

6 Task Theoretical Physics VI - Statistics

6.1 (Debye theory of the heat capacity in solids: 1D)

Hamiltonian of a chain of linearly coupled harmonic oscillators:

$$\begin{aligned}\hat{\mathbf{H}}_{1D} &= \sum_{j=1}^N \frac{\hat{\mathbf{p}}_j^2}{2m} + \frac{k}{2} \sum_{j=1}^{N-1} (\hat{\mathbf{u}}_{j+1} - \hat{\mathbf{u}}_j)^2 + \frac{k}{2} \hat{\mathbf{u}}_1^2 + \frac{k}{2} \hat{\mathbf{u}}_N^2 \\ &= \frac{1}{2m} \hat{\mathbf{p}}_N^T \mathbf{E} \hat{\mathbf{p}}_N + \frac{k}{2} \hat{\mathbf{u}}_N^T \mathbf{V} \hat{\mathbf{u}}_N\end{aligned}$$

with \mathbf{E} being the unitary matrix:

$$\mathbf{E} = \begin{pmatrix} 1 & 0 & \cdots & 0 \\ 0 & 1 & \ddots & \vdots \\ \vdots & \ddots & \ddots & 0 \\ 0 & \cdots & 0 & 1 \end{pmatrix}$$

and \mathbf{V} being the matrix:

$$\mathbf{V} = \begin{pmatrix} 2 & -1 & 0 & \cdots & 0 \\ -1 & 2 & \ddots & \ddots & \vdots \\ 0 & \ddots & \ddots & \ddots & 0 \\ \vdots & \ddots & \ddots & 2 & -1 \\ 0 & \cdots & 0 & -1 & 2 \end{pmatrix}$$

There exists an orthogonal transformation $\hat{\mathbf{X}}$ which relates $\hat{\mathbf{p}}_j$ and $\hat{\mathbf{u}}_j$ to the normal mode coordinates $\hat{\mathbf{P}}_i$ and $\hat{\mathbf{Q}}_i$. With

$$\begin{aligned}\hat{\mathbf{u}}_j &= \sum_{i=1}^N X_{ji} \hat{\mathbf{Q}}_i \\ \hat{\mathbf{p}}_j &= \sum_{i=1}^N X_{ji} \hat{\mathbf{P}}_i\end{aligned}$$

We know, that

$$\hat{\mathbf{X}}^T \mathbf{V} \hat{\mathbf{X}} = \Lambda$$

with

$$\Lambda = \begin{pmatrix} \omega_1^2 & 0 & \cdots & 0 \\ 0 & \omega_2^2 & \ddots & \vdots \\ \vdots & \ddots & \ddots & 0 \\ 0 & \cdots & 0 & \omega_N^2 \end{pmatrix}$$

and:

$$\hat{\mathbf{X}}^T = \begin{pmatrix} x_{11} & x_{21} & \cdots & x_{N-1,1} & x_{N1} \\ x_{12} & x_{22} & & & \vdots \\ \vdots & & \ddots & & \vdots \\ \vdots & & & x_{N-1,N-1} & \vdots \\ x_{1N} & \cdots & \cdots & x_{N-1,N} & x_{NN} \end{pmatrix}$$

$$\hat{\mathbf{X}} = \begin{pmatrix} x_{11} & x_{12} & \cdots & x_{1,N-1} & x_{1N} \\ x_{21} & x_{22} & & & \vdots \\ \vdots & & \ddots & & \vdots \\ \vdots & & & x_{N-1,N-1} & \vdots \\ x_{N1} & \cdots & \cdots & x_{N,N-1} & x_{NN} \end{pmatrix}$$

6.2 (Debye theory of the heat capacity in solids: 3D)

(a)

We are considering a cube with sides of length L consisting of N atoms. In k space there is now one k -state in each $\left(\frac{2\pi}{L}\right)^3$ volume. Therefore the state density is ($V = L^3$):

$$D(k) = \frac{1}{\left(\frac{2\pi}{L}\right)^3} = \frac{L^3}{(2\pi)^3} = \frac{V}{(2\pi)^3}$$

Now we are looking for the number of states which are smaller or equal to k , which we get by integrating over a sphere with radius k in k -space. Therefore the number of states is:

$$N = \int_{sphere} D(k) dk = \int_0^k dk k^2 D(k) \int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\varphi = \left(\frac{L}{2\pi}\right)^3 \frac{4\pi}{3} k^3$$

Using now the definition for the density of state in frequency dependance:

$$D(\omega) = \frac{dN}{d\omega} = \frac{dN}{dk} \cdot \frac{dk}{d\omega} = \left(\frac{L}{2\pi}\right)^3 4\pi k^2 \frac{dk}{d\omega} = \left(\frac{L}{2\pi}\right)^3 4\pi k^2 \frac{1}{v} = \frac{V\omega^2}{2\pi^2 v^3} \quad (1)$$

while we used debye approximation $\omega = v \cdot k$, $\frac{d\omega}{dk} = v$ (while v is the velocity of the mode/groupvelocity). Integration to the cutoff frequency - debye frequency ω_D should give $3N$ states, that are contained in the N lattice with 3 different modes of the same mode-velocity for each of the gridpoints:

$$3N = \int_0^{\omega_D} D(\omega) d\omega = \int_0^{\omega_D} \frac{V\omega^2}{2\pi^2 v^3} d\omega = \frac{V\omega_D^3}{6\pi^2 v^3}$$

this equation can be rearranged to derive the debye frequency:

$$\omega_D^3 = \frac{18\pi^2 N v^3}{V}$$

We can now instantly rewrite 1 to the term we have been looking for the total density of states in terms of the number of atoms N and the Debye frequency ω_D :

$$D(N, \omega_D, \omega) = \frac{V\omega^2}{2\pi^2 v^3} = \frac{9N}{\omega_D^3} \cdot \omega^2 \quad (2)$$

with $\frac{V}{2\pi^2 v^3} = \frac{9N}{\omega_D^3}$.

(b)

We now have to calculate the mean energy and the heat capacity.

Definition of mean energy (taken from the lecture):

$$\langle E \rangle = \frac{1}{2} \int_0^{\omega_D} \hbar\omega D(\omega) d\omega + \int_0^{\omega_D} n(\omega) D(\omega) d\omega$$

with

$$n(\omega) = \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}$$

inserting 2:

$$\begin{aligned} \langle E \rangle &= \frac{9N}{\omega_D^3} \frac{1}{2} \int_0^{\omega_D} \hbar\omega \cdot \omega^2 d\omega + \frac{9N}{\omega_D^3} \int_0^{\omega_D} \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \cdot \omega^2 d\omega \\ &= \frac{9N\hbar}{2\omega_D^3} \int_0^{\omega_D} \omega^3 d\omega + \frac{9N}{\omega_D^3} \int_0^{\omega_D} \frac{\hbar\omega^3}{e^{\beta\hbar\omega} - 1} d\omega \\ &= \frac{9}{8} N \hbar \omega_D + \frac{9N}{\omega_D^3} \int_0^{\omega_D} \frac{\hbar\omega^3}{e^{\beta\hbar\omega} - 1} d\omega \end{aligned} \quad (3)$$

Definition of heat capacity:

$$C_v = \frac{\partial \langle E \rangle}{\partial T}$$

inserting 3:

$$\begin{aligned} C_v(T) &= \frac{9N}{\omega_D^3} \frac{\partial}{\partial T} \int_0^{\omega_D} \frac{\hbar\omega^3}{e^{\beta\hbar\omega} - 1} d\omega \\ &= \frac{9N}{\omega_D^3} \int_0^{\omega_D} \hbar\omega^3 \frac{\partial}{\partial T} \left(e^{\frac{\hbar\omega}{k_B T}} - 1 \right)^{-1} d\omega \\ &= \frac{9N}{\omega_D^3} \int_0^{\omega_D} d\omega \hbar\omega^3 \frac{(-1)}{\left(e^{\frac{\hbar\omega}{k_B T}} - 1 \right)^2} \cdot e^{\frac{\hbar\omega}{k_B T}} \cdot \left(-\frac{\hbar\omega}{k_B T^2} \right) \\ &= \frac{9N\hbar}{\omega_D^3} \frac{\hbar}{k_B T^2} \int_0^{\omega_D} d\omega \frac{\omega^4 e^{\frac{\hbar\omega}{k_B T}}}{\left(e^{\frac{\hbar\omega}{k_B T}} - 1 \right)^2} \end{aligned}$$

now we want to get to the standard form, this is possible by using the substitution $x = \frac{\hbar\omega}{k_B T} \Leftrightarrow \omega = \frac{k_B T}{\hbar} x \Rightarrow d\omega = \frac{k_B T}{\hbar} dx$ and $T_D = \frac{\hbar\omega_D}{k_B}$:

$$\begin{aligned} C_v(T) &= \frac{9N\hbar}{\omega_D^3} \left(\frac{\hbar}{k_B T}\right) \frac{1}{T} \left(\frac{k_B T}{\hbar}\right)^5 \int_0^{\beta\hbar\omega_D} dx \frac{x^4 e^x}{(e^x - 1)^2} \\ &= 9Nk_B \left(\frac{k_B T}{\hbar\omega_D}\right)^3 \int_0^{\beta\hbar\omega_D} dx \frac{x^4 e^x}{(e^x - 1)^2} \\ &= 9Nk_B \left(\frac{T}{T_D}\right)^3 \int_0^{\beta\hbar\omega_D} dx \frac{x^4 e^x}{(e^x - 1)^2} \end{aligned}$$

The case $\beta \rightarrow \infty$:

$$C_v(T) = \frac{12}{5} \pi^4 \frac{Nk_B}{T_D^3} T^3$$

which is the famous Debye T^3 -law.

The case $\beta \rightarrow 0$:

$$C_v(T) = 3Nk_B$$

6.3 (Simplified polymer model)

(a)

We are meant to show, that the number of configurations $\Omega(E)$ for which the energy of the polymer is between E and $E + \delta E$ is equal to:

$$\Omega(E) = \frac{2^N \delta E}{al\sqrt{2\pi N}} e^{-\frac{E^2}{2Nl^2 a^2}}$$

for $N \gg 1$, $al \ll \delta E \ll E$ and $|E| \ll Nal$.

From **task 1.2 b)** we know, that the binomial distribution can be rewritten in the gaussian distribution for $N \gg 1$:

$$P_N(k) = \frac{N!}{(N-k)!k!} q^k (1-q)^{N-k} = \frac{1}{\sqrt{2\pi Nq(1-q)}} \exp\left(-\frac{1}{2} \frac{1}{Nq(1-q)} (k - Nq)^2\right)$$

for our problem the possibility for a chain link to be “left” or “right” is equal, this means the possibility for a chain link to be “right” is $q = \frac{1}{2}$, resulting in:

$$P_N(k) = \sqrt{\frac{2}{\pi N}} \exp\left(-\frac{2}{N} \left(k - \frac{N}{2}\right)^2\right) \quad (4)$$

The energy of the polymer should be between E and $E + \delta E$, we can think of k links to be right and $(N - k)$ links to be left therefore (with $x_i = il$):

$$E(k) = -akl - a(N - k)l = (N - 2k)al$$

Which can be rewritten to:

$$k = \frac{N}{2} - \frac{E}{2al}$$

inserted in 4 this leads to:

$$P_N(k) = \sqrt{\frac{2}{\pi N}} \exp\left(-\frac{E^2}{2Nl^2a^2}\right)$$

While there are two possible settings for the links with N links in total, the total number of settings for the whole system is 2^N . Multiplying this with the possibility for a special setting k gives us the number of configurations for the setting k :

$$\Omega(E(k)) = \frac{2^N}{\sqrt{\frac{1}{2}\pi N}} \exp\left(-\frac{E(k)^2}{2Nl^2a^2}\right) \quad (5)$$

while we want to find the number of configurations for the case of the energy interval E to $E + \delta E$ we have to sum over $\Omega(E(k))$ since we are in a discrete case:

$$\Omega(E) \Big|_{E \in [E', E' + \delta E]} = \sum_{E'=E}^{E+\delta E} \frac{2^N}{\sqrt{\frac{1}{2}\pi N}} \exp\left(-\frac{E^2}{2Nl^2a^2}\right)$$

We have a look at the sum, while δE is very small, the possibility changes will also be very small. The possibility is directly linked to $k = \frac{N}{2} - \frac{E}{2al}$, with $E \rightarrow E + \delta E$ this becomes:

$$k' = \frac{Nal - (E + \delta E)}{2al}$$

now with $\delta E \ll E$ and $|E| \ll Nal$ the change in energy will “not” influence $k \approx k'$, therefore $E(k') \approx E(k)$ and we can write, while the energy can be written in front of the sum:

$$\begin{aligned} \Omega(E) \Big|_{E \in [E', E' + \delta E]} &= \Omega(E(k)) \sum_E \\ &= \Omega(E(k)) \delta k \end{aligned}$$

while δk is the number of states in $[E, E + \delta E]$, it is a small number because of δE being small, with

$$\begin{aligned} \delta k &= k - k' \\ &= \frac{N}{2} - \frac{E}{2al} - \frac{N}{2} + \frac{E + \delta E}{2al} \\ &= \frac{\delta E}{2al} \end{aligned}$$

inserting this, we get:

$$\Omega(E) \Big|_{E \in [E', E' + \delta E]} = \frac{2^N \delta E}{al\sqrt{2\pi N}} \exp\left(-\frac{E^2}{2Nl^2a^2}\right)$$

□

(b)

definition of entropy:

$$S(E) = k_B \ln \Omega(E)$$

while we want the entropy at energy E we cannot use the expression from **a**), but instead we can use 5, which gives the energy for a given k :

$$\begin{aligned} S(E(k)) &= k_B \ln \left[\frac{2^N}{\sqrt{\frac{1}{2}\pi N}} \exp\left(-\frac{E(k)^2}{2Nl^2a^2}\right) \right] \\ &= k_B \left(N \ln 2 - \frac{1}{2} \ln\left(\frac{1}{2}\pi N\right) - \frac{E(k)^2}{2Nl^2a^2} \right) \end{aligned}$$

If we want the entropy for an interval $[E, E + \delta E]$ (seems unlikely, because entropy doesn't have physical meaning for intervals), we get:

$$\begin{aligned} S(E) &= k_B \ln \Omega(E) \Big|_{E \in [E', E' + \delta E]} \\ &= k_B \ln \left[\frac{2^N \delta E}{al\sqrt{2\pi N}} \exp\left(-\frac{E^2}{2Nl^2a^2}\right) \right] \\ &= k_B \left[\ln\left(\frac{2^N \delta E}{al\sqrt{2\pi N}}\right) - \frac{E^2}{2Nl^2a^2} \right] \end{aligned}$$

(c)

With $T = \text{const.}$ (polymer immersed in solution in thermal equilibrium) and $E \neq \text{const.}$ (energy fluctuations) we have to calculate the problem in the canonical ensemble, therefore:

$$D(E) = \frac{d\Omega}{dE}$$

using 5 we get:

$$\begin{aligned} D(E) &= \frac{2^N}{\sqrt{\frac{1}{2}\pi N}} \frac{d}{dE} \exp\left(-\frac{E^2}{2Nl^2a^2}\right) \\ &= \frac{2^N}{\sqrt{\frac{1}{2}\pi N}} \left(\frac{-2 \cdot E}{2Nl^2a^2} \right) \exp\left(-\frac{E^2}{2Nl^2a^2}\right) \\ &= -\frac{E 2^N}{Nl^2a^2 \sqrt{\frac{1}{2}\pi N}} \exp\left(-\frac{E^2}{2Nl^2a^2}\right) \end{aligned}$$

Definition of partition function:

$$Z_N(T, V) = c_N \int_{-Nal}^{Nal} dE D(E) e^{-\beta E}$$

inserting $D(E)$ and $\alpha^2 = \frac{1}{2Nl^2a^2}$, $\gamma = \frac{2^N}{Nl^2a^2\sqrt{\frac{1}{2}\pi N}}$ with $c_N = 1$ leads to:

$$Z_N(T, V) = -\gamma \int_{-Nal}^{Nal} dE E e^{-\alpha^2 E^2 - \beta E}$$

rewriting the exponent leads to:

$$\begin{aligned} Z_N(T, V) &= -\gamma \int_{-Nal}^{Nal} dE E e^{-\left(\alpha^2 E^2 + \beta E + \frac{\beta^2}{4\alpha^2}\right) + \frac{\beta^2}{4\alpha^2}} \\ &= -\gamma e^{\frac{\beta^2}{4\alpha^2}} \int_{-Nal}^{Nal} dE E e^{-\left(\alpha E + \frac{\beta}{2\alpha}\right)^2} \end{aligned}$$

substituting $\alpha E + \frac{\beta}{2\alpha} = x \Rightarrow E = \frac{x}{\alpha} - \frac{\beta}{2\alpha^2}$ and $\frac{dx}{\alpha} = dE$, also using $N \gg 1 \Rightarrow Nal \rightarrow \infty$ we get:

$$Z_N(T, V) = -\frac{\gamma}{\alpha^2} e^{\frac{\beta^2}{4\alpha^2}} \int_{-\infty}^{\infty} dx \left(x e^{-x^2} - \frac{\beta}{2\alpha} e^{-x^2} \right)$$

the first integral cancels because of symmetry, so we only have to calculate the second one:

$$\begin{aligned} Z_N(T, V) &= -\frac{\gamma\beta}{2\alpha^3} e^{-\frac{\beta^2}{4\alpha^2}} \int_{-\infty}^{\infty} dx e^{-x^2} \\ &= -\frac{\gamma\beta}{2\alpha^3} e^{-\frac{\beta^2}{4\alpha^2}} \cdot \sqrt{\pi} \\ &= -\frac{\gamma\sqrt{\pi}}{2\alpha^3} \cdot \beta e^{-\frac{\beta^2}{4\alpha^2}} \end{aligned}$$

Definition of mean energy:

$$\begin{aligned} \langle E \rangle &= -\frac{\partial}{\partial \beta} \ln Z_N \\ &= \frac{\partial}{\partial \beta} \ln \left(-\frac{\gamma\sqrt{\pi}}{2\alpha^3} \cdot \beta e^{-\frac{\beta^2}{4\alpha^2}} \right) \\ &= \frac{\partial}{\partial \beta} \ln \beta - \frac{\partial}{\partial \beta} \left(\frac{\beta^2}{4\alpha^2} \right) \\ &= \frac{1}{\beta} - \frac{2\beta}{4\alpha^2} \\ &= \frac{1}{\beta} - \frac{\beta}{2\alpha^2} \end{aligned}$$

inserting $\alpha^2 = \frac{1}{2Nl^2a^2}$ leads to:

$$\langle E \rangle = k_B T - \frac{Nl^2a^2}{k_B T}$$

Having a look at the special cases for physical insights. $T \rightarrow \infty$ the energy will turn to infinity, while using:

$$E = -ax_N \Rightarrow x_N = -\frac{E}{a} \Rightarrow x_N = \frac{k_B T}{a} + \frac{Nl^2 a}{k_B T}$$

also the chain length will turn to infinity. For $T \rightarrow 0$ we have the case of energy turning to negative infinity. The chain length will then again turn to infinity. The length of infinity might result of the assumption that $N \gg 1 \Rightarrow Nal \rightarrow \infty$. The special case of $x_N = 0$ is defined by:

$$x_N = 0 = \frac{k_B T}{a} + \frac{Nl^2 a}{k_B T} \Rightarrow T^2 = -\frac{Nl^2 a^2}{k_B^2} \Rightarrow T = \pm i\sqrt{N} \frac{la}{k_B}$$

which means, there is no temperature, where the chain length will become zero. This seems very unlikely, therefore this solution seems to be wrong!

We have a second try, this time we use the function given in **a**) which results from:

$$\begin{aligned} D(E) &= \frac{d\Omega}{dE} \\ &= \lim_{\Delta E \rightarrow 0} \frac{\Omega(E + \Delta E) - \Omega(E)}{\Delta E} \\ &= \lim_{\Delta E \rightarrow 0} \frac{1}{\Delta E} \left(\sum_{E'=0}^{E+\Delta E} \Omega(E'(k)) - \sum_{E'=0}^E \Omega(E'(k)) \right) \end{aligned}$$

while $\Delta E \approx \delta E$ for $\Delta E \rightarrow 0$ we can rewrite that:

$$\begin{aligned} D(E) &= \frac{1}{\delta E} \lim_{\delta E \rightarrow 0} \sum_{E'=E}^{E+\delta E} \Omega(E'(k)) \\ &= \frac{1}{\delta E} \Omega(E) \Big|_{E \in [E', E'+\delta E]} \\ &= \frac{2^N}{al\sqrt{2\pi N}} \exp\left(-\frac{E^2}{2Nl^2 a^2}\right) \end{aligned}$$

From here it is now relatively easy, since we already did quite the equivalent calculation before, with some minor differences, starting with the partition function:

$$Z_N(T, V) = c_N \int_{-Nal}^{Nal} dE D(E) e^{-\beta E}$$

inserting $D(E)$ and $\alpha^2 = \frac{1}{2Nl^2 a^2}$, $\gamma = \frac{2^N}{al\sqrt{2\pi N}}$ with $c_N = 1$ leads to:

$$Z_N(T, V) = -\gamma \int_{-Nal}^{Nal} dE e^{-\alpha^2 E^2 - \beta E}$$

rewriting the exponent leads to:

$$Z_N(T, V) = -\gamma e^{\frac{\beta^2}{4\alpha^2}} \int_{-Nal}^{Nal} dE e^{-(\alpha E + \frac{\beta}{2\alpha})^2}$$

substituting $\alpha E + \frac{\beta}{2\alpha} = x$ and $\frac{dx}{\alpha} = dE$, also using $N \gg 1 \Rightarrow Nal \rightarrow \infty$ we get:

$$\begin{aligned} Z_N(T, V) &= -\frac{\gamma}{\alpha} e^{\frac{\beta^2}{4\alpha^2}} \int_{-\infty}^{\infty} dx e^{-x^2} \\ &= -\frac{\gamma}{\alpha} e^{\frac{\beta^2}{4\alpha^2}} \sqrt{\pi} \end{aligned}$$

Definition of mean energy:

$$\begin{aligned} \langle E \rangle &= -\frac{\partial}{\partial \beta} \ln Z_N \\ &= \frac{\partial}{\partial \beta} \ln \left(-\frac{\gamma \sqrt{\pi}}{\alpha} e^{\frac{\beta^2}{4\alpha^2}} \right) \\ &= -\frac{\partial}{\partial \beta} \left(\frac{\beta^2}{4\alpha^2} \right) \\ &= -\frac{2\beta}{4\alpha^2} \\ &= -\frac{\beta}{2\alpha^2} \end{aligned}$$

inserting $\alpha^2 = \frac{1}{2Nl^2a^2}$ leads to:

$$\langle E \rangle = -\frac{Nl^2a^2}{k_B T}$$

Same special cases for this equation lead to more physical results. First we get ourselves

$$x_N = -\frac{E}{a} = \frac{Nl^2a}{k_B T} \text{ from } E = -ax_N$$

which this time can become zero for infinitely high temperature, while the average energy will be zero then, which seems to be correct, when we look at $E = -ax_N$, what before wasn't fulfilled. Now for low temperature the energy will turn to minus infinity, while the length of the chain therefore will turn to infinity, which seems ok too, since we used $N \gg 1 \Rightarrow Nal \rightarrow \infty$, therefore we already observed an infinitely long chain.

Definition energy fluctuations:

$$\Delta E^2 = \frac{-\partial \langle H \rangle}{\partial \beta} = k_B T^2 \frac{\partial \langle E \rangle}{\partial T}$$

inserting $\langle E \rangle$ therefore leads to:

$$\Delta E^2 = k_B T^2 \frac{Nl^2a^2}{k_B T^2} = Nl^2a^2$$

this means the energy fluctuations are:

$$\Delta E = \sqrt{N}al$$

which we already saw quantitatively in the lecture $\Delta E \propto \sqrt{N}$.

Or if we take the normalised energy fluctuations:

$$\frac{\Delta E}{\langle E \rangle} = \frac{\sqrt{N}al}{-\frac{Nl^2a^2}{k_B T}} = -\sqrt{\frac{1}{N}} \frac{k_B T}{la}$$

for $N \rightarrow \infty$ the energy fluctuations tend to go to 0.

(d)

In thermal equilibrium the forces of the marker drawn by the electric field and the force of the polymer on the marker, should add to zero. Therefore

$$F_{field} = F_{polymer}$$

with the definition of force:

$$F = -\frac{\partial E}{\partial x}$$

with E the electric energy ($E = -ax_N$) and $x = x_N$ we can write:

$$F = a$$

Further using $-\frac{\langle E \rangle}{x_N} = a$:

$$F = -\frac{\langle E \rangle}{x_N} = \frac{Nl^2a^2}{k_B T x_N} = a$$

which can finally be rewritten to:

$$F = \frac{k_B T}{Nl^2} \cdot x_N$$

6.4 (Rotating ideal gas)

Cubic box with infinitely hard walls of volume $V = L^3$. Distance between H and Cl is $d = 1.3 = 1.3 \cdot 10^{-10} m$.

(a)

We first only consider translations. Starting with the particle in the box picture in three dimensions, while we think of HCl to be one particle. This is justified by the assumption of HCl being rigid, therefore the mass of this particle is $M = m_{\text{H}} + m_{\text{Cl}}$. At first only for the x -coordinate:

$$V(x) = \begin{cases} 0 & -\frac{L}{2} \leq x \leq \frac{L}{2} \\ \infty & |x| > \frac{L}{2} \end{cases}$$

with the border condition $\varphi(x = -\frac{L}{2}) = 0$ and $\varphi(x = \frac{L}{2}) = 0$, also for the first derivative, this leads to the energy values:

$$E_{n_x} = \frac{\hbar^2}{2M} \left(\frac{\pi}{L}\right)^2 n_x^2$$

for $n_x \in \mathbb{N}$. This means E_{n_x} got a lowest energy with $n_x = 1$:

$$E_{n_x, \min} = \frac{\hbar^2}{2M} \left(\frac{\pi}{L} \right)^2$$

Now extending the problem to three dimensions. We can just sum the one-dimensional energies, while the dimensions are not coupled:

$$E_{n_x n_y n_z} = \frac{\hbar^2 \pi^2}{2ML^2} (n_x^2 + n_y^2 + n_z^2)$$

therefore the spacing between the translational energy levels isn't constant. The lowest level can be found for all of the $n_i = 1$ to be:

$$E_{111} = \frac{3\hbar^2 \pi^2}{2ML^2}$$

the next highest level can be found for one of the n 's being 2 and the others being 1, therefore the lowest spacing between two translational energy levels is:

$$E_{211} - E_{111} = \frac{\hbar^2 \pi^2}{2ML^2} (6 - 3) = \frac{3\hbar^2 \pi^2}{2ML^2} \approx 2.7 \cdot 10^{-38} J$$

with $L = 10^{-2} m$. The translational energy levels therefore might be considered as continuous to some respect.

(b)

Definition of partition function:

$$Z = Z_N(T, V) = c_N \int d^{3N} q d^{3N} p e^{-\beta H(\vec{q}_N, \vec{p}_N)}$$

for the discrete (quantized case):

$$Z_N(T) = Tr \left(e^{-\beta \hat{H}} \right)$$

with the hamiltonian:

$$\hat{H} = \hat{H}_{trans} + \hat{H}_{rot} = \sum_i \frac{p_i^2}{2M} + \frac{\hbar^2}{2\mu d^2} \hat{L}^2$$

while translation and rotation are independent, we can find simultaneous eigenkets:

$$\hat{H}|\psi\rangle = \hat{H}|n_x n_y n_z\rangle_{trans} \otimes |l\rangle_{rot} = \left(\frac{\hbar^2 \pi^2}{2ML^2} (n_x^2 + n_y^2 + n_z^2) + \frac{\hbar^2 l(l+1)}{2\mu d^2} \right) |\psi\rangle$$

Inserting this in the partition function and considering the degeneracy of $2l+1$ leads to:

$$\begin{aligned} Z_N(T) &= Tr \left(e^{-\beta \hat{H}} \right) \\ &= \sum_{n_x, n_y, n_z=0}^{\infty} \sum_{l=0}^{\infty} (2l+1) \langle n_x n_y n_z; l | \exp \left(-\beta \hat{H} \right) | n_x n_y n_z; l \rangle \\ &= \sum_{n_x, n_y, n_z=0}^{\infty} \sum_{l=0}^{\infty} (2l+1) \exp \left(-\beta \left[\frac{\hbar^2 \pi^2}{2ML^2} (n_x^2 + n_y^2 + n_z^2) + \frac{\hbar^2 l(l+1)}{2\mu d^2} \right] \right) \end{aligned}$$

we now have to consider the temperature, when rotations become important. Therefore we assume, that the relevance starts, when the exponent becomes about $-l(l+1)$ or better to say:

$$\begin{aligned}\beta \frac{\hbar^2}{2\mu d^2} &= 1 \\ \frac{\hbar^2}{2k_B \mu d^2} &= T \\ T &\approx 14.6 K\end{aligned}$$

now using $\alpha = \frac{\hbar^2 \pi^2}{2ML^2}$ and $\gamma = \frac{\hbar^2}{2\mu d^2}$ we can rewrite:

$$Z_N(T) = \sum_{n_x, n_y, n_z=0}^{\infty} \sum_{l=0}^{\infty} (2l+1) \exp(-\beta [\alpha (n_x^2 + n_y^2 + n_z^2) + \gamma (l^2 + l)])$$

for high temperatures (especially $k_B \cdot 14.6 K \approx 2 \cdot 10^{-22} J$, which is much higher than the spacing between translational energy levels) now, there are many energy levels that can be reached (as seen in **a**)) therefore the energy distribution becomes continuous and we can rewrite in integrals (for the n 's this would already be possible for $T = 14.6 K$):

$$Z_N(T) = \int_0^{\infty} d^3n \exp(-\beta \alpha (n_x^2 + n_y^2 + n_z^2)) \int_0^{\infty} dl (2l+1) \exp(-\beta \gamma (l^2 + l))$$

the first kind of integral is well known, the second one can be rewritten:

$$Z_N(T) = \left(\frac{\pi}{4\alpha\beta}\right)^{\frac{3}{2}} e^{\frac{\beta\gamma}{4}} \int_0^{\infty} dl (2l+1) \exp\left(-\beta\gamma \left(l + \frac{1}{2}\right)^2\right)$$

this time we cannot use the symmetry, while the interval that we are using for the integration isn't symmetric. Therefore we have to do it by hand, first starting with the substitution $l + \frac{1}{2} = x \Rightarrow x - \frac{1}{2} = l$ and $dl = dx$:

$$Z_N(T) = \left(\frac{\pi}{4\alpha\beta}\right)^{\frac{3}{2}} e^{\frac{\beta\gamma}{4}} \int_{\frac{1}{2}}^{\infty} dx 2x \exp(-\beta\gamma x^2)$$

this integral can be calculated using:

$$\begin{aligned}\frac{\partial}{\partial x} \exp(-\beta\gamma x^2) &= -2\beta\gamma x \exp(-\beta\gamma x^2) \\ &\Leftrightarrow \\ x \exp(-\beta\gamma x^2) &= \frac{-1}{2\beta\gamma} \frac{\partial}{\partial x} \exp(-\beta\gamma x^2)\end{aligned}$$

this inserted in the integral:

$$\begin{aligned}
\int_{\frac{1}{2}}^{\infty} dx x \exp(-\beta\gamma x^2) &= \frac{-1}{2\beta\gamma} \int_{\frac{1}{2}}^{\infty} dx \frac{\partial}{\partial x} \exp(-\beta\gamma x^2) \\
&= \frac{-1}{2\beta\gamma} [\exp(-\beta\gamma x^2)]_{\frac{1}{2}}^{\infty} \\
&= \frac{-1}{2\beta\gamma} \left[-\exp\left(-\frac{\beta\gamma}{4}\right) \right] \\
&= \frac{e^{-\frac{\beta\gamma}{4}}}{2\beta\gamma}
\end{aligned}$$

therefore we get:

$$\begin{aligned}
Z_N(T) &= \left(\frac{\pi}{4\alpha\beta} \right)^{\frac{3}{2}} e^{\frac{\beta\gamma}{4}} \frac{e^{-\frac{\beta\gamma}{4}}}{2\beta\gamma} \\
&= \left(\frac{\pi}{4\alpha\beta} \right)^{\frac{3}{2}} \frac{1}{\beta\gamma}
\end{aligned}$$

inserting α and γ :

$$Z_N(T) = \left(\frac{\pi}{4 \left(\frac{\hbar^2 \pi^2}{2ML^2} \right) \beta} \right)^{\frac{3}{2}} \frac{1}{\beta \frac{\hbar^2}{2\mu d^2}} = \left(\frac{k_B T M L^2}{2\hbar^2 \pi} \right)^{\frac{3}{2}} \frac{2\mu d^2 k_B T}{\hbar^2} = \left(\frac{M L^2}{2\hbar^2 \pi} \right)^{\frac{3}{2}} \frac{2\mu d^2}{\hbar^2} (k_B T)^{\frac{5}{2}}$$

While this is the partition function for one particle the systems partition function is defined by $Z_{sys} = (Z_N(T))^N$ leading to:

$$Z_{sys}(T) = \left(\frac{M L^2}{2\hbar^2 \pi} \right)^{\frac{3}{2}N} \left(\frac{2\mu d^2}{\hbar^2} \right)^N (k_B T)^{\frac{5}{2}N} \quad (6)$$

(c)

While we should calculate some expressions, we first have to think about what temperature would be suitable, while the rotational degrees of freedom should make an important contribution. This is only for $T \gg 14.6 K$, therefore we can use 6.

Definition free energy:

$$\begin{aligned}
F &= -k_B T \ln Z \\
&= -k_B T N \ln \left[\left(\frac{M L^2}{2\hbar^2 \pi} \right)^{\frac{3}{2}} \frac{2\mu d^2}{\hbar^2} (k_B T)^{\frac{5}{2}} \right] \\
&= -k_B T N \left[\frac{3}{2} \ln \left(\frac{M L^2}{2\hbar^2 \pi} \right) + \ln \left(\frac{2\mu d^2}{\hbar^2} \right) + \frac{5}{2} \ln (k_B T) \right] \\
&= -k_B T N \left[\frac{3}{2} \ln \left(\frac{M L^2}{2\pi} \right) + \ln (2\mu d^2) - \frac{5}{2} \ln \hbar^2 + \frac{5}{2} \ln (k_B T) \right]
\end{aligned}$$

Definition entropy:

$$\begin{aligned}
S &= -\left.\frac{\partial F}{\partial T}\right|_V \\
&= k_B N \frac{\partial}{\partial T} T \left[\frac{3}{2} \ln \left(\frac{ML^2}{2\pi} \right) + \ln(2\mu d^2) - \frac{5}{2} \ln \hbar^2 + \frac{5}{2} \ln(k_B T) \right] \\
&= k_B N \left(\frac{3}{2} \ln \left(\frac{ML^2}{2\pi} \right) + \ln(2\mu d^2) - \frac{5}{2} \ln \hbar^2 + \frac{5}{2} \ln(k_B T) + T \frac{\partial}{\partial T} \left[\frac{5}{2} \ln T \right] \right) \\
&= k_B N \left(\frac{3}{2} \ln \left(\frac{ML^2}{2\pi} \right) + \ln(2\mu d^2) - \frac{5}{2} \ln \hbar^2 + \frac{5}{2} \ln(k_B T) + \frac{5}{2} T \frac{1}{T} \right) \\
&= k_B N \left(\frac{3}{2} \ln \left(\frac{ML^2}{2\pi} \right) + \ln(2\mu d^2) - \frac{5}{2} \ln \hbar^2 + \frac{5}{2} \ln(k_B T) + \frac{5}{2} \right)
\end{aligned}$$

Definition of heat capacity:

$$\begin{aligned}
C_V &= T \left.\frac{\partial S}{\partial T}\right|_{N,V} \\
&= T \frac{\partial}{\partial T} \left(N k_B \left(\frac{3}{2} \ln \left(\frac{ML^2}{2\pi} \right) + \ln(2\mu d^2) - \frac{5}{2} \ln \hbar^2 + \frac{5}{2} \ln(k_B T) + \frac{5}{2} \right) \right) \\
&= \frac{5}{2} N k_B T \frac{\partial}{\partial T} \ln T \\
&= \frac{5}{2} N k_B
\end{aligned}$$

This result can be physically interpreted. The lineare molecules, will have two rotational axes (one rotational axis has no momentum, the molecule binding axis, the other two orthogonal to that one give one degree of freedom each) and three translational degrees of freedom (there are no vibrational degrees of freedom, the molecule got a “rigid bonding”), resulting in 5 degrees of freedom f , while we got $\frac{5}{2} = \frac{f}{2}$ this is perfectly fulfilled in the prediction for the heat capacity.