1. The partition function for this chain is:

$$Z = (g_0 e^{-\beta\epsilon_0+\beta f\ell_0} + g_1 e^{-\beta(\epsilon_0+\Delta\epsilon)+\beta f(\ell_0-\Delta\ell)})^N$$

Notice that this is not one of the partition functions we have seen before. It is a generalized ensemble (see IMSM section 3.5 for more information on this). Though this has only been mentioned in class thus far, you can think of it in analogy to the grand canonical ensemble replacing N with L and μ for f.

(a) For this question just consider the partition function for a single segment:

$$\begin{aligned}\langle n_i\rangle &= \frac{(0) * g_0 e^{-\beta\epsilon_0+\beta f\ell_0} + (1) * g_1 e^{-\beta(\epsilon_0+\Delta\epsilon)+\beta f(\ell_0-\Delta\ell)}}{g_0 e^{-\beta\epsilon_0+\beta f\ell_0} + g_1 e^{-\beta(\epsilon_0+\Delta\epsilon)+\beta f(\ell_0-\Delta\ell)}}\\ &= \frac{r}{e^{\beta(\Delta\epsilon+f\Delta\ell)}+r}\end{aligned}$$

(b) There are a few ways to approach this. One would be to perform the following derivative:

$$\langle L\rangle = \left(\frac{\partial \ln Z}{\partial \beta f}\right)_{\beta,N}$$

Alternatively, one could just use the result from part (a):

$$\langle L\rangle = N(\ell_0 - \Delta\ell\langle n_i\rangle)$$

(c) Just as in part (c), this can be done with a derivative (remember to keep βf constant) :

$$\langle E\rangle = \left(\frac{\partial \ln Z}{\partial(-\beta)}\right)_{\beta f,N}$$

or by using part (a):

$$\langle E\rangle = N(\epsilon_0 + \Delta\epsilon\langle n_i\rangle)$$

(d) To evaluate the mean square fluctuations in length, consider the following:

$$\begin{aligned}\langle(\delta L)^2\rangle &= \langle(L-\langle L\rangle)^2\rangle\\ &= \langle(\sum_{i=1}^{N}\ell_i - N\langle\ell\rangle)^2\rangle\\ &= \langle\sum_{i=1}^{N}\sum_{j=1}^{N}\ell_i\ell_j - 2N\langle\ell\rangle\sum_{i=1}^{N}\ell_i + N^2\langle\ell\rangle^2\rangle\\ &= \langle\sum_{i=1}^{N}\ell_i^2\rangle + \langle\sum_{i\neq j}\ell_i\ell_j\rangle - 2N\langle\ell\rangle\langle\sum_{i=1}^{N}\ell_i\rangle + N^2\langle\ell\rangle^2\end{aligned}$$

where the sum $\sum_{i\neq j}$ is a double sum over i and j such that $i \neq j$. This distinction must be made so as to appropriately account for the types of terms present. In calculating the number of terms in this sum, there are N choices for the first segment and $N-1$ for the second, since the same segment cannot be selected twice. This considered, we have

$$\begin{aligned}\langle(\delta L)^2\rangle &= N\langle\ell^2\rangle + N(N-1)\langle\ell\rangle^2 - 2N^2\langle\ell\rangle^2 + N^2\langle\ell\rangle^2 \\ &= N\langle\ell^2\rangle + N(N-1)\langle\ell\rangle^2 - N^2\langle\ell\rangle^2 \\ &= N\langle(\delta\ell)^2\rangle\end{aligned}$$

Notice that the mean square fluctuations are extensive, as expected. Continuing the work from above:

$$\begin{aligned}\langle(\delta L)^2\rangle &= N\Big\langle\,(\ell_i - \langle\ell\rangle)^2\,\Big\rangle \\ &= N\left\langle\Big(\ell_0 - n_i\Delta\ell - (\ell_0 - \Delta\ell\langle n_i\rangle)\Big)^2\right\rangle \\ &= N\Delta\ell^2(\langle n_i^2\rangle - \langle n_i\rangle^2) \\ &= N\Delta\ell^2\langle n_i\rangle(1-\langle n_i\rangle) \\ &= N\Delta\ell^2\frac{re^{\beta(\Delta\epsilon+f\Delta\ell)}}{(e^{\beta(\Delta\epsilon+f\Delta\ell)}+r)^2}\end{aligned}$$

(e) Using properties of generalized ensembles, it is easy to show:

$$\langle(\delta L)^2\rangle = \left(\frac{\partial^2\ln Z}{\partial(\beta f)^2}\right)_{\beta,N} = \left(\frac{\partial\langle L\rangle}{\partial(\beta f)}\right)_{\beta,N}$$

(f) This is a simple Taylor expansion that will use results from parts (e) and (b):

$$\langle L\rangle \approx \langle L\rangle|_{f=0} + \left(\frac{\partial\langle L\rangle}{\partial(\beta f)}\right)_{\beta,N}\Bigg|_{f=0} * \beta f$$

$$\langle L\rangle \approx N\ell_0 - N\Delta\ell\left(\frac{r}{e^{\beta\Delta\epsilon}+r}\right) + N\beta f\Delta\ell^2\left(\frac{re^{\beta\Delta\epsilon}}{(e^{\beta\Delta\epsilon}+r)^2}\right)$$

(g) To get the constant tension heat capacity recall its definition in terms of enthalpy (analogous to the constant pressure heat capacity):

$$C_f = \left(\frac{\partial H}{\partial T}\right)_f$$

where the enthalpy is defined as $H = E - fL$. We can just differentiate this expression:

$$C_f = \left(\frac{\partial E}{\partial T}\right)_f - f\left(\frac{\partial L}{\partial T}\right)_f$$

In the thermodynamic limit, $E = \langle E\rangle$ and $L = \langle L\rangle$. So we can use our expressions from parts (b) and (c):

$$C_f = N(\Delta\epsilon + f\Delta\ell)\left(\frac{\partial\langle n_i\rangle}{\partial T}\right)_f = \frac{N(\Delta\epsilon+f\Delta\ell)^2}{k_BT^2}\left(\frac{re^{\beta(\Delta\epsilon+f\Delta\ell)}}{(e^{\beta(\Delta\epsilon+f\Delta\ell)}+r)^2}\right)$$

Notice how the heat capacity is extensive (proportional to N). It should be obvious that this expression will go to zero as we approach zero temperature.

2. (a) The canonical partition function for $N = 1$ is q.

$$
\begin{aligned}
q &= h^{-3}\int d\vec{p}\int d\vec{r}\mathrm{e}^{-\beta\left(\frac{\vec{p}^2}{2m}+V(x)\right)} \\
&= \left(\frac{2\pi m}{h^2\beta}\right)^{3/2}\int_{-\frac{L}{2}}^{\frac{L}{2}} dx e^{-\beta\alpha|x|}\int_{-\frac{L}{2}}^{\frac{L}{2}} dy\int_{-\frac{L}{2}}^{\frac{L}{2}} dz \\
&= \left(\frac{2\pi m}{h^2\beta}\right)^{3/2}\left[2\int_0^{\frac{L}{2}} dx e^{-\beta\alpha x}\right]\times L^2 \\
&= \left(\frac{2\pi m}{h^2\beta}\right)^{3/2}\left[\frac{2L^2}{\beta\alpha}\left(1-e^{-\frac{\beta\alpha L}{2}}\right)\right]
\end{aligned}
$$

Since N are indistinguishable, $Q(N, V, T)$ is simply

$$
\begin{aligned}
Q(N,V,T) &= \frac{q(V,T)^N}{N!} \\
&= \frac{1}{N!}\left(\frac{2\pi m}{h^2\beta}\right)^{3N/2}\left[\frac{2L^2}{\beta\alpha}\left(1-e^{-\frac{\beta\alpha L}{2}}\right)\right]^N
\end{aligned}
$$

(b)

$$
\begin{aligned}
\langle E\rangle &= -\frac{\partial\ln Q}{\partial\beta} \\
&= \frac{3N}{2\beta}+N\left(\frac{1}{\beta}-\frac{\frac{\alpha L}{2}e^{-\beta\alpha L/2}}{1-e^{-\beta\alpha L/2}}\right) \\
&= N\left(\frac{5}{2\beta}-\frac{\frac{\alpha L}{2}e^{-\beta\alpha L/2}}{1-e^{-\beta\alpha L/2}}\right)
\end{aligned}
$$

We use the fact that $C_v = \beta^2 k_B\langle\delta E^2\rangle$ to make the next two computations simpler. First we compute $\langle\delta E^2\rangle$.

$$
\begin{aligned}
\langle\delta E^2\rangle &= -\frac{\partial\langle E\rangle}{\partial\beta} \\
&= \frac{5N}{2\beta^2}-N\left\{\frac{(\alpha L/2)^2 e^{-\beta\alpha L}}{(1-e^{-\beta\alpha L/2})^2}\left[e^{\beta\alpha L/2}(1-e^{-\beta\alpha L/2})+1\right]\right\} \\
&= N\left[\frac{5}{2\beta^2}-\left\{\frac{\left(\frac{\alpha L}{2}\right)^2 e^{-\beta\alpha L/2}}{\left(1-e^{-\beta\alpha L/2}\right)^2}\right\}\right]
\end{aligned}
$$

and then

$$
C_v = Nk_B\left[\frac{5}{2}-\left\{\frac{\left(\frac{\beta\alpha L}{2}\right)^2 e^{-\beta\alpha L/2}}{\left(1-e^{-\beta\alpha L/2}\right)^2}\right\}\right]
$$

The relative fluctuations in energy is then:

$$\begin{aligned}
\frac{\langle \delta E^2 \rangle^{1/2}}{\langle E \rangle} &= \frac{N^{1/2}\left[\frac{5}{2\beta^2} - \left\{\frac{\left(\frac{\alpha L}{2}\right)^2 e^{-\beta\alpha L/2}}{\left(1-e^{-\beta\alpha L/2}\right)^2}\right\}\right]^{1/2}}{N\left(\frac{5}{2\beta} - \frac{\frac{\alpha L}{2} e^{-\beta\alpha L/2}}{1-e^{-\beta\alpha L/2}}\right)} \\
&= \frac{1}{\sqrt{N}}\left\{\left[\frac{5}{2\beta^2} - \left\{\frac{\left(\frac{\alpha L}{2}\right)^2 e^{-\beta\alpha L/2}}{\left(1-e^{-\beta\alpha L/2}\right)^2}\right\}\right]^{1/2}\left(\frac{5}{2\beta} - \frac{\frac{\alpha L}{2} e^{-\beta\alpha L/2}}{1-e^{-\beta\alpha L/2}}\right)^{-1}\right\}
\end{aligned}$$

which do indeed scale as $1/\sqrt{N}$.

(c)

$$\begin{aligned}
A &= -k_B T \ln Q \\
p &= -\left(\frac{\partial A}{\partial V}\right)_{N,T} \\
&= k_B T \left(\frac{\partial lnQ}{\partial V}\right)_{N,T} \\
&= k_B T \left(\frac{\partial \ln Q}{\partial L}\right)_{N,T} \frac{\partial L}{\partial V} \\
&= \frac{k_B T}{3V^{2/3}} \left(\frac{\partial \ln Q}{\partial L}\right)_{N,T} \\
&= \frac{k_B T}{3V^{2/3}} \left[\frac{2N}{L} + \frac{N\beta\alpha}{2} \times \frac{e^{-\beta\alpha L/2}}{1-e^{-\beta\alpha L/2}}\right] \\
&= \frac{2N}{3\beta V} + \frac{N\alpha}{6V^{2/3}} \times \frac{e^{-\beta\alpha L/2}}{1-e^{-\beta\alpha L/2}}
\end{aligned}$$

First, let's take the high T limit as $k_B T \gg \alpha L$.

$$\begin{aligned}
p &\approx \frac{2N}{3\beta V} + \frac{N\alpha}{6V^{2/3}}\left(\frac{2}{\beta\alpha L} - 1\right) \\
&\approx \frac{N}{\beta V} - \frac{N\alpha}{6V^{2/3}} \\
&\approx \frac{N}{\beta V}\left(1 - \frac{\beta\alpha L}{6}\right) \\
&\approx \frac{N}{\beta V}
\end{aligned}$$

And we get the ideal gas law! This makes sense as at high T, the small perturbation at the bottom of the box has vanishingly little impact, so the behavior will be ideal gas-like. Now let's take the low T limit as $k_B T \ll \alpha L$.

$$\begin{aligned}
p &\approx \frac{2N}{3\beta V} + \frac{N\alpha}{6V^{2/3}} e^{-\beta\alpha L/2} \\
&\approx \frac{2N}{3\beta V}\left(1 + \frac{\beta\alpha L}{4} e^{-\beta\alpha L/2}\right) \\
&\approx \frac{2N}{3\beta V}
\end{aligned}$$

At low T the gas only has $2/3$ of the normal ideal gas pressure, due to the large confining potential in x. It is only free to exert pressure against the walls in the y and z directions- no longer the x direction.

(d)

$$\begin{aligned}
\lim_{\alpha\to 0} Q &= \frac{1}{N!}\left(\frac{2\pi m}{\beta h^2}\right)^{3N/2}\left(\frac{2L^2}{\beta\alpha}\left[1-e^{-\beta\alpha L/2}\right]\right)^N \\
&= \frac{1}{N!}\left(\frac{2\pi m}{\beta h^2}\right)^{3N/2}\left(\frac{2L^2}{\beta\alpha} * \frac{\beta\alpha L}{2}\right)^N \\
&= \frac{L^{3N}}{N!}\left(\frac{2\pi m}{\beta h^2}\right)^{3N/2} \\
&= \frac{V^N}{N!}\left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2}
\end{aligned}$$

(e)

$$\begin{aligned}
\Xi &= \sum_N e^{\beta\mu N} Q(N,V,T) \\
&= \exp\left(e^{\beta\mu} V \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\right)
\end{aligned}$$

Since $\langle N\rangle = \frac{\partial \ln \Xi}{\partial \beta\mu}$, we get

$$\langle N\rangle = \ln \Xi$$

Since we know that

$$\ln \Xi = \beta p V$$

we get,

$$\begin{aligned}
\langle N\rangle &= \beta p V \\
pV &= N k_B T
\end{aligned}$$

which is the ideal gas law.

3. (a) Recall that the average energy can be calculated from

$$\langle E\rangle = \left(\frac{\partial \ln Q}{\partial(-\beta)}\right)_{V,N}$$

In this case, we can compute the partition function explicitly.

$$\begin{aligned}
Q &= \sum_{i=1}^{\infty} e^{-\beta(n+1/2)\hbar\omega} \\
&= \frac{e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega}}
\end{aligned}$$

Taking the derivative with respect to β of the log of the inverse of the above expression, we get a simple expression for the average energy,

$$
\begin{aligned}
\langle E \rangle &= \left(\frac{\partial}{\partial(\beta)}\right)_{V,N} \ln\left(\frac{e^{-\beta\hbar\omega/2}}{e^{\beta\hbar\omega} - e^{-\beta\hbar\omega}}\right), \\
&= \frac{\hbar\omega}{2} + \hbar\omega\frac{e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}}, \\
&= \hbar\omega\left(\frac{1}{2} + \left(e^{\beta\hbar\omega} - 1\right)^{-1}\right).
\end{aligned}
$$

(b) We are trying to determine the behavior of $\langle E \rangle$ at large T, or as $\beta \to 0$. To do this, we Taylor expand $\exp(\beta\hbar\omega)$ to first order in β, giving

$$
\begin{aligned}
\langle E \rangle &= \hbar\omega\left(\frac{1}{2} + (\beta\hbar\omega)^{-1}\right) \\
&= k_B T + \hbar\omega/2 \\
&= k_B T
\end{aligned}
$$

(c) Here we can compute the partition function yet again. In the classical limit, we can perform the sum as an integral and can separate the terms of the Hamiltonian:

$$
\begin{aligned}
Q &= \int dp\ dx\ e^{-\beta H(x,p)}, \\
&= \int dp\ e^{-\beta p^2/2m} \int dx\ e^{-\beta m^2\omega^2 x^2/2}, \\
&= \sqrt{2\pi m k_B T}\sqrt{\frac{2\pi k_B T}{m\omega^2}}, \\
&= \frac{2\pi}{\omega\beta}.
\end{aligned}
$$

Now, it is straightforward to compute the average energy,

$$
\langle E \rangle = \frac{\omega\beta}{2\pi}\frac{2\pi}{\omega\beta^2} = k_B T = \frac{1}{\beta}.
$$

Note that the quantum and classical results agree (per degree of freedom).

4. (a) First it will be shown that

$$
\langle \delta N_i \delta N_j \rangle = \left(\frac{\delta\langle N_i \rangle}{\delta\beta\mu_j}\right)_{\beta,\beta\mu_i,V},
$$

where $\delta N_i = N_i - \langle N_i \rangle$. Here two different expressions will be shown to be equivalent to an intermediate expression and thus are equal to each other. The first expression is the lefthand side of the above equation:

$$
\begin{aligned}
\langle \delta N_i \delta N_j \rangle &= \langle (N_i - \langle N_i \rangle)(N_j - \langle N_j \rangle) \rangle \\
&= \langle N_i N_j \rangle - \langle N_i \rangle\langle N_j \rangle - \langle N_i \rangle\langle N_j \rangle + \langle N_i \rangle\langle N_j \rangle \\
&= \langle N_i N_j \rangle - \langle N_i \rangle\langle N_j \rangle.
\end{aligned}
$$

Now for the righthand side:

$$\begin{aligned}
\left(\frac{\partial\langle N_i\rangle}{\partial\beta\mu_j}\right)_{\beta,\beta\mu_l,V} &= \left[\frac{\partial}{\partial\beta\mu_j}\left(\frac{\partial\ln\Xi}{\partial\beta\mu_i}\right)_{\beta,\beta\mu_j,V}\right]_{\beta,\beta\mu_i,V} \\
&= \left[\frac{\partial}{\partial\beta\mu_j}\frac{1}{\Xi}\left(\frac{\partial\Xi}{\partial\beta\mu_i}\right)_{\beta,\beta\mu_j,V}\right]_{\beta,\beta\mu_i,V} \\
&= \frac{\partial}{\partial\beta\mu_j}\left(\frac{\sum_\nu N_i\exp\left(-\beta E_\nu+\beta\mu_i N_i+\beta\mu_j N_j\right)}{\sum_\nu\exp\left(-\beta E_\nu+\beta\mu_i N_i+\beta\mu_j N_j\right)}\right)_{\beta,\beta\mu_i,V}.
\end{aligned}$$

Let $e^x=\exp\left(-\beta E_\nu+\beta\mu_i N_i+\beta\mu_j N_j\right)$. Then we have

$$\begin{aligned}
&= \frac{\sum_\nu -N_i e^x}{\sum_\nu e^{2x}}\sum_\nu N_j e^x+\frac{\sum_\nu N_iN_je^x}{\sum_\nu e^x} \\
&= \frac{\sum_\nu N_iN_je^x}{\sum_\nu e^x}-\frac{\sum_\nu N_ie^x\sum_{\nu'}N_je^x}{\sum_\nu e^x\sum_{\nu'}e^x} \\
&= \langle N_iN_j\rangle-\langle N_i\rangle\langle N_j\rangle.
\end{aligned}$$

Since both quantities can be expressed as $\langle N_iN_j\rangle-\langle N_i\rangle\langle N_j\rangle$, they must be equal.
A similar format will be used to derive the higher dimensional expression. On one hand, we have

$$\begin{aligned}
\langle\delta N_i\delta N_j\delta N_l\rangle &= \langle(N_i-\langle N_i\rangle)(N_j-\langle N_j\rangle)(N_l-\langle N_l\rangle)\rangle \\
&= \langle N_iN_jN_l\rangle+2\langle N_i\rangle\langle N_j\rangle\langle N_l\rangle-\langle N_iN_j\rangle\langle N_l\rangle-\langle N_iN_l\rangle\langle N_j\rangle-\langle N_i\rangle\langle N_jN_l\rangle.
\end{aligned}$$

On the other, we have

$$\begin{aligned}
\left(\frac{\partial^2\langle N_i\rangle}{\partial\beta\mu_j\partial\beta\mu_l}\right)_{\beta,\beta\mu_i,V} &= \left[\frac{\partial^2}{\partial\beta\mu_j\partial\beta\mu_l}\frac{1}{\Xi}\left(\frac{\partial\Xi}{\partial\beta\mu_i}\right)_{\beta,\beta\mu_l,\beta\mu_j,V}\right]_{\beta,\beta\mu_i,V} \\
&= \left(\frac{\partial^2}{\partial\beta\mu_j\partial\beta\mu_l}\frac{\sum_\nu N_ie^x}{\sum_\nu e^x}\right)_{\beta,\beta\mu_i,V},
\end{aligned}$$

where $e^x=\exp\left(-\beta E_\nu+\beta\mu_iN_i+\beta\mu_jN_j+\beta\mu_lN_l\right)$ and Ξ is the grand canonical partition function for a three component system. Then

$$\begin{aligned}
&= \frac{\partial}{\partial\beta\mu_l}\left[\frac{\sum_\nu N_iN_je^x}{\sum_\nu e^x}-\frac{\sum_\nu N_ie^x\sum_{\nu'}N_je^x}{\sum_\nu e^x\sum_{\nu'}e^x}\right] \\
&= \left[\frac{\sum_\nu -N_iN_je^x\sum_{\nu'}N_le^x}{\sum_\nu e^{2x}}+\frac{\sum_\nu N_iN_jN_le^x}{\sum_\nu e^x}\right. \\
&\left.-\left(\frac{\sum_\nu N_ie^x\sum_{\nu'}N_je^x\sum_{\nu''}-2N_le^x}{\sum_\nu e^{3x}}+\frac{\sum_\nu N_ie^x\sum_{\nu'}N_jN_le^x}{\sum_\nu e^{2x}}+\frac{\sum_\nu N_iN_le^x\sum_{\nu'}N_je^x}{\sum_\nu e^{2x}}\right)\right] \\
&= -\langle N_iN_j\rangle\langle N_l\rangle+\langle N_iN_jN_l\rangle+2\langle N_i\rangle\langle N_j\rangle\langle N_l\rangle-\langle N_i\rangle\langle N_jN_l\rangle-\langle N_iN_l\rangle\langle N_j\rangle.
\end{aligned}$$

Since the two expressions are equal to the same intermediate expression, it must be that

$$\langle \delta N_i \delta N_j \delta N_l \rangle = \left(\frac{\partial^2 \langle N_i \rangle}{\partial \beta\mu_j \partial \beta\mu_l} \right)_{\beta, \beta\mu_i, V}.$$

The second part of this question is more difficult than the first. The solutions will follow a derivation of an expression with useful equations inserted along the way. For convenience, numbers will be introduced for lines of the equation being derived, and letters will be used for the helping expressions.

First, we begin by writing the total differential of energy as a function of β, V, and $\beta\mu$:

$$dE = \left(\frac{\partial E}{\partial \beta} \right)_{V,\beta\mu} d\beta + \left(\frac{\partial E}{\delta V} \right)_{\beta,\beta\mu} dV + \left(\frac{\partial E}{\partial \beta\mu} \right)_{\beta,V} d\beta\mu \tag{1}$$

Now just imagine that the system undergoes a process in which temperature is changed while the volume and number of particles are fixed. Then we have

$$\left(\frac{\partial E}{\partial \beta} \right)_{V,N} = \left(\frac{\partial E}{\partial \beta} \right)_{V,\beta\mu} + \left(\frac{\partial E}{\partial \beta\mu} \right)_{\beta,V} d\beta\mu \tag{2}$$

Now, noting use of the chain rule,

$$\left(\frac{\partial \beta\mu}{\partial \beta} \right)_{V,N} = -\left(\frac{\partial \beta\mu}{\partial N} \right)_{\beta,V} \left(\frac{\partial N}{\partial \beta} \right)_{\beta\mu,V} \tag{A}$$

Then using Eq. A, Eq. 1 becomes

$$\left(\frac{\partial E}{\partial \beta} \right)_{V,N} = \left(\frac{\partial E}{\partial \beta} \right)_{V,\beta\mu} - \left(\frac{\partial E}{\partial \beta\mu} \right)_{\beta,V} \frac{(\partial N/\partial \beta)_{\beta\mu,V}}{(\partial N/\partial \beta\mu)_{\beta,V}}. \tag{3}$$

A second note, which originates in using the partition function to calculate thermodynamic quantities:

$$\begin{aligned} -\left(\frac{\partial E}{\partial \beta\mu} \right)_{\beta,V} &= -\left(\frac{\partial}{\partial \beta\mu} \left(\frac{\partial \ln Z}{\partial(-\beta)} \right)_{V,\beta\mu} \right)_{\beta,V} \\ &= -\left(\frac{\partial}{\partial(-\beta)} \left(\frac{\partial \ln Z}{\partial \beta\mu} \right)_{\beta,V,} \right)_{V,\beta\mu} \\ &= \left(\frac{\partial N}{\partial \beta} \right)_{V,\beta\mu}. \end{aligned} \tag{B}$$

Using Eq. B in Eq. 3,

$$\left(\frac{\partial E}{\partial \beta} \right)_{V,N} = \left(\frac{\partial E}{\partial \beta} \right)_{V,\beta\mu} + \left[\left(\frac{\partial N}{\partial \beta} \right)_{\beta,V} \right]^2 / \left(\frac{\partial N}{\partial \beta\mu} \right)_{\beta,V}. \tag{4}$$

Note that the denominator gives the mean-square fluctuations in number:

$$\left(\frac{\partial N}{\partial \beta\mu} \right)_{\beta,V} = \langle (\delta N)^2 \rangle.$$

Now to relate these density fluctuations to the compressibility κ_T, we can do the following:

$$
\begin{aligned}
\left(\frac{\partial N}{\partial \beta\mu}\right)_{\beta,V} &= \frac{1}{\beta}\left(\frac{\partial N}{\partial \mu}\right)_{\beta,V} && \text{(C)}\\
&= -\frac{1}{\beta}\left(\frac{\partial N}{\partial V}\right)_{\beta,\mu}\left(\frac{\partial V}{\partial \mu}\right)_{\beta,N} && \text{(D)}\\
&= -\frac{1}{\beta}\left(\frac{\partial p}{\partial \mu}\right)_{\beta}\left(\frac{\partial V}{\partial \mu}\right)_{\beta,N} && \text{(E)}\\
&= -\frac{1}{\beta}\left[\left(\frac{\partial p}{\partial \mu}\right)_{\beta}\right]^2\left(\frac{\partial V}{\partial p}\right)_{\beta} && \text{(F)}\\
&= -\frac{1}{\beta}\left(\frac{N}{V}\right)^2\left(\frac{\partial V}{\partial p}\right)_{\beta,N} && \text{(G)}\\
&= \frac{1}{\beta}N\rho\left[-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{\beta,N}\right] && \text{(H)}\\
&= \frac{1}{\beta}N\rho\kappa_T. && \text{(J)}
\end{aligned}
$$

Above Eq. A was used once more, a Maxwell relation originating from the Gibbs free energy differential was utilized, and the Gibbs-Duhem equation was applied. Substituting the result in line J into Eq. 4, we obtain

$$\left(\frac{\partial E}{\partial \beta}\right)_{V,N} = \left(\frac{\partial E}{\partial \beta}\right)_{V,\beta\mu} + \left[\left(\frac{\partial N}{\partial \beta}\right)_{\beta,V}\right]^2\frac{\beta}{N\rho\kappa_T}. \tag{5}$$

Multiplying through by

$$\frac{d\beta}{dT} = -\frac{1}{k_B T^2} = -k_B\beta, \tag{K}$$

we finally have the result

$$C_{V,N} = C_{V,\beta\mu} - \frac{k_B\beta^2}{N\rho\kappa_T}\left[\left(\frac{\partial N}{\partial \beta}\right)_{\beta,V}\right]^2. \tag{6}$$

(b) See solutions manual.

5. (a) Here we only take the potential energy of the rigid rod into account, since the integral of the partition function due to the kinetic energy would evaluate to a constant with respect to the field (the field only alters the potential of the rod).

This said, the potential energy is just given by $u(\theta, \phi)$. Then we have

$$\begin{aligned} q_{\text{rot}} &= \int_0^{2\pi} d\phi \int_{-1}^{1} d(\cos\theta) e^{\beta\epsilon\cos\theta} \\ &= \frac{2\pi}{\beta\epsilon} e^{\beta\epsilon\cos\theta}\Big|_{-1}^{1} \\ &= \frac{2\pi}{\beta\epsilon}[e^{\beta\epsilon} - e^{-\beta\epsilon}] \\ &= \frac{4\pi}{\beta\epsilon}\sinh(\beta\epsilon) \\ &= \frac{4\pi k_B T}{\epsilon}\sinh(\frac{\epsilon}{k_B T}) \end{aligned}$$

For the sake of the rest of the problem, the solutions will be written in terms of the exponentials and not in the hyperbolic trigonometric functions.

(b) Note that since $u(\theta, \phi) = -\epsilon\cos\theta$, $\langle\cos\theta\rangle = -\frac{1}{\epsilon}\langle u\rangle$. Also,

$$\ln q_{\text{rot}} = \ln 2\pi - \ln\beta\epsilon + \ln(e^{\beta\epsilon} - e^{-\beta\epsilon}).$$

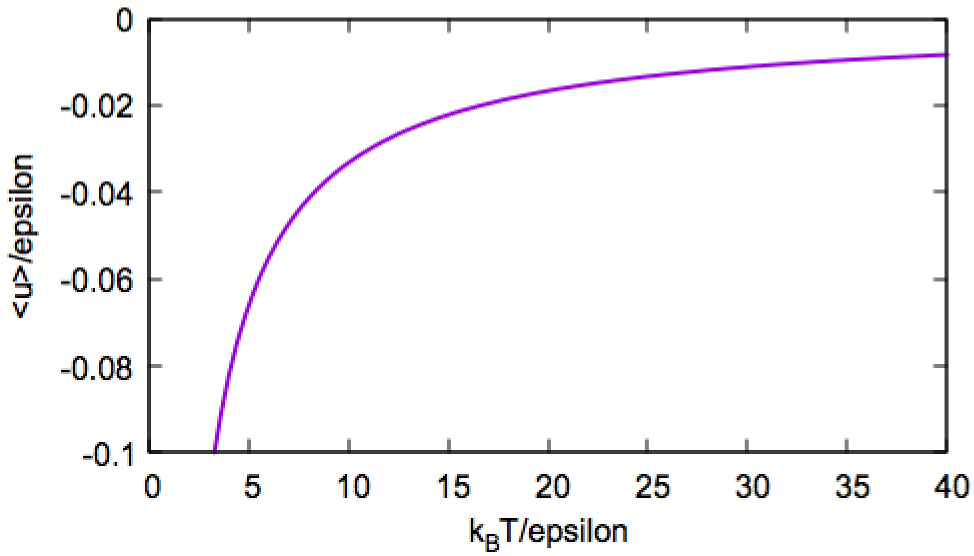
Then

$$\begin{aligned} \langle\cos\theta\rangle &= \left(\frac{\partial \ln q_{\text{rot}}}{\partial\beta\epsilon}\right) \\ &= -\frac{1}{\beta\epsilon} + \frac{e^{\beta\epsilon} + e^{-\beta\epsilon}}{e^{\beta\epsilon} - e^{-\beta\epsilon}}, \end{aligned}$$

so

$$\begin{aligned} \langle u\rangle &= \frac{1}{\beta} - \epsilon\frac{e^{\beta\epsilon} + e^{-\beta\epsilon}}{e^{\beta\epsilon} - e^{-\beta\epsilon}} \\ &= \frac{1}{\beta} - \epsilon\frac{e^{2\beta\epsilon} + 1}{e^{2\beta\epsilon} - 1}. \end{aligned}$$

The plot of $\langle u\rangle/\epsilon$ versus $k_B T/\epsilon$ is shown below.



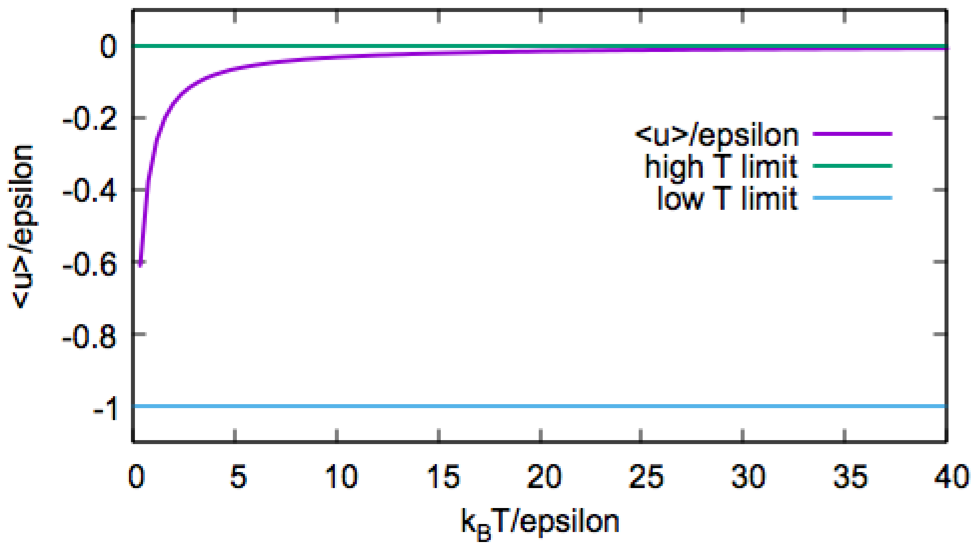
(c) Let us take a Taylor expansion of $\langle u \rangle$ at high temperature, *i.e.*, small $\beta\epsilon$.

$$\begin{aligned}
\langle u \rangle &= \frac{1}{\beta} - \epsilon \frac{e^{2\beta\epsilon}+1}{e^{2\beta\epsilon}-1} \\
&\approx \frac{1}{\beta} - \epsilon \frac{1+(1+2\beta\epsilon+...)}{-1+(1+2\beta\epsilon+...)} \\
&= \frac{1}{\beta} - \epsilon \frac{2+2\beta\epsilon+...}{2\beta\epsilon+...} \\
&\approx \frac{1}{\beta} - \epsilon \frac{1}{\beta\epsilon} \\
&= 0.
\end{aligned}$$

(d) Consider the behavior of $\langle u \rangle$ at low temperature, *i.e.*, large $\beta\epsilon$.

$$\begin{aligned}
\langle u \rangle &= \frac{1}{\beta} - \epsilon \frac{e^{2\beta\epsilon}+1}{e^{2\beta\epsilon}-1} \\
&\approx -\epsilon \frac{e^{2\beta\epsilon}}{e^{2\beta\epsilon}} \\
&= -\epsilon.
\end{aligned}$$

(e) Plots are shown below, with the high temperature limit in green and the low temperature limit in blue.



(f) The fluctuations in energy, $\langle \delta u^2 \rangle$, can be calculated from $\langle u \rangle$ straightforwardly:

$$\begin{aligned}\langle \delta u^2 \rangle &= -\left(\frac{\partial \langle u \rangle}{\partial \beta}\right)_{N,V} \\ &= \frac{1}{\beta^2} - 2\epsilon^2 e^{2\beta\epsilon}\frac{e^{2\beta\epsilon}+1}{(e^{2\beta\epsilon}-1)^2} \\ &= \frac{1}{\beta^2} - \frac{4\epsilon^2 e^{2\beta\epsilon}}{(e^{2\beta\epsilon}-1)^2}\end{aligned}$$

So then we have that the heat capacity is

$$\begin{aligned}C_{\text{rot}} &= \frac{\langle \delta u^2 \rangle}{k_B T^2} \\ &= k_B - \frac{4\epsilon^2}{k_B T^2}\frac{e^{2\epsilon/k_B T}}{(e^{2\epsilon/K_B T}-1)^2}.\end{aligned}$$

(g) From part (c), the high temperature heat capacity is 0. The energy is constant, and so the fluctuations are also constant, and more specifically, 0.
From part (d), the low temperature fluctuations are

$$\begin{aligned}\langle \delta u^2 \rangle &= -\frac{\partial}{\partial \beta}\left[\frac{1}{\beta} - \epsilon\right] \\ &= \frac{1}{\beta^2},\end{aligned}$$

so

$$C_{\text{rot}} = k_B.$$

(h) Physically the high temperature limit can be thought of in terms of populations of states. In the high temperature limit, there is bountiful energy to populate even high energy orientational states, so all states are essentially equally populated. Thus there is no "cost" to move between states, and thus the heat capacity is zero.

In the low temperature limit, limited energy is available, and so most orientational states are inaccessible. Only the ground orientational state is populated in the limit that the temperature approaches zero. The fluctuations are not zero because there still would be a "cost" associated with increasing energy if it were available. There are two rotational degrees of freedom, in θ and in ϕ, and so these would give a combined contribution of $k_B T$ to the heat capacity.