. It occupies one of two possible states: horizontal, which contributes length a to the chain, or vertical, which contributes nothing to the length. The segments are linked so that they cannot come apart. The chain is in contact with a heat bath at temperature T.

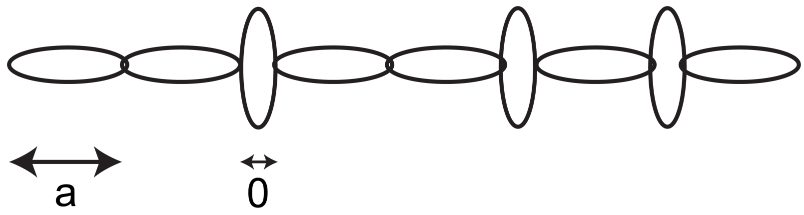

FIG. 1: One-dimensional chain containing a large number N of linked rigid segments.

a) If there is **no** energy difference between the the two states, what (expressed in terms of Na, and T) is the average length of the chain?

Solution:

We first need to compute the partition function. Since the segments do not interaction (and are distinguishable), we have for the partition function

$$Z_c(T, N) = [Z_c(T, 1)]^N$$

where

$$Z_c(T, 1) = \exp(-\beta E_h) + \exp(-\beta E_v) = 2\exp(-\beta E)$$

where

$$E_h = E_v = E$$

are the energies of the horizontal and vertical links.

The average length of each segment is now given by

$$\langle l \rangle = \frac{0 \times \exp(-\beta E_v) + a\exp(-\beta E_h)}{Z_c(T, 1)} = \frac{a\exp(-\beta E)}{2\exp(-\beta E)} = \frac{a}{2}$$

and the length of the entire chain is

$$\langle L \rangle = N\langle l \rangle = \frac{Na}{2}$$

b) The chain is now fixed at one end to a wall and stretched horizontally at the other end by a weight with mass m hung over a pulley that supplies a horizontal force F. (See figure 2.) Determine the average length of the chain (again in terms of Na, and T) at any temperature. Find the average length in the limits that $T \to 0$ and $T \to \infty$.

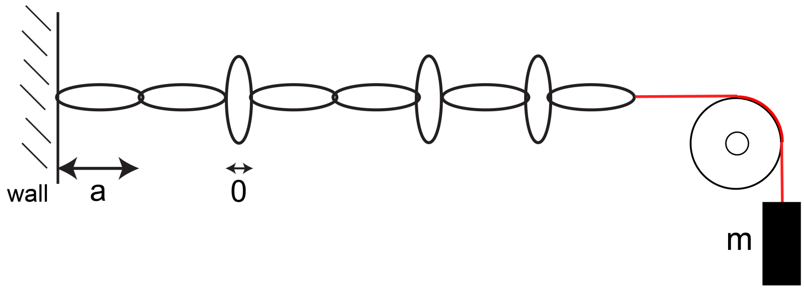

FIG. 2: One-dimensional chain fixed to a wall and and stretched horizontally at the other end by a weight with mass m hung over a pulley.

Solution:

When a chain segment of length a is horizonal, the potential energy of the mass m is lowered and the total energy is

$$E_h = E - mga = E - Fa$$

Thus we have

$$\begin{aligned} Z_c(T,1) &= \exp(-\beta E_v) + \exp(-\beta E_h) = \exp(-\beta E) + \exp[-\beta(E - Fa)] \\ &= \exp(-\beta E)[1 + \exp(\beta F a)] \end{aligned}$$

Now the average length is a single segment becomes

$$\begin{aligned} \langle l \rangle &= \frac{0 \times \exp(-\beta E_v) + a\exp(-\beta E_h)}{Z_c(T,1)} = \frac{a\exp[-\beta(E - Fa)]}{\exp(-\beta E)[1 + \exp(\beta F a)]} \\ &= \frac{a\exp[\beta F a]}{[1 + \exp(\beta F a)]} = \frac{a}{[1 + \exp(-\beta F a)]} \end{aligned}$$

and

$$\langle L \rangle = N\langle l \rangle = \frac{Na}{[1 + \exp(-\beta F a)]}$$

For $T \longrightarrow 0$

$$\langle L \rangle = N\langle l \rangle = \frac{Na}{[1 + \exp(-\beta F a)]} = Na$$

For $T \longrightarrow \infty$

$$\langle L \rangle = N \langle l \rangle = \frac{Na}{[1 + \exp(-\beta F a)]} = \frac{Na}{2}$$

c) What is the requirement on temperature T and force F such that Hooke's Law (that the change in length from equilibrium is proportional to F) applies?

Solution:

We can expand for small $\beta F a$

$$\begin{aligned}\langle L \rangle = N \langle l \rangle &= \frac{Na}{[1 + \exp(-\beta F a)]} \approx \frac{Na}{[1 + 1 - \beta F a]} \approx \frac{Na}{2[1 - \beta F a/2]} \\ &= \frac{Na}{2}[1 + \beta F a/2] = \frac{Na}{2} + \frac{N}{k_B T}\left(\frac{a}{2}\right)^2 F\end{aligned}$$

Thus Hooke's law holds if

$$\begin{aligned}\beta F a &\ll 1 \\ F a &\ll k_B T\end{aligned}$$

which is the high temperature limit.

d) As the temperature is raised do we need more or less force to stretch the rubber band? If you warm up the band while applying a fixed force, will it expand or contract?

Solution:

The above result

$$\langle L \rangle = N \langle l \rangle = \frac{Na}{[1 + \exp(-\beta F a)]}$$

shows that F needs to increase with increasing temperature to keep $\langle L \rangle$ constant, and that for constant F, $\langle L \rangle$ becomes smaller.

Problem 3

A spacecraft is in orbit around the Sun at distance R. It is shielded from the Sun's heat by a flat panel that is oriented perpendicular to the Sun and absorbs all of the incoming solar radiation. The Sun can be regarded a black body with surface temperature T_S, the radius of the sun is R_S, and the Boltzmann constant is given by σ.

a) Derive the formula giving the solar energy flux (the power per unit area) arriving at the panel.

Solution:

The solar energy flux of the sun is given by

$$j_S = \sigma T_S^4$$

The total surface of the sun is

$$A_S = 4\pi R_S^2$$

such that the total power emitted by the sun is

$$P_S = j_S A_S = \sigma T_S^4 4\pi R_S^2$$

To obtain the energy flux arriving at the panel, we need to divide P by the area of a sphere with radius R, which yields

$$j_P = \frac{P_S}{4\pi R^2} = \sigma T_S^4 \left(\frac{R_S}{R}\right)^2$$

b) The shielding panel is thermally insulated so that it only loses heat via photons re-radiated from its front surface. Assuming that the panel
can be treated as a black body, calculate the equilibrium temperature of the panel in terms of T_S, R_S and R.

Solution:

We have

$$j_P = \sigma T_P^4 = \sigma T_S^4 \left(\frac{R_S}{R}\right)^2$$

and hence

$$T_P = T_S \sqrt{\frac{R_S}{R}}$$

c) The free energy of a volume V of black-body radiation is

$$F(T, V) = -\gamma V T^4$$

where γ is some constant that depends on k_B, $\hbar$ and the speed of light c (you do not need to compute it). Use a thermodynamic relationto express the internal energy U, the entropy S, and the pressure P of the volume of gas in terms of γ, V, and T. Hence find the dimensionless constant ζ such that $P = \zeta U/V$.

Solution:

Perform a Legendre transformation using

$$S = -\frac{\partial F(T, V)}{\partial T} = 4\gamma V T^3$$

and

$$U = F + TS = -\gamma V T^4 + 4\gamma V T^4 = 3\gamma V T^4$$

Moreover, the pressure is given by

$$p = -\frac{\partial F(T, V)}{\partial V} = \gamma T^4 = \zeta \frac{U}{V} = \zeta 3\gamma T^4$$

and hence

$$\zeta = \frac{1}{3}$$

d) Assuming that the incoming energy flux (the answer to part (a)) is Q_{in}, compute P_{in}, the force per unit area due to the impact of the
photons on the panel. Compare your answer to the energy density in the incoming radiation. Does the constant from part (c) still apply?
If not why not?

Solution:

Q_{in} is a measure for the incoming energy per unit time and area, i.e.,

$$Q_{in} = \frac{\Delta E}{A \Delta t}$$

For photons, the relation between energy and momentum p is given by

$$E = cp$$

which yields

$$Q_{in} = \frac{c\Delta p}{A\Delta t} = c\frac{F}{A} = cP$$

where P is the exterted pressure.

The energy that arrives at the panel of area A in time Δt is then given by

$$U = E = A\Delta t Q_{in}$$

This energy is contained in the volume

$$V = Ac\Delta t$$

Thus we have

$$\frac{U}{V} = \frac{A\Delta t Q_{in}}{Ac\Delta t} = \frac{Q_{in}}{c} = P$$

Thus the constant is now 1 and not 1/3 since the volume (in front of the panel) does not contain a blackbody any longer.

Problem 4

Consider a model for n identical xenon atoms of mass m that are trapped on the surface of a solid. A xenon atom can be tightly bound to one of N adsorption sites with binding energy E_a (a positive number), or it may be free to move over the two-dimensional surface whose total area is A. When it is free to move along the surface, the xenon atom has both kinetic energy $\varepsilon_{kin} = mv^2/2 = p^2/2m$ and constant potential energy $\varepsilon_{pot} = V$. You may assume that the number n of xenon atoms is much smaller than the number of adsorption sites N, and that each adsorption site can bind at most one atom.

a) Consider first the two-dimensional gas composed of the n_g atoms that are free to move. Evaluate the partition function of the gas as a function of $n_g, A, m, \hbar, k_B$ and the temperature T. Also compute the free energy $F_g = E - TS$ and the chemical potential

$$\mu_g = \frac{\partial F_g}{\partial n_g}$$

as a function of the gas density n_g/A. (You may assume that the temperature is high enough that you may use Boltzmann statistics.)

Solution:

This is a two-dimensional canonical ensemble with partition function

$$\begin{aligned}
Z &= \frac{1}{n_g! h^{2n_g}} \int d^{2n_g}q d^{2n_g}p \exp\left[-\beta H(q,p)\right] \\
&= \frac{1}{n_g! h^{2n_g}} \int d^{2n_g}q d^{2n_g}p \exp\left[-\beta \sum_{i=1}^{n_g}\left(\frac{\vec{p}_i^{\,2}}{2m} + V\right)\right] \\
&= \frac{1}{n_g! h^{2n_g}} \left[e^{-\beta V} A\right]^{n_g} \int d^{2n_g}p \exp\left[-\beta \sum_{i=1}^{n_g} \frac{\vec{p}_i^{\,2}}{2m}\right] \\
&= \frac{1}{n_g! h^{2n_g}} \left[e^{-\beta V} A\right]^{n_g} \prod_{i=1}^{n_g} \int d^2p_i \exp\left[-\beta \frac{\vec{p}_i^{\,2}}{2m}\right] \\
&= \frac{1}{n_g! h^{2n_g}} \left[e^{-\beta V} A\right]^{n_g} \prod_{i=1}^{n_g} \left(\sqrt{\frac{2m\pi}{\beta}}\right)^2 \\
&= \frac{1}{n_g! h^{2n_g}} \left[e^{-\beta V} A \frac{2m\pi}{\beta}\right]^{n_g}
\end{aligned}$$

The free energy is given by

$$F_g = -k_B T \ln\left(\frac{1}{n_g!}\left[\frac{e^{-\beta V} A}{h^2}\frac{2m\pi}{\beta}\right]^{n_g}\right) = -k_B T n_g \ln\left(\frac{e^{-\beta V} A}{h^2}\frac{2m\pi}{\beta}\right) + k_B T \ln n_g!$$
$$= n_g V - k_B T n_g \ln\left(\frac{A}{h^2}\frac{2m\pi}{\beta}\right) + k_B T n_g \ln n_g - k_B T n_g$$
$$= n_g V - k_B T n_g \left[1 + \ln\left(\frac{A}{n_g h^2}\frac{2m\pi}{\beta}\right)\right]$$

And we have

$$\mu_g = \frac{\partial F_g}{\partial n_g} = V - k_B T\left[1 + \ln\left(\frac{A}{n_g h^2}\frac{2m\pi}{\beta}\right)\right] + k_B T n_g \frac{1}{n_g}$$
$$= V - k_B T \ln\left(\frac{A}{n_g}\frac{2m\pi k_B T}{h^2}\right)$$
$$= V + k_B T \ln\left(\frac{n_g}{A}\frac{h^2}{2m\pi k_B T}\right)$$

b) Now consider the $n_b = n - n_g$ atoms that are bound to the adsorption sites. Find the mean energy, entropy, free-energy and chemical potential for these particles.

Solution:

$$U = \langle E \rangle = -n_b E_a$$

and

$$S = k_B \ln \Omega$$

where

$$\Omega = \frac{N!}{n_b!\,(N - n_b)!}$$

Hence, the free energy is given by

$$F_b = U - TS = -n_b E_a - T k_B \ln\left(\frac{N!}{n_b!\,(N - n_b)!}\right)$$
$$= -n_b E_a - k_B T\left[\ln(N!) - \ln[n_b!] - \ln[(N - n_b)!]\right]$$
$$\approx -n_b E_a - k_B T\left[N \ln N - N - n_b \ln n_b + n_b - (N - n_B)\ln(N - n_b) + N - n_B\right]$$
$$= -n_b E_a - k_B T\left[N \ln N - n_b \ln n_b - (N - n_B)\ln(N - n_b)\right]$$
$$= -n_b E_a - k_B T\left[-N \ln \frac{N - n_b}{N} - n_b \ln \frac{n_b}{N - n_b}\right]$$
$$= -n_b E_a - k_B T\left[-N \ln\left(1 - \frac{n_b}{N}\right) - n_b \ln \frac{n_b}{N - n_b}\right]$$
$$\approx -n_b E_a - k_B T n_b\left[1 - \ln \frac{n_b}{N}\right]$$

c) Show that in equilibrium the number n_g is determined by $n_b + n_g = n$ together with

$$\frac{n_b A}{n_g N} = C(T) \exp\left(\frac{E_a + V}{k_B T}\right)$$

You should express the function $C(T)$ in terms of $T, m, \hbar$ and k_B.

Solution:

In equilibrium, the free energy per particle is the same

$$\begin{aligned}
\frac{F_g}{n_g} &= \frac{F_b}{n_b} \\
V - k_B T\left[1 + \ln\left(\frac{A}{n_g h^2}\frac{2m\pi}{\beta}\right)\right] &= -E_a - k_B T + k_B T \ln\frac{n_b}{N} \\
-k_B T - k_B T \ln\left(\frac{A}{n_g h^2}\frac{2m\pi}{\beta}\right) - k_B T \ln\frac{n_b}{N} &= -E_a - V - k_B T \\
-\ln\left(\frac{A}{n_g h^2} 2m\pi k_B T\right) - \ln\frac{n_b}{N} &= \frac{E_a + V}{k_B T} \\
\frac{2m\pi k_B T}{h^2}\frac{n_b A}{n_g N} &= \exp\left(\frac{E_a + V}{k_B T}\right) \\
\frac{n_b}{N} \Big/ \frac{n_g}{A} &= \frac{h^2}{2m\pi k_B T}\exp\left(\frac{E_a + V}{k_B T}\right)
\end{aligned}$$

and hence

$$C(T) = \frac{h^2}{2m\pi k_B T}$$

$$\mu_g = V + k_B T \ln\left(\frac{n_g}{A}\frac{h^2}{2m\pi k_B T}\right)$$

$$\begin{aligned}
\mu_b &= -E_a - k_B T\left[1 - \ln\frac{n_b}{N}\right] + k_B T \\
&= -E_a + k_B T \ln\frac{n_b}{N}
\end{aligned}$$

Problem 5

Consider a paramagnetic material consisting of a volume V of N non-interacting spin-1 particles with magnetic dipole moment

$$\vec{\mu} = \frac{\mu}{\hbar}\vec{S} \qquad S_z = m\hbar \qquad m = 0, \pm 1$$

that are located in a magnetic field $\vec{B} = B_0\hat{z}$ at temperature T.

(a) Write the partition function in terms of k_BT and $\varepsilon = \mu B_0$.

Solution:

As the moments are non-interacting, we can write the partition function as

$$Z(T, V, B, N) = [Z(T, V, B, 1)]^N$$

The energy of a magnetic moment in a magnetic field is given by

$$H = -\vec{\mu}\cdot\vec{B} = -\frac{\mu}{\hbar}\vec{S}\cdot\vec{B} = -\frac{\mu}{\hbar}m\hbar B_0 = -\mu m B_0$$

Thus we obtain

$$\begin{aligned} Z(T, B, 1) &= \sum_{m=0,\pm 1} \exp\left[-\beta\left(-\mu m B_0\right)\right] = 1 + \exp\left[\beta\mu B_0\right] + \exp\left[-\beta\mu B_0\right] \\ &= 1 + \exp\left[\frac{\varepsilon}{k_BT}\right] + \exp\left[-\frac{\varepsilon}{k_BT}\right] \end{aligned}$$

and hence

$$Z(T, B, N) = \left(1 + \exp\left[\frac{\varepsilon}{k_BT}\right] + \exp\left[-\frac{\varepsilon}{k_BT}\right]\right)^N$$

b) Compute the average spin $\langle S_z\rangle$.

Solution:

$$\begin{aligned} \langle S_z\rangle &= \frac{\sum_{m=0,\pm 1} m\hbar \exp\left[-\beta\left(-\mu m B_0\right)\right]}{Z(T, B, 1)} \\ &= \hbar\frac{1\times\exp\left[\frac{\varepsilon}{k_BT}\right] + (-1)\exp\left[-\frac{\varepsilon}{k_BT}\right]}{1 + \exp\left[\frac{\varepsilon}{k_BT}\right] + \exp\left[-\frac{\varepsilon}{k_BT}\right]} \\ &= \hbar\frac{\exp\left[\frac{\varepsilon}{k_BT}\right] - \exp\left[-\frac{\varepsilon}{k_BT}\right]}{1 + \exp\left[\frac{\varepsilon}{k_BT}\right] + \exp\left[-\frac{\varepsilon}{k_BT}\right]} \end{aligned}$$

(c) Calculate the average energy $\langle E \rangle$ of the N spins, and find the approximate functional form of $\langle E \rangle$ in the low- and high-temperature limits. Provide a qualitative argument to explain your results in these two limits. What is the relation between $\langle E \rangle / N$ and $\langle S_z \rangle$? Explain

Solution:

We have for the energy of a single spin

$$\begin{aligned}
\langle E_S \rangle &= \frac{1}{Z(T,B,1)} \sum_{m=0,\pm 1} (-\mu m B_0) \exp\left[-\beta\left(-\mu m B_0\right)\right] \\
&= \frac{0 \times 1 - \varepsilon \exp\left[\frac{\varepsilon}{k_B T}\right] + \varepsilon \exp\left[-\frac{\varepsilon}{k_B T}\right]}{1 + \exp\left[\frac{\varepsilon}{k_B T}\right] + \exp\left[-\frac{\varepsilon}{k_B T}\right]} \\
&= -\varepsilon \frac{\exp\left[\frac{\varepsilon}{k_B T}\right] - \exp\left[-\frac{\varepsilon}{k_B T}\right]}{1 + \exp\left[\frac{\varepsilon}{k_B T}\right] + \exp\left[-\frac{\varepsilon}{k_B T}\right]}
\end{aligned}$$

and hence

$$\langle E \rangle = -N\varepsilon \frac{\exp\left[\frac{\varepsilon}{k_B T}\right] - \exp\left[-\frac{\varepsilon}{k_B T}\right]}{1 + \exp\left[\frac{\varepsilon}{k_B T}\right] + \exp\left[-\frac{\varepsilon}{k_B T}\right]}$$

In the low temperature limit $k_B T \ll \varepsilon$, we have

$$\langle E \rangle \approx -N\varepsilon \frac{\exp\left[\frac{\varepsilon}{k_B T}\right]}{1 + \exp\left[\frac{\varepsilon}{k_B T}\right]} = -N\varepsilon \frac{1}{1 + \exp\left[-\frac{\varepsilon}{k_B T}\right]} = -N\varepsilon \left[1 - \exp\left(-\frac{\varepsilon}{k_B T}\right)\right]$$

In the high temperature limit $k_B T \gg \varepsilon$, we have

$$\langle E \rangle \approx -N\varepsilon \frac{1 + \frac{\varepsilon}{k_B T} - 1 + \frac{\varepsilon}{k_B T}}{1 + 1 + \frac{\varepsilon}{k_B T} + 1 - \frac{\varepsilon}{k_B T}} = -N\varepsilon \frac{2\frac{\varepsilon}{k_B T}}{3} = -\frac{2}{3} N \frac{\varepsilon^2}{k_B T}$$