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

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

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

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]

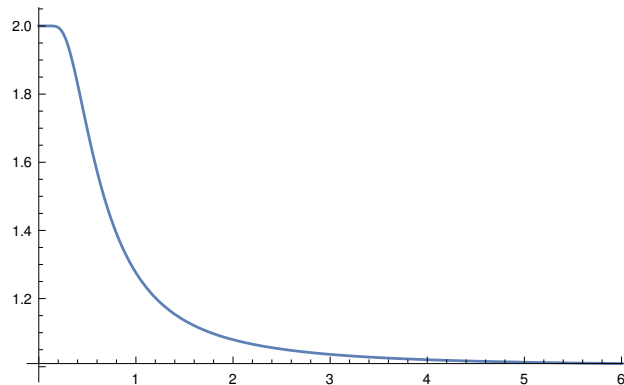
Out[30]= ConditionalExpression[2 k, Ef k \[Mu] > 0]

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 free energy is extremized. 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*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):

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

Expanding

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

we get

$$\mathcal{Z}(r) \approx 16\pi^2 + \frac{16\pi^2}{3} D_1^2 D_2^2 \frac{\beta^2}{r^6} + \dots$$

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[Sin[[Theta]1]*Sin[[Theta]2]*[[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[Sin[[Theta]1]*Sin[[Theta]2]*[[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 [[Phi]^4 [[Beta]^2)/(4 R^6)
```

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

$$\mathcal{Z}(r) = \int \exp(-\beta U(r)) = \int d\Omega [1 - \beta U(r)] = 16\pi^2 [1 - \beta U(r)]$$

we can now read off

$$U(r) = -\frac{1}{\beta} \frac{1}{3} D_1^2 D_2^2 \frac{\beta^2}{r^6} = \boxed{-\frac{D_1^2 D_2^2}{3k_B T r^6}}$$

(c) For this problem we just repeat the computation, but also integrating over D_1, D_2 with extra Boltzmann weights $\exp[-\beta(D_1^2/2\chi_1 + D_2^2/2\chi_2)]$:

$$\mathcal{Z}'(r) = \int_0^\infty dD_1 \int_0^\infty dD_2 \int_0^{2\pi} d\phi_1 \int_0^{2\pi} d\phi_2 \int_0^\pi \sin\theta_1 d\theta_1 \int_0^\pi \sin\theta_2 d\theta_2 \exp(\beta V) \exp[-\beta(D_1^2/2\chi_1 + D_2^2/2\chi_2)]$$

where now we no longer treat D_1, D_2 as constants. Letting Mathematica do the work we get to low order

$$\mathcal{Z}'(r) \approx \frac{8\pi^3}{\beta\sqrt{\chi_1\chi_2}} + \frac{8\pi^3(\chi_1\chi_2)^{3/2}}{3\beta r^6} + \dots \approx \frac{8\pi^3}{\beta\sqrt{\chi_1\chi_2}} \left(1 + \frac{(\chi_1\chi_2)^2}{3r^6}\right)$$

(d) Using the same approach as before, we can simply read off the effective potential:

$$U'(r) = -\frac{1}{\beta} \frac{(\chi_1\chi_2)^2}{3r^6} = \boxed{-k_B T \frac{\chi_1^2 \chi_2^2}{3r^6}}$$

Mathematica code:

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

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

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

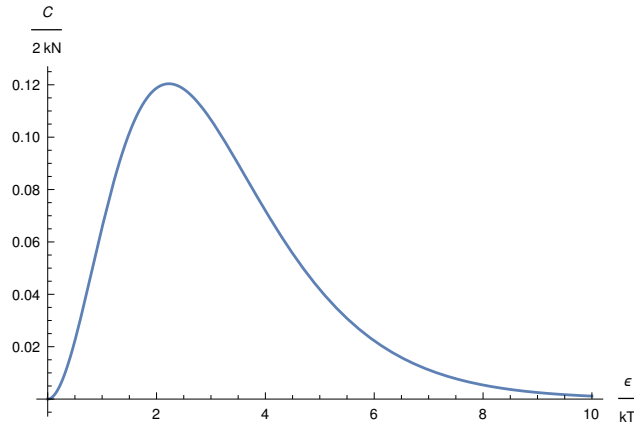
$$C = \frac{dE}{dT} = \frac{2N\epsilon^2}{k_B} \frac{e^{\epsilon/k_B T}}{T^2 (1 + 2e^{\epsilon/k_B T})^2}$$

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:

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

So,

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

(b) The Gibbs free energy is

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

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

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

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,

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

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

- (d) By definition,

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

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:

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

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...

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

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 β 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

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

(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:

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

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

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

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:

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

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

Heat capacity contribution from each defect:

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

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

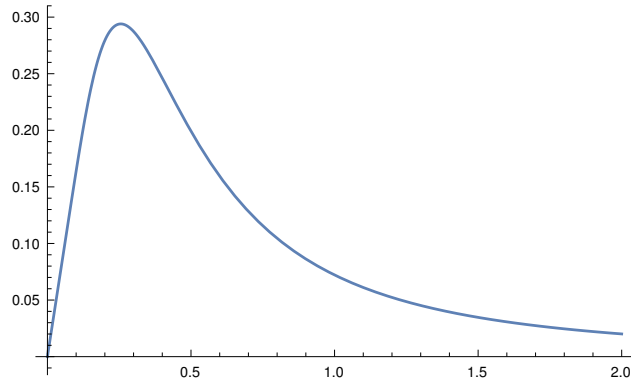
$$\begin{aligned} C(T) &= \int_0^\Delta d\delta \rho(\delta) \frac{\delta^2}{4k_B T^2} \operatorname{sech}^2 \left(\frac{\delta}{2k_B T} \right) \\ &= \int_0^\Delta d\delta \rho \frac{\delta^2}{4k_B T^2} \operatorname{sech}^2 \left(\frac{\delta}{2k_B T} \right) \\ &= \boxed{-2k^2 \rho T \operatorname{Li}_2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

From here we find that

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

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.**