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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 $\mathcal{H} = \sum_n^N \mathcal{H}(n)$ 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.

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

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

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

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 (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:

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

Hence, we have

$$\langle x^2\rangle = \int x^2\rho\, dV = \frac{1}{\mathcal{Z}^{1/N}}\frac{1}{(N!)^{1/N}h^3}\frac{8\pi^3}{\beta^2\sqrt{K\beta}(\beta/m)^{3/2}(K-m\Omega^2)^2} = \frac{1}{\beta(K-m\Omega^2)} = \boxed{\frac{1}{\beta m(\omega^2-\Omega^2)}}$$

$$\langle y^2\rangle = \frac{(N!)^{1/N}h^3}{\beta(K-m\Omega^2)} = \boxed{\frac{1}{\beta m(\omega^2-\Omega^2)}} \qquad \text{by symmetry}$$

$$\langle z^2\rangle = \frac{1}{\mathcal{Z}^{1/N}}\int z^2\rho\, dV = \frac{1}{\mathcal{Z}^{1/N}}\frac{1}{(N!)^{1/N}h^3}\frac{8\pi^3}{(K\beta)^{3/2}(\beta/m)^{3/2}\beta(K-m\Omega^2)} = \boxed{\frac{1}{K\beta}}$$

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

$$\begin{aligned}
\mathcal{Z}_{\text{rot}} &= \frac{1}{h^2}\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \int dp_\phi\, dp_\theta \exp\left(-\frac{\beta}{2I}\left(p_\theta^2 + \frac{p_\phi^2}{\sin^2\theta}\right) + \beta E\mu\cos\theta\right) \\
&= \boxed{\frac{8I\pi^2 \sinh(\beta\mu E)}{Eh^2\beta^2\mu}}
\end{aligned}$$

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

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

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

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

where instead of naivly plugging in $E = 0$ we have taken the limit $E \to 0$ 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:

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

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

(e) Heat capacity is

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

We find

$$\lim_{T\to 0} C = 2k_B$$
$$\lim_{T\to\infty} C = k_B.$$

Mathematica code:

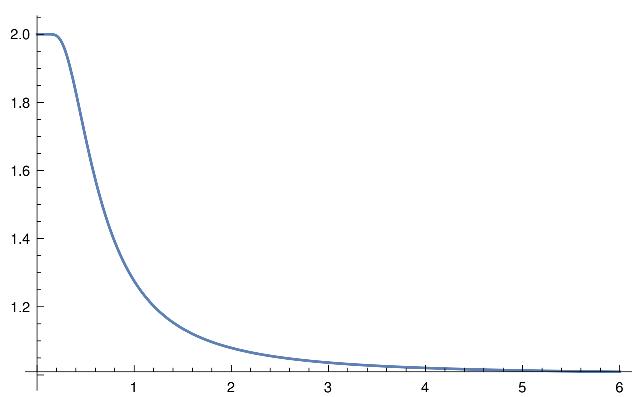
```
In[30]:= Limit[2 k - (Ef^2 \[Mu]^2 Csch[(Ef \[Mu])/(k T)]^2)/(k T^2),
T -> 0]

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 $k_BT \approx E\mu$.

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

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

(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

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

where

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

(c)

4. Fluctuation-induced dipole interactions.

(a)

(b)

(c)

(d)

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 $\boxed{2^N}$ choices for which the energy is minimal, $E_{\text{min}} = 0$.

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

(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}.

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

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

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

(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

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

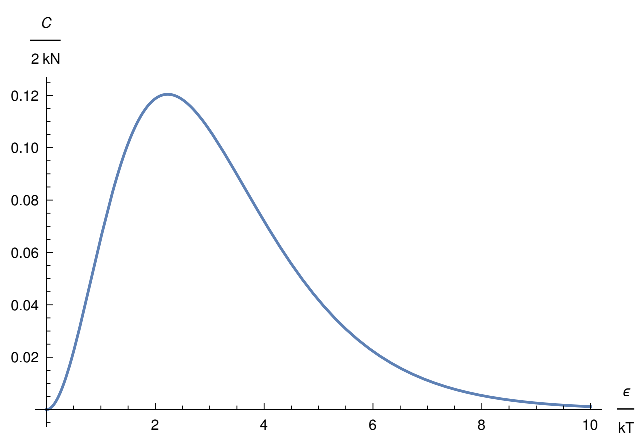
The heat capacity is given by

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

Letting $x = \epsilon/k_BT$ then we can write

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

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:

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

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

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

6. Curie susceptibility.

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

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

Now we want to evaluate what each Z is:

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

So,

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

(b) The Gibbs free energy is

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

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

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

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

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

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

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

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 textook:

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

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 $c = N\mu^2 s(1 + s)/3k_B$.

(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 $\lambda(T) = h/\sqrt{2\pi m k_B T}$

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

(b) The grand partition function is a weighted sum over all microstates. Given $\mathcal{N}$ 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:

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

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

(c) The fraction of occupied surface sites is

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

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

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

where

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

(d)

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

With this,

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

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

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

(e) Setting $m=2$ we find

$$\langle N^2\rangle_c = -k_BT\frac{\partial^2\mathcal{G}}{\partial\mu^2}\bigg|_T.$$

Observe that

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

We thus find

$$\boxed{\langle N^2\rangle_c = k_BT\frac{\partial\langle N\rangle}{\partial\mu}\bigg|_T}$$

(f) We just calculate away...

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

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)

(b)

(c)

(d)

(e)

9. (Optional) Classical virial theorem.

(a)

(b)

10. (Optional) Disordered gas.

(a)

(b)

(c)