

Name: **Huan Q. Bui**  
 Course: **8.333 - Statistical Mechanics I**  
 Problem set: **#4**

**1. Rotating gas.** The Hamiltonian is

$$\mathcal{H} = \sum_{n=1}^N \left[ \frac{(p^{(n)})^2}{2m} + \frac{K}{2} (r^{(n)})^2 \right]$$

(a) The components of the angular momentum of particle  $n$  is  $L_i^{(n)} = \epsilon_{ijk} r_j^{(n)} p_k^{(n)}$ . To show that  $\{\vec{L}^{(n)}, \mathcal{H}\} = 0$  we may show that  $\{L_i^{(n)}, \mathcal{H}\} = 0$ .

$$\begin{aligned} \{L_i^{(n)}, \mathcal{H}\} &= \epsilon_{ijk} \{r_j^{(n)} p_k^{(n)}, \mathcal{H}\} \\ &= \epsilon_{ijk} \{r_j^{(n)}, \mathcal{H}\} p_k^{(n)} + \epsilon_{ijk} r_j^{(n)} \{p_k^{(n)}, \mathcal{H}\} \end{aligned}$$

Since there is no interaction, the only nontrivial Poisson brackets are those with partial derivatives with respect to the canonical variables associated with the particle ( $n$ ) (we can also show this explicitly by definition but it's just a matter of notation). If we write  $\mathcal{H} = \sum_n \mathcal{H}^{(n)}$  then we have

$$\begin{aligned} \{L_i^{(n)}, \mathcal{H}\} &= \epsilon_{ijk} \{r_j^{(n)}, \mathcal{H}^{(n)}\} p_k^{(n)} + \epsilon_{ijk} r_j^{(n)} \{p_k^{(n)}, \mathcal{H}^{(n)}\} \\ &= \frac{1}{2m} \epsilon_{ijk} \{r_j^{(n)}, p_a^{(n)} p_a^{(n)}\} p_k^{(n)} + \frac{K}{2} \epsilon_{ijk} r_j^{(n)} \{p_k^{(n)}, r_b^{(n)} r_b^{(n)}\} \\ &= -\frac{1}{2m} \epsilon_{ijk} \{p_a^{(n)} p_a^{(n)}, r_j^{(n)}\} p_k^{(n)} - \frac{K}{2} \epsilon_{ijk} r_j^{(n)} \{r_b^{(n)} r_b^{(n)}, p_k^{(n)}\} \\ &= -\frac{1}{m} \epsilon_{ijk} \{p_a^{(n)}, r_j^{(n)}\} p_a^{(n)} p_k^{(n)} - K \epsilon_{ijk} \{r_b^{(n)}, p_k^{(n)}\} r_b^{(n)} r_j^{(n)} \\ &= \frac{1}{m} \epsilon_{ijk} \delta_{aj} p_a^{(n)} p_k^{(n)} + K \epsilon_{ijk} \delta_{bk} r_b^{(n)} r_j^{(n)} \\ &= \frac{1}{m} \epsilon_{ijk} p_j^{(n)} p_k^{(n)} + K \epsilon_{ijk} r_k^{(n)} r_j^{(n)} \\ &= 0, \end{aligned}$$

where we have used the fact that  $\vec{a}^{(n)} \times \vec{a}^{(n)} = \vec{0}$  for any  $\vec{a}^{(n)}$ .

(b) The generalized canonical distribution is

$$p[\mu \equiv \{\vec{p}_i, \vec{r}_i\}] = \frac{1}{\mathcal{Z}(\beta, \vec{\Omega})} \exp \left( -\beta \mathcal{H}(\mu) - \beta \vec{\Omega} \cdot \vec{L} \right)$$

Assuming that  $\vec{\Omega} = \Omega \hat{z}$  where  $\Omega < \sqrt{k/m}$ , so that  $\vec{\Omega} \cdot \vec{L} = \Omega L_z$ , we may compute  $\mathcal{Z}$  as follows.

$$\begin{aligned} \mathcal{Z}(\beta, \Omega) &= \frac{1}{N! h^{3N}} \int d\mu \exp \left( -\beta \mathcal{H}(\mu) - \beta \vec{\Omega} \cdot \vec{L} \right) \\ &= \frac{1}{N! h^{3N}} \prod_{n=1}^N \int d\mu^{(n)} \exp \left( -\beta \mathcal{H}^{(n)}(\mu^{(n)}) \right) \exp \left( -\beta \Omega L_z^{(n)} \right) \\ &= \frac{1}{N! h^{3N}} \left[ \int d^3 r d^3 p \exp \left( \beta \left( \frac{p^2}{2m} + \frac{K}{2} r^2 \right) \right) \exp \left( -\beta \Omega (x p_y - y p_x) \right) \right]^N \\ &= \frac{1}{N! h^{3N}} \left[ \frac{8\pi^3 \sqrt{m}}{\sqrt{K} \beta^3 (K/m - \Omega^2)} \right]^N = \boxed{\frac{1}{N! h^{3N}} \left[ \frac{8\pi^3}{\omega \beta^3 (\omega^2 - \Omega^2)} \right]^N} \end{aligned}$$

where we have called  $\omega = \sqrt{K/m}$ . Mathematica code:

```

Integrate[
Exp[-\[Beta]*((px^2 + py^2 + pz^2)/(2*m) + K*(x^2 + y^2 + z^2)/2)]*
Exp[-\[Beta]*\[CapitalOmega]*(x*py - y*px)], {px, -Infinity,
Infinity}, {py, -Infinity, Infinity}, {pz, -Infinity, Infinity},
{x, -Infinity, Infinity}, {y, -Infinity, Infinity}, {z, -Infinity,
Infinity}]

>>> ConditionalExpression[(8 \[Pi]^3)/(
Sqrt[K \[Beta]] (\[Beta]/m)^(5/2)
Abs[m] Abs[
K - m \[CapitalOmega]^2]), (m > 0 && Re\[Beta] > 0) || (m < 0 &&
Re\[Beta] < 0)]

```

(c) By symmetry,  $\langle L_z \rangle = \sum_{n=1}^N \langle L_z^{(n)} \rangle = N \langle L_z^{(n)} \rangle$ , so

$$\begin{aligned}
\langle L_z \rangle &= \frac{N}{\mathcal{Z}(\beta, \vec{\Omega})} \int d^3r d^3p (xp_y - yp_x) \exp\left(\beta\left(\frac{p^2}{2m} + \frac{K}{2}r^2\right)\right) \exp(-\beta\Omega(xp_y - yp_x)) \left[\int d\mu \Pr[\mu]\right]^{N-1} \\
&= \frac{N}{\mathcal{Z}^{1/N}} \int d^3r d^3p (xp_y - yp_x) \exp\left(\beta\left(\frac{p^2}{2m} + \frac{K}{2}r^2\right)\right) \exp(-\beta\Omega(xp_y - yp_x)) \\
&= \frac{N}{\mathcal{Z}^{1/N}} \frac{1}{h^3(N!)^{1/N}} \frac{-16m^2\pi^3\sqrt{K\beta}\Omega}{K\beta^4\sqrt{\beta/m}(K - m\Omega)^2} \\
&= N \frac{\omega\beta^3(\omega^2 - \Omega^2)}{8\pi^3} \frac{-16\pi^3\Omega}{\beta^4\omega(\omega^2 - \Omega^2)^2} \\
&= \boxed{\frac{-2N\Omega}{\beta(\omega^2 - \Omega^2)}}
\end{aligned}$$

Mathematica code:

```

In[6]:= Integrate[(x*py - y*px)*
Exp[-\[Beta]*((px^2 + py^2 + pz^2)/(2*m) + K*(x^2 + y^2 + z^2)/2)]*
Exp[-\[Beta]*\[CapitalOmega]*(x*py - y*px)], {px, -Infinity,
Infinity}, {py, -Infinity, Infinity}, {pz, -Infinity, Infinity},
{x, -Infinity, Infinity}, {y, -Infinity, Infinity}, {z, -Infinity,
Infinity}]

Out[6]= ConditionalExpression[-((
16 m^2 \[Pi]^3 Sqrt[K \[Beta]] \[CapitalOmega])/
K \[Beta]^4 Sqrt[\[Beta]/m] (K - m \[CapitalOmega]^2)^2)),
Re\[Beta] (1/m - \[CapitalOmega]^2/K)] > 0]

(*Find 1/N * <Lz>*)
In[16]:= -((16 m^2 \[Pi]^3 Sqrt[K \[Beta]] \[CapitalOmega])/
K \[Beta]^4 Sqrt[\[Beta]/m] (K - m \[CapitalOmega]^2)^2))/((
8 \[Pi]^3)/(
Sqrt[K \[Beta]] (\[Beta]/m)^(5/2)
Abs[m] Abs[
K - m \[CapitalOmega]^2])) // FullSimplify

Out[16]= -((
2 \[CapitalOmega] Abs[
m (K - m \[CapitalOmega]^2)]/(\[Beta] (K - m \[CapitalOmega]^2)^2)
)

```

(d) The probability density of finding a particle at location  $(x, y, z)$  is taken by integrating out all momentum parts. Since we also don't have interaction, we simply look at one-particle partition function  $\mathcal{Z}^{1/N}$  and 1-particle densities only:

$$\begin{aligned}
\rho(x, y, z) &= \frac{1}{\mathcal{Z}^{1/N}} \left[ \int d^3p \exp\left(-\beta\frac{p^2}{2m} - \beta\frac{K}{2}(x^2 + y^2 + z^2) - \beta\Omega(xp_y - yp_x)\right) \right] \\
&= \frac{1}{\mathcal{Z}^{1/N}} \frac{1}{(N!)^{1/N} h^3} 2\sqrt{2}\pi^{3/2} \left(\frac{m}{\beta}\right)^{3/2} \exp\left(-\frac{\beta K}{2}(x^2 + y^2 + z^2)\right) \exp(-\Omega^2(x^2 + y^2)).
\end{aligned}$$

Hence, we have

$$\begin{aligned}\langle x^2 \rangle &= \int x^2 \rho dV = \frac{1}{\mathcal{Z}^{1/N}} \frac{1}{(N!)^{1/N} h^3} \frac{8\pi^3}{\beta^2 \sqrt{K\beta} (\beta/m)^{3/2} (K - m\Omega^2)^2} = \frac{1}{\beta(K - m\Omega^2)} = \boxed{\frac{1}{\beta m(\omega^2 - \Omega^2)}} \\ \langle y^2 \rangle &= \frac{(N!)^{1/N} h^3}{\beta(K - m\Omega^2)} = \boxed{\frac{1}{\beta m(\omega^2 - \Omega^2)}} \quad \text{by symmetry} \\ \langle z^2 \rangle &= \frac{1}{\mathcal{Z}^{1/N}} \int z^2 \rho dV = \frac{1}{\mathcal{Z}^{1/N}} \frac{1}{(N!)^{1/N} h^3} \frac{8\pi^3}{(K\beta)^{3/2} (\beta/m)^{3/2} \beta(K - m\Omega^2)} = \boxed{\frac{1}{K\beta}}\end{aligned}$$

Mathematica code:

```
(*x^2*)
In[25]:= Integrate[
x^2*(2 Sqrt[2]
E^(-(1/2) \[Beta] (K (x^2 + y^2 + z^2) -
m (x^2 + y^2) \[CapitalOmega]^2)) m \[Pi]^((
3/2))/(\[Beta] Sqrt[\[Beta]/m]), {x, -Infinity,
Infinity}, {y, -Infinity, Infinity}, {z, -Infinity, Infinity}]

Out[25]= ConditionalExpression[(
8 \[Pi]^3)/(\[Beta]^2 Sqrt[K \[Beta]] (\[Beta]/m)^((
3/2) (K - m \[CapitalOmega]^2)^2), And[
Or[
Element[\[Beta] (K - m \[CapitalOmega]^2), Reals],
Re[\[Beta] (K - m \[CapitalOmega]^2)] > 0],
Re[\[Beta] (K - m \[CapitalOmega]^2)] >= 0,
Re[m \[Beta] \[CapitalOmega]^2] < Re[K \[Beta]]]]

(*Simplify for x^2*)
In[28]:= ((
8 \[Pi]^3)/(\[Beta]^2 Sqrt[K \[Beta]] (\[Beta]/m)^((
3/2) (K - m \[CapitalOmega]^2)^2))/((8 \[Pi]^3)/((
Sqrt[K \[Beta]] (\[Beta]/m)^((5/2)
Abs[m] Abs[K - m \[CapitalOmega]^2]))

Out[28]= (
Abs[m] Abs[
K - m \[CapitalOmega]^2])/(m \[Beta] (K - m \[CapitalOmega]^2)^2)

(*z^2*)
In[29]:= Integrate[
z^2*(2 Sqrt[2]
E^(-(1/2) \[Beta] (K (x^2 + y^2 + z^2) -
m (x^2 + y^2) \[CapitalOmega]^2)) m \[Pi]^((
3/2))/(\[Beta] Sqrt[\[Beta]/m]), {x, -Infinity,
Infinity}, {y, -Infinity, Infinity}, {z, -Infinity, Infinity}]

Out[29]= ConditionalExpression[(
8 \[Pi]^3)/((K \[Beta])^((3/2) (\[Beta]/m)^((
3/2) (K \[Beta] - m \[Beta] \[CapitalOmega]^2))),
Re[\[Beta] (K - m \[CapitalOmega]^2)] > 0]

(*Simplify for z^2*)
In[31]:= ((
8 \[Pi]^3)/((K \[Beta])^((3/2) (\[Beta]/m)^((
3/2) (K \[Beta] - m \[Beta] \[CapitalOmega]^2))))/((8 \[Pi]^3)/((
Sqrt[K \[Beta]] (\[Beta]/m)^((5/2)
Abs[m] Abs[K - m \[CapitalOmega]^2]))

Out[31]= (
Abs[m] Abs[
K - m \[CapitalOmega]^2])/(K m (K \[Beta] -
m \[Beta] \[CapitalOmega]^2))
```

**2. Polar rods.** The Hamiltonian is

$$\mathcal{H}_{\text{rot}} = \frac{1}{2I} \left( p_\theta^2 + \frac{p_\phi^2}{\sin^2 \theta} \right) - \mu E \cos \theta.$$

- (a) The contribution of the rotational degrees of freedom of each dipole to the classical partition function is

$$\mathcal{Z}_{\text{rot}} = \frac{1}{h^2} \int_0^{2\pi} d\phi \int_0^\pi d\theta \int dp_\phi dp_\theta \exp\left(-\frac{\beta}{2I} \left(p_\theta^2 + \frac{p_\phi^2}{\sin^2 \theta}\right) + \beta E \mu \cos \theta\right)$$

$$= \boxed{\frac{8I\pi^2 \sinh(\beta\mu E)}{Eh^2\beta^2\mu}}$$

Mathematica code:

```
In[1]:= (1/h^2) Integrate[
2*Pi*Exp[-(\[Beta]/(2*II))* (p\[Theta]^2 +
p\[Phi]^2/Sin\[Theta]^2) + \[Beta]*Ef*\[Mu]*
Cos\[Theta]], {\[Theta], 0, Pi}, {p\[Theta], -Infinity,
Infinity}, {p\[Phi], -Infinity, Infinity}]

Out[1]= (8 II \[Pi]^2 Sinh[Ef \[Beta] \[Mu]])/(Ef h^2 \[Beta]^2 \[Mu])
```

- (b) The mean polarization is

$$P = \langle \mu \cos \theta \rangle = \frac{\partial}{\partial(\beta E)} \ln \mathcal{Z}_{\text{rot}} = \frac{\partial}{\partial(\beta E)} [\ln \sinh(\beta\mu E) - \ln E\beta] = \boxed{\mu \coth(\beta\mu E) - \frac{1}{E\beta}}$$

Brute-forcing using the definition (using Mathematica) also works. Mathematica code:

```
(1/((8 II \[Pi]^2 Sinh[Ef \[Beta] \[Mu]])/(
Ef h^2 \[Beta]^2 \[Mu]))) (1/
h^2) Integrate[(\[Mu]*Cos\[Theta])*2*Pi*
Exp[-(\[Beta]/(2*II))* (p\[Theta]^2 +
p\[Phi]^2/Sin\[Theta]^2) + \[Beta]*Ef*\[Mu]*
Cos\[Theta]], {\[Theta], 0, Pi}, {p\[Theta], -Infinity,
Infinity}, {p\[Phi], -Infinity, Infinity}]

Out[2]= (Csch[
Ef \[Beta] \[Mu]] (Ef \[Beta] \[Mu] Cosh[Ef \[Beta] \[Mu]] -
Sinh[Ef \[Beta] \[Mu]])/(Ef \[Beta])

In[6]:= (Csch[
Ef \[Beta] \[Mu]] (Ef \[Beta] \[Mu] Cosh[Ef \[Beta] \[Mu]] -
Sinh[Ef \[Beta] \[Mu]])/(Ef \[Beta]) // FullSimplify

Out[6]= -(1/(Ef \[Beta])) + \[Mu] Coth[Ef \[Beta] \[Mu]]
```

- (c) The zero-field polarizability is

$$\chi_T = \left. \frac{\partial P}{\partial E} \right|_{E=0} = \lim_{E \rightarrow 0} \left[ -\beta\mu^2 \text{csch}^2(E\beta\mu) + \frac{1}{E^2\beta} \right] = \boxed{\frac{\beta\mu^2}{3}}$$

where instead of naively plugging in  $E = 0$  we have taken the limit  $E \rightarrow 0$  to get this result.

Mathematica code:

```
In[8]:= D[-(1/(Ef \[Beta])) + \[Mu] Coth[Ef \[Beta] \[Mu]],
Ef] // FullSimplify

Out[8]= 1/(Ef^2 \[Beta]) - \[Beta] \[Mu]^2 Csch[Ef \[Beta] \[Mu]]^2

In[9]:= Limit[
1/(Ef^2 \[Beta]) - \[Beta] \[Mu]^2 Csch[Ef \[Beta] \[Mu]]^2, Ef -> 0]

Out[9]= (\[Beta] \[Mu]^2)/3
```

- (d) The rotational energy per particle for a given  $E$  is

$$\langle E_{\text{rot}} \rangle = -\frac{\partial}{\partial \beta} \ln \mathcal{Z}_{\text{rot}} = \boxed{\frac{2}{\beta} - E\mu \coth(E\mu\beta)}$$

Mathematica code:

```

In[11]:= -D[
Log[(8 II \[Pi]^2 Sinh[Ef \[Beta] \[Mu]])/(
Ef h^2 \[Beta]^2 \[Mu])], \[Beta]] // FullSimplify

Out[11]= 2/\[Beta] - Ef \[Mu] Coth[Ef \[Beta] \[Mu]]

```

To see what  $\langle E_{\text{rot}} \rangle$  behaves like in the high/low temperature limits we may write it more explicitly:

$$\langle E_{\text{rot}} \rangle = 2k_B T - E\mu \frac{e^{2E\mu/k_B T} + 1}{e^{2E\mu/k_B T} - 1}.$$

In the high temperature limit,  $\langle E_{\text{rot}} \rangle \sim 2k_B T$ , while in the low temperature limit  $\langle E_{\text{rot}} \rangle \sim 2k_B T - E\mu$ .

(e) Heat capacity is

$$C = \frac{d\langle E_{\text{rot}} \rangle}{dT} = 2k_B - \frac{E^2 \mu^2}{k_B T^2} \text{csch}\left(\frac{E\mu}{k_B T}\right) = 2k_B - \frac{E^2 \mu^2}{k_B T^2} \frac{2e^{E\mu/k_B T}}{e^{2E\mu/k_B T} - 1}.$$

We find

$$\lim_{T \rightarrow 0} C = 2k_B$$

$$\lim_{T \rightarrow \infty} C = k_B.$$

Mathematica code:

```

In[30]:= Limit[2 k - (Ef^2 \[Mu]^2 Csch[(Ef \[Mu])/(k T)]^2)/(k T^2),
T -> 0]

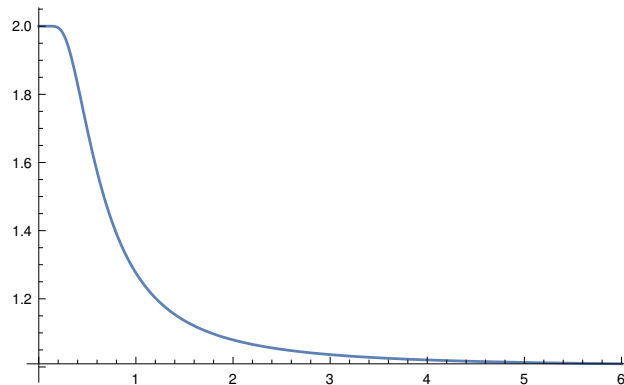
Out[30]= ConditionalExpression[2 k, Ef k \[Mu] > 0]

In[31]:= Limit[2 k - (Ef^2 \[Mu]^2 Csch[(Ef \[Mu])/(k T)]^2)/(k T^2),
T -> Infinity]

Out[31]= k

```

Sketch of rotational heat capacity per dipole. Setting  $k_B = 1$ : The point where the curve begins to



decrease fast is where  $k_B T \approx E\mu$ .

Mathematica code:

```

Plot[2 - Csch[1/T]^2/T^2, {T, 0, 6}, PlotRange -> Full]

```

### 3. Atomic/molecular hydrogen.

(a) Given  $N_1$  hydrogen atoms with

$$\mathcal{H}_a = \sum_{i=1}^{N_1} \frac{p_i^2}{2m}$$

the partition function  $\mathcal{Z}_a(N_1, T, V)$  is

$$\mathcal{Z}_a(N_1, T, V) = \frac{V^{N_1}}{N_1! h^{3N_1}} \left[ \int \exp\left(-\beta \frac{p^2}{2m}\right) d^3p \right]^{N_1} = \boxed{\frac{V^{N_1}}{N_1! h^{3N_1}} \left( \frac{2\pi m}{\beta} \right)^{3N_1/2}}$$

(b) Given

$$\mathcal{H}_m = \sum_{i=1}^{N_2} \left[ \frac{p_i^2}{4m} + \frac{L_i^2}{2I} - \epsilon \right] = \sum_{i=1}^{N_2} \left[ \frac{(p^{(i)})^2}{4m} + \frac{1}{2I} \left( (p_\theta^{(i)})^2 + \frac{(p_\phi^{(i)})^2}{\sin^2 \theta} \right) - \epsilon \right]$$

in view of the previous problem. The external and internal degrees of freedom of the molecule completely decouple. Also, the extra factor of  $\exp(\beta\epsilon)$  simply carries along. So, we have

$$\mathcal{Z}_m(N_2, T, V) = \frac{V^{N_2}}{N_2! h^{3N_2}} \left( \frac{4\pi m}{\beta} \right)^{3N_2/2} e^{N_2\beta\epsilon} \mathcal{Z}_{\text{rot}}$$

where

$$\mathcal{Z}_{\text{rot}} = \frac{1}{h^{2N_2}} \left\{ \int_0^{2\pi} d\phi \int_0^\pi d\theta \int dp_\phi dp_\theta \exp \left[ -\frac{\beta}{2I} \left( p_\theta^2 + \frac{p_\phi^2}{\sin^2 \theta} \right) \right] \right\}^{N_2} = \left( \frac{8I\pi^2}{h^2\beta} \right)^{N_2}$$

Mathematica code:

```
In[1]:= Integrate[
2*Pi*Exp[(-\[Beta]/(2*II))*(p\[Theta]^2 +
p\[Phi]^2/Sin\[Theta]^2)], {\[Theta], 0,
Pi}, {p\[Theta], -Infinity, Infinity}, {p\[Phi], -Infinity,
Infinity}]

Out[1]= (8 II \[Pi]^2)/\[Beta]
```

So we have

$$\mathcal{Z}_m(N_2, T, V) = \boxed{\frac{V^{N_2}}{N_2! h^{3N_2}} \left( \frac{4\pi m}{\beta} \right)^{3N_2/2} \left( \frac{8I\pi^2}{h^2\beta} \right)^{N_2} e^{N_2\beta\epsilon}}$$

(c) At equilibrium, the total entropy is maximized. This implies that  $\mathcal{Z}_a \mathcal{Z}_m$  is extremized i.e.  $\ln \mathcal{Z}_a + \ln \mathcal{Z}_m$  is extremized (since the log is a monotonically increasing function). Using the Stirling approximation we find

$$\begin{aligned} \ln \mathcal{Z}_a &= -N_1 \ln N_1 + \ln \frac{V^{N_1}}{h^{3N_1}} + \frac{3N_1}{2} \log \frac{2\pi m}{\beta} \\ \ln \mathcal{Z}_m &= -N_2 \ln N_2 + \ln \frac{V^{N_2}}{h^{3N_2}} + \frac{3N_2}{2} \log \frac{4\pi m}{\beta} + N_2 \log \left[ \frac{8I\pi^2}{h^2\beta} e^{\beta\epsilon} \right]. \end{aligned}$$

Setting  $N_2 = (N - N_1/2)$  and writing

$$\frac{\partial}{\partial N_1} [\ln \mathcal{Z}_a + \ln \mathcal{Z}_m] = 0$$

gives us

$$\ln \left[ \frac{2n_m}{n_a^2} \right] = \ln \left[ \frac{2N_2 V}{N_1^2} \right] = \ln \left[ \frac{(N - N_1)V}{N_1^2} \right] = 1 + 3 \ln h + \frac{1}{2} \ln(256\pi) + \frac{3}{2} \ln(k_B m T) - \ln \left( \frac{I k_B T e^{\epsilon/k_B T}}{h^2} \right)$$

And so we have

$$\frac{n_m}{n_a^2} = \frac{8\sqrt{\pi} h I}{m^{3/2} \sqrt{k_B T}} e^{1+\epsilon/k_B T}$$

Mathematica code:

```
In[52]:= A = (8 II \[Pi]^2)/(h^2*\[Beta])*Exp\[Beta]*e;

In[56]:= N2 = (n - N1)/2;

In[57]:= D[-N1*Log[N1] + 
Log[V^N1/(h^(3*N1))] + (3*N1/2) Log[2*Pi*m*k*T] 
- N2*Log[N2] + Log[V^N2/(h^(3*N2))] + (3*N2/2)*Log[2*Pi*m*k*T] + 
N2*Log[A], N1] // FullSimplify

Out[57]= 1/4 (-2 - 6 Log[h] + 2 Log[n - N1] - 4 Log[N1] - 
Log[256 \[Pi]] + 3 Log[k m T] + 2 Log[V] - 
2 Log[(E^(e \[Beta]) II)/(h^2 \[Beta]))]

In[62]:= B = -1 - 
3 Log[h] - (1/2) Log[256 \[Pi]] + (3/2) Log[k m T] - 
Log[(E^(e \[Beta]) II)/(h^2 \[Beta])];

In[63]:= (1/2)*Exp[-B] /. {\[Beta] -> 1/(k*T)} // FullSimplify

Out[63]= (8 E^(1 + e/(k T)) h II k Sqrt[\[Pi]] T)/(k m T)^(3/2)
```

#### 4. Fluctuation-induced dipole interactions.

(a) We may rewrite  $V(r)$  as

$$V(r) = \frac{1}{r^3} \left[ 3D_1 D_2 \cos \theta_1 \cos \theta_2 - \vec{D}_1 \cdot \vec{D}_2 \right]$$

putting things in coordinate form we have

$$V(r) = \frac{D_1 D_2}{r^3} \left[ 2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos(\phi_1 - \phi_2) \right]$$

where I have used the fact that

$$\vec{D}_1 \cdot \vec{D}_2 = D_1 D_2 (\cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \cos(\phi_1 - \phi_2))$$

With this we can calculate the partition function as follows (ignoring factors of  $h$  for now):

$$\mathcal{Z}(r) = \int_0^{2\pi} d\phi_1 \int_0^{2\pi} d\phi_2 \int_0^\pi d\theta_1 \int_0^\pi d\theta_2 \exp(\beta V)$$

Expanding

$$\exp(\beta V) \approx 1 + \beta V + \frac{1}{2} \beta^2 V^2 + \dots$$

we get

$$\mathcal{Z}(r) \approx 4\pi^4 + 0 + \frac{9}{4} D_1^2 D_2^2 \pi^4 \frac{\beta^2}{r^6} + \dots$$

Mathematica code:

```

(*D1 dot D2*)
In[28]:= v1 = {D1*Sin[[Theta]1]*Cos[[Phi]1],
D1*Sin[[Theta]1]*Sin[[Phi]1], D1*Cos[[Theta]1]}

Out[28]= {D1 Cos[[Phi]1] Sin[[Theta]1],
D1 Sin[[Theta]1] Sin[[Phi]1], D1 Cos[[Theta]1]}

In[29]:= v2 = {D2*Sin[[Theta]2]*Cos[[Phi]2],
D2*Sin[[Theta]2]*Sin[[Phi]2], D2*Cos[[Theta]2]}

Out[29]= {D2 Cos[[Phi]2] Sin[[Theta]2],
D2 Sin[[Theta]2] Sin[[Phi]2], D2 Cos[[Theta]2]}

In[31]:= Dot[v1, v2] // FullSimplify

Out[31]= D1 D2 (Cos[[Theta]1] Cos[[Theta]2] +
Cos[[Phi]1 - \[Phi]2] Sin[[Theta]1] Sin[[Theta]2])

(*First order*)
In[33]:= (*First order*)

In[34]:= Integrate[[Beta] (D1*D2)/(R^3)*(2*Cos[[Theta]1]*
Cos[[Theta]2] -
Sin[[Theta]1]*Sin[[Theta]2]*
Cos[[Phi]1 - \[Phi]2]), {{Theta]1, 0, Pi}, {Theta]2, 0,
Pi}, {{Phi]1, 0, 2 Pi}, {Phi]2, 0, 2 Pi}}

Out[34]= 0

(*Second order*)
In[32]:= (*Second order*)

In[25]:= Integrate[(\[Beta]^2/
2)*(D1*D2)^2/(R^6)*(2*Cos[[Theta]1]*Cos[[Theta]2] -
Sin[[Theta]1]*Sin[[Theta]2]*
Cos[[Phi]1 - \[Phi]2])^2, {{Theta]1, 0, Pi}, {Theta]2, 0,
Pi}, {{Phi]1, 0, 2 Pi}, {Phi]2, 0, 2 Pi}}

Out[25]= (9 D1^2 D2^2 \[Pi]^4 \[Beta]^2)/(4 R^6)

```

(b) From  $\mathcal{Z}(r)$  we can find  $U(r)$  as follows:

*blah*

(c)

*blah*

(d)

*blah*

## 5. Molecular adsorption.

(a) The smallest energy is attained whenever all molecules lie on the  $xy$  plane. Each molecule has two choices for its alignment. With  $N$  molecules, there are  $2^N$  choices for which the energy is minimal,  $E_{\min} = 0$ .

The largest microstate energy is attained whenever all molecules are aligned in the  $z$ -direction. The energy associated with this microstate is  $E_{\max} = N\epsilon$ .

(b) The total energy is  $E = N_z\epsilon$  where  $N_z$  is the number of molecules aligned in the  $z$ -direction. This leaves  $N - N_z$  molecules in the  $xy$  plane. The number of microcanonical microstates is obtained by counting how many ways we could pick  $N_z$  molecules out of  $N$  molecules, multiplied the number of ways to configure the  $N - N_z$  molecules on the  $xy$  plane, which is  $2^{N-N_z}$ .

$$\Omega(E, N) = \binom{N}{N_z} 2^{N-N_z} = \frac{N!}{N_z!(N - N_z)!} 2^{N-N_z}$$



The entropy is given by

$$S(E, N) = k_B \ln \Omega(E, N) \\ = k_B \ln \frac{N!}{N_z!(N - N_z)!} + k_B(N - N_z) \ln 2.$$

We recognize that the first term is simply the entropy for a two-level system (Eq. 4.18 in our textbook), so using Stirling's approximation and using  $N_z = E/\epsilon$  we find

$$S(E, N) = -Nk_B \left[ \frac{E}{N\epsilon} \ln \frac{E}{N\epsilon} + \left(1 - \frac{E}{N\epsilon}\right) \ln \left(1 - \frac{E}{N\epsilon}\right) \right] + k_B \left(N - \frac{E}{\epsilon}\right) \ln 2$$

- (c) To find what the heat capacity is we must first find the energy as a function of temperature via the entropy. We know that  $\partial E/\partial S = T$  so inverting gives  $\partial S/\partial E = 1/T$ . So,

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{k_B}{\epsilon} \left[ \log \left(1 - \frac{E}{N\epsilon}\right) - \log \left(\frac{2E}{N\epsilon}\right) \right]$$

from which we find

$$E(T) = \frac{N\epsilon}{1 + 2e^{\epsilon/k_B T}}.$$

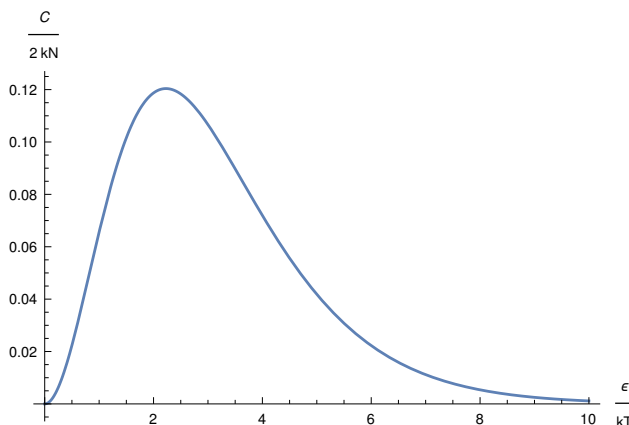
The heat capacity is given by

$$C = \frac{dE}{dT} = \frac{2N\epsilon^2}{k_B} \frac{e^{\epsilon/k_B T}}{T^2 (1 + 2e^{\epsilon/k_B T})^2}$$

Letting  $x = \epsilon/k_B T$  then we can write

$$\frac{C(x)}{2k_B N} = x^2 \frac{e^x}{(1 + 2e^x)^2}.$$

Now we can sketch:



Mathematica code:

```
In[33]:= S = -N*
k*((En/(N*e))*Log[En/(N*e)] + (1 - En/(N*e))*Log[1 - En/(N*e)]) +
k*(N - En/e)*Log[2];

In[36]:= D[S, En] // FullSimplify
```

```

Out[36]= (k (Log[1 - En/(e N)] - Log[(2 En)/(e N)]))/e
In[37]:= Solve[
1/T == (k (Log[1 - En/(e N)] - Log[(2 En)/(e N)]))/e, En]
Out[37]= {{En -> (e N)/(1 + 2 E^(e/(k T)))}}
In[42]:= HC = D[(e N)/(1 + 2 E^(e/(k T))), T] // FullSimplify
Out[42]= (2 e^2 E^(e/(k T)) N)/(k (T + 2 E^(e/(k T)) T)^2)
(*Plotting*)
In[48]:= Plot[x^2*Exp[x]/(1 + 2*Exp[x])^2, {x, 0, 10},
AxesLabel -> {\[Epsilon]/kT, C/(2 kN)}]

```

- (d) There are  $N_z$  molecules that are standing up, so the probability that any specific molecule is standing up is simply  $N_z/N$ :

$$\text{Pr} = \frac{N_z}{N} = \frac{E}{N\epsilon} = \frac{1}{1 + 2e^{\epsilon/k_B T}}$$

- (e) Since the heat capacity is positive for all  $T > 0$ , the energy  $E(T)$  is always increasing as  $T \rightarrow \infty$ . However, it turns out that  $E$  approach as a limit:

$$E_{\max} = \lim_{T \rightarrow \infty} \frac{N\epsilon}{1 + 2e^{\epsilon/k_B T}} = \frac{N\epsilon}{3}$$

## 6. Curie susceptibility.

- (a) In general, the Gibbs partition function is given by

$$\begin{aligned}
\mathcal{Z}(N, T, B) &= \sum \exp(\beta \vec{B} \cdot \vec{M}) \\
&= \sum_{\text{states}} \exp\left(\beta \mu B \sum_{i=1}^N m_i\right) \\
&= \left[ \sum_{m_i=-s, \dots, s} \exp(\beta \mu B m_i) \right]^N \\
&= Z^N
\end{aligned}$$

Now we want to evaluate what each  $Z$  is:

$$\begin{aligned}
Z &= \exp(\beta \mu B(-s)) + \exp(\beta \mu B(-s+1)) + \dots + \exp(\beta \mu B s) \\
&= \exp(\beta \mu B(-s)) [1 + \exp(\beta \mu B) + \exp(2\beta \mu B) + \dots + \exp(2\beta \mu s)] \\
&= \exp(\beta \mu B(-s)) \frac{1 - \exp((2s+1)\beta \mu B)}{1 - \exp(\beta \mu B)} \\
&= \frac{\exp(-\beta \mu B s) - \exp(\beta \mu B(s+1))}{1 - \exp(\beta \mu B)}.
\end{aligned}$$

So,

$$\mathcal{Z}(N, T, B) = \left[ \frac{\exp(-\beta \mu B s) - \exp(\beta \mu B(s+1))}{1 - \exp(\beta \mu B)} \right]^N$$

(b) The Gibbs free energy is

$$G = -k_B T \ln \mathcal{Z} = -k_B T N \ln \left[ \cosh(s\beta\mu B) + \coth\left(\frac{\beta\mu B}{2}\right) \sinh(\beta\mu B s) \right]$$

Mathematica code:

```
In[62]:= Z = (Exp[-\[Beta]*\[Mu]*B*s] -
Exp[\[Beta]*\[Mu]*B*(s + 1)])/(1 - Exp[\[Beta]*\[Mu]*B]);

In[63]:= G = -kB*T*Log[Z];

In[65]:= G // FullSimplify

Out[65]= -kB T Log[
Cosh[B s \[Beta] \[Mu]] +
Coth[(B \[Beta] \[Mu])/2] Sinh[B s \[Beta] \[Mu]]]
```

To obtain  $G$  for small  $B$ , we may Taylor-expand  $G$  in powers of  $B$  near  $B = 0$  in Mathematica. The result is

$$G(B) \approx -k_B T N \ln(1 + 2s) - \frac{N}{6} B^2 [k_B s(1 + s) T \beta^2 \mu^2] + O(B)^4$$

Mathematica code:

```
In[68]:= Series[G, {B, 0, 3}] // FullSimplify

Out[68]= SeriesData[B, 0, {-kB T Log[1 + 2 s], 0,
Rational[-1, 6] kB s (1 + s) T \[Beta]^2 \[Mu]^2}, 0, 4, 1]
```

Notice that

$$G(B = 0) = \lim_{B \rightarrow 0} -k_B T N \ln \left[ \cosh(s\beta\mu B) + \coth\left(\frac{\beta\mu B}{2}\right) \sinh(\beta\mu B s) \right] = -k_B T N \ln(1 + 2s).$$

Mathematica code:

```
In[69]:= Limit[(Exp[-\[Beta]*\[Mu]*B*s] -
Exp[\[Beta]*\[Mu]*B*(s + 1)])/(1 - Exp[\[Beta]*\[Mu]*B]), B -> 0]

Out[69]= 1 + 2 s
```

Therefore, we have

$$G(B) \approx G(0) - \frac{N\mu^2 B^2 s(1 + s)}{6k_B T} + O(B^4)$$

as desired.

- (c) **I believe we actually want to calculate  $\chi = \partial \langle M_z \rangle / \partial B$ , since otherwise if we stay with the definition in the problem then we don't get  $B$ -dependence.** With this, let us calculate  $\langle M_z \rangle$  by following the steps in the textbook:

$$\langle M_z \rangle = \left\langle \sum_{i=1}^N m_i \right\rangle = \frac{1}{\beta} \frac{\partial}{\partial B} \ln \mathcal{Z} = \frac{\partial}{\partial B} (k_B T \ln \mathcal{Z}) = -\frac{\partial G}{\partial B}.$$

With this,

$$\chi = \left. \frac{\partial \langle M_z \rangle}{\partial B} \right|_{B=0} = -\left. \frac{\partial^2 G}{\partial B^2} \right|_{B=0} \approx \frac{N\mu^2 s(1 + s)}{3k_B T}$$

which is consistent with Curie's law:  $\chi = c/T$  where  $c = N\mu^2 s(1 + s)/3k_B$ .

(d) By definition,

$$C_B - C_M = -B \frac{\partial \langle M_z \rangle}{\partial T} = \left( \frac{N \mu^2 s(1+s)}{3k_B} \right) \frac{B^2}{T^2} = \frac{cB^2}{T^2}$$

as desired, where we have used the fact that the magnetic field  $B$  is independent of temperature  $T$ .

Mathematica code:

```
In[75]:= GB = G0 - N*[Mu]^2*B^2*s (1 + s)/(6*kB*T)
Out[75]= G0 - (B^2 N s (1 + s) \[Mu]^2)/(6 kB T)
In[77]:= -B*D[-D[GB, B], T] // FullSimplify
Out[77]= (B^2 N s (1 + s) \[Mu]^2)/(3 kB T^2)
```

## 7. Langmuir isotherms.

(a) Following pages 114-115 of the textbook we may use  $\lambda(T) = h/\sqrt{2\pi m k_B T}$

$$\mu = k_B T \ln \left( \frac{N}{V} \lambda^3 \right) = k_B T \ln \left[ \frac{P}{k_B T} \frac{h^3}{(2\pi m k_B T)^{3/2}} \right] = k_B T \left[ \ln(P T^{-5/2}) + \underbrace{\ln \left( \frac{h^3}{k_B^{5/2} (2\pi m)^{3/2}} \right)}_{A_0} \right]$$

(b) The grand partition function is a weighted sum over all microstates. Given  $N$  sites, we must choose  $N$  sites which will receive a gas particle. The weight associated with this assignment is  $\exp(-\beta \epsilon N) \exp(\beta \mu N)$ . Then, we have to sum over all possible configurations:

$$Q = \sum_{N=0}^N \binom{N}{N} e^{-\beta \epsilon N} e^{\beta \mu N} = \left[ 1 + e^{\beta(\mu - \epsilon)} \right]^N$$

where we have used the fact that this is simply a binomial expansion.

(c) The fraction of occupied surface sites is

$$f = \frac{\langle N \rangle}{N} = \frac{1}{\beta N} \frac{\partial}{\partial \mu} \ln Q = \frac{1}{1 + e^{\beta(\epsilon - \mu)}} = \frac{1}{1 + e^{\beta \epsilon} e^{-\beta \mu}}$$

where we have followed Eq 4.103 in the textbook. Mathematica code:

```
In[82]:= (1/(\[Beta]*N))*
D[Log[(1 + E^(\[Beta] (-\[Epsilon] + \[Mu])))]^
N], \[Mu]] // FullSimplify
Out[82]= 1/(1 + E^(\[Beta] (\[Epsilon] - \[Mu])))
```

Now, since the gas and the surface has the same temperature and chemical potential we have

$$e^{-\beta \mu} = \left( \frac{N}{V} \lambda^3 \right)^{-1} = \frac{k_B T}{P \lambda^3}.$$

With this, we find

$$f = f(T, P) = \frac{1}{1 + e^{\beta \epsilon} \frac{k_B T}{P \lambda^3}} = \frac{P}{P + P_0(T)}$$

where

$$P_0(T) = \frac{k_B T}{\lambda^3} e^{\epsilon/k_B T}$$

(d)

$$\langle e^{-ikN} \rangle = \frac{1}{Q(\beta\mu)} [1 + e^{\beta(\mu-\epsilon)} e^{-ik}]^N = \frac{Q(\beta\mu - ik)}{Q(\beta\mu)}.$$

With this,

$$\begin{aligned} \langle N^m \rangle_c &= \frac{\partial^m}{\partial(-ik)^m} \ln \frac{Q(\beta\mu - ik)}{Q(\beta\mu)} \\ &= \frac{\partial^m}{\partial(-ik)^m} \ln Q(\beta\mu - ik) \\ &= \frac{\partial^m}{\partial(-ik)^m} [-\beta \mathcal{G}(\beta\mu - ik)] \end{aligned}$$

where we have used Eq. 4.105 in the textbook, with  $\mathcal{G}$  denoting the grand potential. With this, we find

$$\langle N^m \rangle_c = -\beta \frac{\partial^m}{\partial(\beta\mu)^m} \mathcal{G}(\beta\mu - ik) \Big|_T = -\beta^{1-m} \frac{\partial^m \mathcal{G}}{\partial \mu^m} \Big|_T = \boxed{-(k_B T)^{m-1} \frac{\partial^m \mathcal{G}}{\partial \mu^m} \Big|_T}$$

(e) Setting  $m = 2$  we find

$$\langle N^2 \rangle_c = -k_B T \frac{\partial^2 \mathcal{G}}{\partial \mu^2} \Big|_T.$$

Observe that

$$\langle N \rangle = \frac{1}{\beta} \partial_\mu \ln Q = \frac{-\beta}{\beta} \partial_\mu \mathcal{G} = -\frac{\partial \mathcal{G}}{\partial \mu}.$$

We thus find

$$\boxed{\langle N^2 \rangle_c = k_B T \frac{\partial \langle N \rangle}{\partial \mu} \Big|_T}$$

(f) We just calculate away...

$$\begin{aligned} \frac{\langle N^2 \rangle_c}{\langle N \rangle_c^2} &= \frac{\langle N^2 \rangle_c}{\langle N \rangle^2} \\ &= \frac{k_B T \partial_\mu \langle N \rangle}{N^2 f^2} \Big|_T \\ &= \frac{k_B T}{N^2 f^2} \left( \frac{\partial}{\partial \mu} \frac{N}{1 + e^{\beta\epsilon - \beta\mu}} \right) \Big|_T \\ &= \frac{1}{N f^2} \frac{e^{\beta(\epsilon - \mu)}}{(e^{\beta\epsilon} + e^{\beta\mu})^2} \Big|_T \\ &= \frac{1}{N f^2} \left[ \frac{1}{1 + e^{\beta\epsilon} e^{-\beta\mu}} \left( 1 - \frac{1}{1 + e^{\beta\epsilon} e^{-\beta\mu}} \right) \right] \Big|_T \\ &= \frac{f(1-f)}{N f^2} \\ &= \boxed{\frac{1-f}{N f}} \end{aligned}$$

Mathematica code:

```

In[93]:= D[1/(
1 + E^(\[Beta] (\[Epsilon] - \[Mu]))), \[Mu]] // FullSimplify

Out[93]= (E^(\[Beta] (\[Epsilon] + \[Mu])) \[Beta])/(E^(\[Beta] \
\[Epsilon]) + E^(\[Beta] \[Mu]))^2

```

## 8. (Optional) One dimensional polymer.

(a) The partition function here is similar to that of a two-level system:

$$\mathcal{Z}(T, N) = \sum_{s_1=0}^1 \sum_{s_2=0}^1 \cdots \sum_{s_N=0}^1 \exp^{-\beta \epsilon \sum_{i=1}^N s_i} = \boxed{[1 + \exp(-\beta \epsilon)]^N}$$

here we keep  $\beta = 1/k_B T$  for simplicity, but it's understood that the variables  $\beta$  and  $T$  are equivalent.

(b) Consider a monomer. The probability that it is aligned along its short axis and along its long axis, respectively, are

$$\boxed{p_{\text{short}} = \frac{e^{-\beta \epsilon}}{1 + e^{-\beta \epsilon}} \quad p_{\text{long}} = \frac{1}{1 + e^{-\beta \epsilon}}}$$

so the relative probability for short versus long alignment is simply the Boltzmann weight  $\boxed{e^{-\beta \epsilon}}$ .

(c) The average length of the polymer is  $N$  times the average length of a monomer:

$$\langle L(T, N) \rangle = N \langle L_1(T) \rangle = \frac{N}{1 + e^{-\beta \epsilon}} [a e^{-\beta \epsilon} + 2a] = \boxed{aN \frac{2 + e^{-\beta \epsilon}}{1 + e^{-\beta \epsilon}}}$$

(d) Since the links are independent, we have

$$\begin{aligned} \langle L(T, N)^2 \rangle_c &= N \langle L_1(T) \rangle_c^2 \\ &= N [\langle L_1(T)^2 \rangle - \langle L_1(T) \rangle^2] \\ &= N \left[ \frac{a^2 e^{-\beta \epsilon} + 4a^2}{1 + e^{-\beta \epsilon}} - a^2 \left( \frac{2 + e^{-\beta \epsilon}}{1 + e^{-\beta \epsilon}} \right)^2 \right] \\ &= \boxed{\frac{Na^2}{2} \frac{1}{1 + \cosh(\beta \epsilon)}} \end{aligned}$$

(e) The central limit theorem says that in the  $N \rightarrow \infty$  limit  $L(T, N)$  follows the normal distribution with the same mean and variance as the binomial which  $L(T, N)$  follows:

$$\boxed{L(T, N) \sim \mathcal{N} \left\{ aN \frac{2 + e^{-\beta \epsilon}}{1 + e^{-\beta \epsilon}}, \frac{Na^2}{2} \frac{1}{1 + \cosh(\beta \epsilon)} \right\} \equiv \mathcal{N} \left\{ \frac{Na}{2} \left[ 3 + \tanh\left(\frac{\beta \epsilon}{2}\right) \right], \frac{Na^2}{2} \frac{1}{1 + \cosh(\beta \epsilon)} \right\}}$$

where  $\mathcal{N} \{\mu, \sigma^2\}$  denotes the normal distribution with mean  $\mu$  and variance  $\sigma^2$ .

Mathematica code:

```

In[7]:= L =
a*(2 + Exp[-\[Beta]*\[Epsilon]])/(1 + Exp[-\[Beta]*\[Epsilon]]);

In[6]:= L2 =
a^2*Exp[-\[Beta]*\[Epsilon]]/(1 + Exp[-\[Beta]*\[Epsilon]]) +
4*a^2/(1 + Exp[-\[Beta]*\[Epsilon]]);

```

```

In[9]:= N*(L2 - L^2) // FullSimplify
Out[9]= (a^2 N)/(2 + 2 Cosh[\[Beta] \[Epsilon]])

In[12]:= ExpToTrig[L] // FullSimplify
Out[12]= 1/2 a (3 + Tanh[(\[Beta] \[Epsilon])/2])

```

## 9. (Optional) Classical virial theorem.

(a) We simply calculate, using the definition and integration by parts:

$$\begin{aligned}
\left\langle \frac{\partial f}{\partial X_i} \right\rangle &= \frac{1}{\mathcal{Z}} \int \frac{\partial f}{\partial X_i} \exp(-\beta \mathcal{H}) d\Gamma \\
&= -\frac{1}{\mathcal{Z}} \int f \frac{\partial}{\partial X_i} \exp(-\beta \mathcal{H}) d\Gamma \\
&= \beta \frac{1}{\mathcal{Z}} \int f \frac{\partial \mathcal{H}}{\partial X_i} \exp(-\beta \mathcal{H}) d\Gamma \\
&= \beta \left\langle f \frac{\partial \mathcal{H}}{\partial X_i} \right\rangle
\end{aligned}$$

(b) With  $f = q_j$  and  $X_i = q_i$  we have

$$k_B T \delta_{ij} = \left\langle q_j \frac{\partial \mathcal{H}}{\partial q_i} \right\rangle = -\langle q_j \dot{p}_i \rangle$$

With  $f = q_j$  and  $X_i = p_i$  we have

$$0 = \beta \left\langle q_j \frac{\partial \mathcal{H}}{\partial p_i} \right\rangle \implies 0 = \langle q_j \dot{q}_i \rangle$$

## 10. (Optional) Disordered glass.

(a) Partition function contribution from one defect:

$$\mathcal{Z}(T) = \exp[-\beta \epsilon] + \exp[-\beta(\epsilon + \delta)] = e^{-\beta \epsilon} (1 + e^{-\beta \delta})$$

If we want the full partition function then we simply put in indices and take the product of the individual partition functions.

Average energy contribution from one defect:

$$E(T) = -\frac{\partial \ln \mathcal{Z}}{\partial \beta} = -\frac{\partial}{\partial \beta} \ln [e^{-\beta \epsilon} (1 + e^{-\beta \delta})] = \epsilon + \frac{\delta}{1 + e^{\beta \delta}}$$

If we want the total average energy then we just sum over  $N$  defects.

Heat capacity contribution from each defect:

$$C(T) = \frac{\partial E}{\partial T} = \frac{\delta^2}{4k_B T^2} \operatorname{sech}^2 \left( \frac{\delta}{2k_B T} \right)$$

Again if we want the full heat capacity then we just add indices in an sum over all defects.

Mathematica code:

```

In[25]:= Z = Exp[-\[Beta]*\[Epsilon]]*(1 + Exp[-\[Beta]*\[Delta]])
Out[25]= E^(-\[Beta] \[Epsilon]) (1 + E^(-\[Beta] \[Delta]))
In[26]:= -D[Log[Z], \[Beta]] // FullSimplify
Out[26]= \[Delta]/(1 + E^(\[Beta] \[Delta])) + \[Epsilon]
In[27]:= D[-D[Log[Z], \[Beta]] /. {\[Beta] -> 1/(k*T)},
T] // FullSimplify
Out[27]= (\[Delta]^2 Sech[\[Delta]/(2 k T)]^2)/(4 k T^2)

```

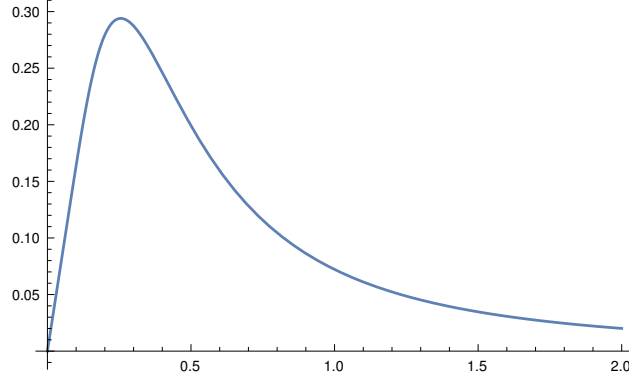
(b) The heat capacity as an integral, assuming  $\rho(\delta) d\delta = \rho d\delta$ , is

$$\begin{aligned}
C(T) &= \int_0^\Delta d\delta \rho(\delta) \frac{\delta^2}{4k_B T^2} \operatorname{sech}^2\left(\frac{\delta}{2k_B T}\right) \\
&= \int_0^\Delta d\delta \rho \frac{\delta^2}{4k_B T^2} \operatorname{sech}^2\left(\frac{\delta}{2k_B T}\right) \\
&= \left[ -2k^2 \rho T \operatorname{Li}_2\left(-e^{\frac{\Delta}{kT}}\right) - \frac{1}{6} \pi^2 k^2 \rho T + \frac{1}{T} \Delta^2 \rho \left(1 - \frac{1}{e^{\frac{\Delta}{kT}} + 1}\right) - 2\Delta k \rho \log\left(e^{\frac{\Delta}{kT}} + 1\right) \right]
\end{aligned}$$

From here we find that

$$\lim_{T \rightarrow 0} C(T) = \lim_{T \rightarrow \infty} C(T) = 0$$

Schematically  $C(T)$  looks like this



Mathematica code:

```

In[30]:= Integrate[\[Rho]*
D[-D[Log[Z], \[Beta]] /. {\[Beta] -> 1/(k*T)}, T], {\[Delta],
0, \[CapitalDelta]] // FullSimplify

Out[30]= ConditionalExpression[-(1/6)
k^2 \[Pi]^2 T \[Rho] + ((1 - 1/(
1 + E^(\[CapitalDelta]/(k T)))) \[CapitalDelta]^2 \[Rho])/T -
2 k \[CapitalDelta] \[Rho] Log[1 + E^(\[CapitalDelta]/(k T))] -
2 k^2 T \[Rho] PolyLog[2, -E^(\[CapitalDelta]/(k T))],
E^(\[CapitalDelta]/(k T)) >= -1]

In[31]:= Limit[-(1/6)
k^2 \[Pi]^2 T \[Rho] + ((1 - 1/(
1 + E^(\[CapitalDelta]/(k T)))) \[CapitalDelta]^2 \[Rho])/T -
2 k \[CapitalDelta] \[Rho] Log[1 + E^(\[CapitalDelta]/(k T))] -
2 k^2 T \[Rho] PolyLog[2, -E^(\[CapitalDelta]/(k T))], T -> 0]

Out[31]= ConditionalExpression[0, \[Rho] \[Element] Reals &&
k \[CapitalDelta] > 0]

```



```

In[32]:= Limit[-(1/6)
k^2 \[Pi]^2 T \[Rho] + ((1 - 1/(
1 + E^(\[CapitalDelta]/(k T)))) \[CapitalDelta]^2 \[Rho])/T -
2 k \[CapitalDelta] \[Rho] Log[1 + E^(\[CapitalDelta]/(k T))] -
2 k^2 T \[Rho] PolyLog[2, -E^(\[CapitalDelta]/(k T))],
T -> Infinity]

Out[32]= 0

```

(c) **No idea how to proceed here.**