

4125 HW 7

Duncan Wilkie

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6.5a

Applying the definition,

$$\begin{aligned} Z &= \sum_s e^{-E(s)/kT} = e^{(-0.05 \text{ eV})(1.6 \times 10^{-19} \text{ J/eV})/(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})} + e^0 \\ &\quad + e^{(0.05 \text{ eV})(1.6 \times 10^{-19} \text{ J/eV})/(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})} \\ &= 8.05 \end{aligned}$$

6.5b

The Boltzmann distribution is

$$P(s) = \frac{1}{Z} e^{-E(s)/kT}$$

Applying it,

$$\begin{aligned} P(-0.05 \text{ eV}) &= \frac{1}{8.05} e^{(0.05 \text{ eV})(1.6 \times 10^{-19} \text{ J/eV})/(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})} = 0.86 \\ P(0 \text{ eV}) &= \frac{1}{8.05} e^0 = 0.12 \\ P(0.05 \text{ eV}) &= \frac{1}{8.05} e^{-(0.05 \text{ eV})(1.6 \times 10^{-19} \text{ J/eV})/(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})} = 0.018 \end{aligned}$$

6.5c

Doing the same calculation,

$$\begin{aligned} Z &= e^0 + e^{-(0.05 \text{ eV})(1.6 \times 10^{-19} \text{ J/eV})/(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})} \\ &\quad + e^{-(0.1 \text{ eV})(1.6 \times 10^{-19} \text{ J/eV})/(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})} = 1.17 \\ P(0 \text{ eV}) &= \frac{1}{Z} e^0 = 0.86 \\ P(0.05 \text{ eV}) &= \frac{1}{1.17} e^{-(0.05 \text{ eV})(1.6 \times 10^{-19} \text{ J/eV})/(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})} = 0.12 \end{aligned}$$

$$P(0.1 \text{ eV}) = \frac{1}{1.17} e^{-(0.1 \text{ eV})(1.6 \times 10^{-19} \text{ J/eV})/(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})} = 0.018$$

The partition function changes, but the probabilities don't. Numerically verifying something whose proof is obvious and is given in the text is pure torture.

6.13

The difference in energy is

$$\Delta E = \Delta mc^2 = (2.3 \times 10^{-30} \text{ kg})(3 \times 10^8 \text{ m/s})^2 = 2.07 \times 10^{-13} \text{ J}$$

The ratio of the probability of a particle being in one state to that of the other is

$$\frac{P(\text{neutron})}{P(\text{proton})} = e^{-\Delta E/kT} = e^{-(2.07 \times 10^{-13} \text{ J})/(1.38 \times 10^{-23} \text{ J/K})(10^{11} \text{ K})} = 0.86$$

We also have $P(\text{neutron}) + P(\text{proton}) = 1 \Leftrightarrow P(\text{neutron}) = 1 - P(\text{proton})$. Substituting this,

$$\begin{aligned} \frac{1}{P(\text{proton})} - 1 &= 0.86 \Rightarrow P(\text{proton}) = \frac{1}{1 + 0.86} = 0.54 \\ \Rightarrow P(\text{neutron}) &= 1 - 0.54 = 0.46 \end{aligned}$$

These will be the fractions of the nucleons that are of each type of particle, respectively.

6.15a

$$\overline{E} = [4(0 \text{ eV}) + 3(1 \text{ eV}) + 2(4 \text{ eV}) + 1(6 \text{ eV})]/10 = 1.7 \text{ eV}$$

6.15b

For 0 eV, it's $4/10 = 0.4$; for 1 eV, it's $3/10 = 0.3$; for 4 eV, it's $2/10 = 0.2$; for 6 eV, it's $1/10 = 0.1$.

6.15c

Applying the formula,

$$\overline{E} = 0.4(0 \text{ eV}) + 0.3(1 \text{ eV}) + 0.2(4 \text{ eV}) + 0.1(6 \text{ eV}) = 1.7 \text{ eV}$$

6.21

Using Sage:

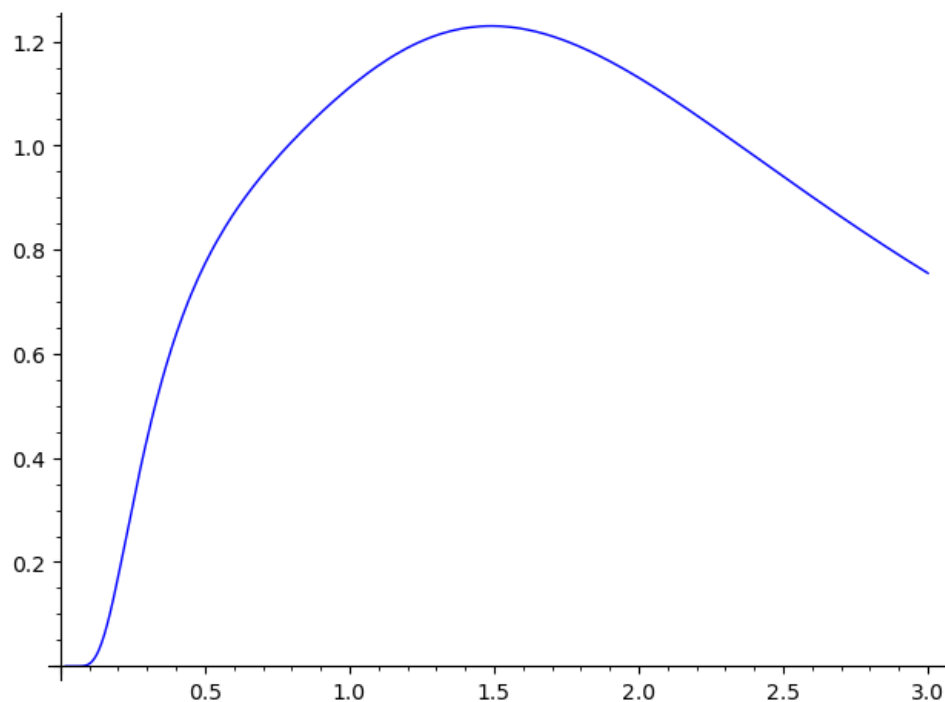
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|-----|
| SageMath version 9.2, Release Date: 2020-10-24 |
| Using Python 3.9.2. Type "help()" to get help. |
|-----|

sage: var('n eps beta T k x')
(n, eps, beta, T, k, x)
sage: E(n) = eps*(1.03*n-0.03*n^2)
sage: Z(beta) = sum(exp(-beta*E), n, 0, 15)
sage: U(beta) = -1/Z(beta)*diff(Z(beta), beta)
sage: C(T) = diff(U(1/(k*T)), T)
sage: C = (C(eps*x/k) / k).full_simplify()
sage: plot(C(x), (x, 0, 3))
# Launched png viewer for Graphics object consisting of 1 graphics primitive

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This produces the following plot of the heat capacity



where the vertical axis is C/k and the horizontal is kT/ϵ (couldn't be bothered to figure out TeX formatting of plot fields in Sage). Including fewer levels results in a faster falloff on the right side of the graph. In the case of the harmonic oscillator, the heat capacity doesn't actually fall off at large T , but approaches a constant value. The vibrational portion of figure 1.13 is more consistent with this anharmonic model, as it doesn't appear to level off as T increases.

6.26

The approximate partition function is

$$Z_{rot} = 1 + 3e^{-2\epsilon/kT}$$

The average energy is then

$$\bar{E} = \frac{1}{Z} \sum_{j=0}^1 E(j)(2j+1)e^{-E(j)/kT} = \frac{1}{1 + 3e^{-2\epsilon/kT}} \left(0 + 6\epsilon e^{-2\epsilon/kT} \right) \approx 6\epsilon e^{-2\epsilon/kT}$$

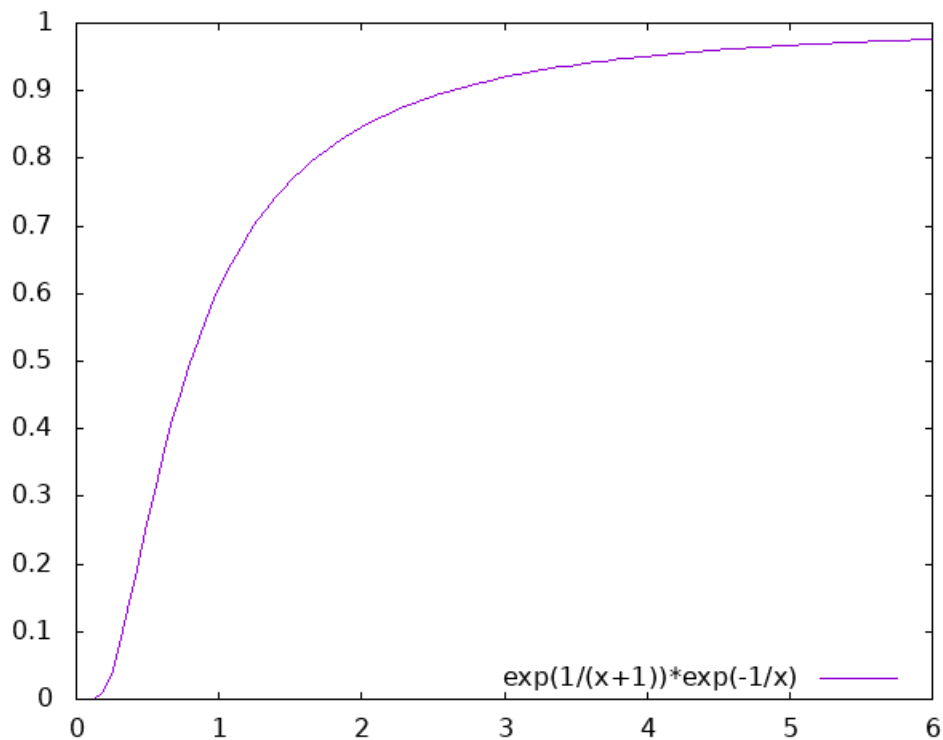
The heat capacity is

$$C_V = \frac{\partial \bar{E}}{\partial T} = \frac{12\epsilon^2}{kT^2} e^{-2\epsilon/kT}$$

The relationship between heat capacity and entropy yields

$$\frac{C_V}{T} = \frac{\partial S}{\partial T} \Rightarrow S = \frac{12\epsilon^2}{k} \int \frac{e^{-2\epsilon/kT}}{T^3} dT$$

In the limit as $T \rightarrow 0$, the numerator of the integrand will fall to zero much faster than the denominator, so this result is consistent with the third law of thermodynamics. The high-temperature limit is a constant, so a simple interpolation between them would be a function that's roughly $e^{-1/T}$ in the limit to zero and constant in the limit to infinity, as shown below.



6.32a

For a continuous probability distribution $P(x)$ the expectation value of x is

$$\langle x \rangle = \int_{\mathbb{R}} x P(x) dx$$

In the case of a particle in a potential well, the probability of the particle being in the position x is

$$P(x) = \frac{e^{-\beta u(x)}}{Z}$$

since the energy state of the particle is determined by its position according to u . Applying the definition of the partition function and writing the sum over an uncountably infinite index as an integral,

$$\langle x \rangle = \int_{\mathbb{R}} x \frac{e^{-\beta u(x)}}{\int_{\mathbb{R}} e^{-\beta u(x)} dx} dx$$

Factoring out the constant,

$$\langle x \rangle = \frac{\int_{\mathbb{R}} x e^{-\beta u(x)} dx}{\int_{\mathbb{R}} e^{-\beta u(x)} dx}$$

as desired.

6.32b

If x_0 is the minimum of the potential, then it must also be a critical point, i.e. $\frac{du}{dx}|_{x_0} = 0$. Plugging the approximation

$$u(x) = u(x_0) + \frac{1}{2}(x - x_0)^2 \frac{d^2 u}{dx^2} \Big|_{x_0}$$

into the above-derived expression for the expectation of position,

$$\langle x \rangle = \frac{e^{-\beta u(x_0)}}{e^{-\beta u(x_0)}} \frac{\int_{\mathbb{R}} x e^{-\beta \frac{u''(x_0)}{2}(x-x_0)^2} dx}{\int_{\mathbb{R}} e^{-\beta \frac{u''(x_0)}{2}(x-x_0)^2} dx} = \frac{\int_{\mathbb{R}} (x + x_0) e^{-ax^2} dx}{\int_{\mathbb{R}} e^{-ax^2} dx}$$

Distributing in the numerator will yield an odd function in the first term, which will be zero, and in the second term everything but x_0 cancels, leaving $\langle x \rangle = x_0$ as desired.

6.32c

Proceeding similarly,

$$\langle x \rangle = \frac{\int_{\mathbb{R}} x e^{-\beta \frac{u''(x_0)}{2}(x-x_0)^2} e^{-\beta \frac{u'''(x_0)}{6}(x-x_0)^3} dx}{\int_{\mathbb{R}} e^{-\beta \frac{u''(x_0)}{2}(x-x_0)^2} e^{-\beta \frac{u'''(x_0)}{6}(x-x_0)^3} dx} \approx \frac{\int_{\mathbb{R}} x e^{-\beta \frac{u''(x_0)}{2}(x-x_0)^2} \left(1 - \left[\beta \frac{u'''(x_0)}{6}(x-x_0)^3\right]\right) dx}{\int_{\mathbb{R}} e^{-\beta \frac{u''(x_0)}{2}(x-x_0)^2} \left(1 - \left[\beta \frac{u'''(x_0)}{6}(x-x_0)^3\right]\right) dx}$$

$$\begin{aligned}
&= \frac{\int_{\mathbb{R}} x_0 e^{-\beta \frac{u''(x_0)}{2} x^2} dx - \int_{\mathbb{R}} (x + x_0) e^{-\beta \frac{u''(x_0)}{2} x^2} \left(\beta \frac{u'''(x_0)}{6} x^3 \right) dx}{\int_{\mathbb{R}} e^{-\beta \frac{u''(x_0)}{2} x^2} dx - \int_{\mathbb{R}} e^{-\beta \frac{u''(x_0)}{2} x^2} \beta \frac{u'''(x_0)}{2} x^3 dx} \\
&= \frac{x_0 \sqrt{\frac{2\pi}{\beta u''(x_0)}} - \frac{\beta u'''(x_0)}{6} \int_{-\infty}^{\infty} x^4 e^{-\beta \frac{u''(x_0)}{2} x^2} dx}{\sqrt{\frac{2\pi}{\beta u''(x_0)}}} \\
&= x_0 - \frac{\beta u'''(x_0)}{6} \sqrt{\frac{\beta u''(x_0)}{2\pi}} \int_{-\infty}^{\infty} x^4 e^{-ax^2} dx
\end{aligned}$$

This integral is in the appendix, and evaluates to $\frac{3\sqrt{\pi}}{4a^{5/2}}$. We therefore have

$$\begin{aligned}
&= x_0 - \frac{\beta u'''(x_0)}{6} \sqrt{\frac{\beta u''(x_0)}{2\pi}} \frac{3\sqrt{\pi}}{4(\beta u''(x_0)/2)^{5/2}} = x_0 - \frac{\beta u'''(x_0)}{8} \sqrt{\frac{\beta u''(x_0)}{2(\beta u''(x_0)/2)^5}} = x_0 - \frac{\beta u'''(x_0)}{8} \frac{4}{\beta^2 u''(x_0)^2} \\
&= x_0 - \frac{u'''(x_0)}{2u''(x_0)^2} \frac{1}{\beta}
\end{aligned}$$

Subtracting x_0 from both sides, this proves that $\langle x \rangle - x_0$ is proportional to $kT = \frac{1}{\beta}$ by a proportionality constant

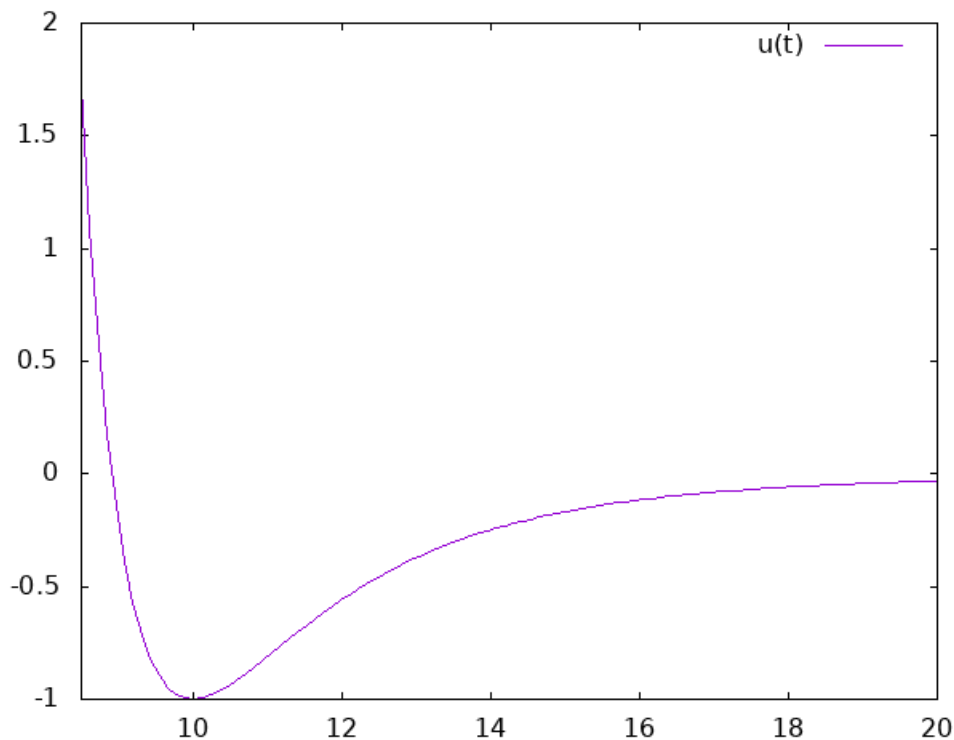
$$-\frac{u'''(x_0)}{2u''(x_0)^2}$$

In terms of the Taylor coefficients, $u'''(x_0) = 6a_3$ and $u''(x_0) = 2a_2$, so the proportionality constant may be written

$$-\frac{6a_3}{8u''(x_0)^2} = -\frac{3a_3}{4a_2^2}$$

6.32d

This potential with y -axis in units of u_0 and $x_0 = 10$ is plotted below.



The minimum occurs at

$$u'(x) = 0 \Leftrightarrow 12u_0 \left[\frac{x_0^6}{x^7} - \frac{x_0^{12}}{x^{13}} \right] = 0 \Leftrightarrow x^6 = x_0^6 \Leftrightarrow x = x_0$$

We only need the two derivatives

$$u''(x_0) = 12u_0 \left[13 \frac{x_0^{12}}{x_0^{14}} - 7 \frac{x_0^6}{x_0^8} \right] = \frac{72u_0}{x_0^2}$$

and

$$u'''(x_0) = 12u_0 \left[7 \cdot 8 \frac{x_0^6}{x_0^9} - 13 \cdot 14 \frac{x_0^{12}}{x_0^{15}} \right] = -\frac{1512u_0}{x_0^3}$$

to compute the proportionality constant

$$-\frac{u'''(x_0)}{2u''(x_0)^2} = \frac{1512u_0/x_0^3}{2 \cdot 72^2 u_0^2/x_0^4} = \frac{7x_0}{48u_0}$$

This proportionality constant is equal to $\alpha x_0/k$, since the derivative of the average linear interatomic spacing with respect to temperature is k times this proportionality constant, and we must divide

by the initial spacing to obtain the formula for α . Computing α with the given numbers,

$$\alpha = k \frac{7}{48u_0} = (1.38 \times 10^{-23} \text{ J/K}) \frac{7}{48(0.01 \text{ eV})} = 0.0013$$

which is roughly twice the measured value (possibly due to our assumption of x_0 as the initial length; this number would likely agree better if one multiplied it by the ratio x_0/x_m where x_m is the measured interatomic spacing at 80 K).

6.38

Using the change of variables given in the book to simplify the integral of the Maxwell distribution,

$$\begin{aligned} x_{min} = v_{min} \sqrt{m/2kT} &= (300 \text{ m/s}) \sqrt{(28 \text{ amu})(1.66 \times 10^{-27} \text{ kg/amu})/2(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})} \\ &= 0.71 \end{aligned}$$

The integral corresponding to the proportion of the particles above 300 m/s is then, following the text,

$$\frac{4}{\sqrt{\pi}} \int_{0.71}^{\infty} x^2 e^{-x^2} = \frac{4}{\sqrt{\pi}} (0.35) = 0.79$$

The proportion below 300 m/s is one minus this number, or 0.21

6.42a

The result for one oscillator is immediate:

$$F = -kT \ln Z = -kT \ln \left(\frac{1}{1 - e^{-\beta\epsilon}} \right) = kT \ln (1 - e^{-\beta\epsilon})$$

The Helmholtz free energy is extensive, so if we have N oscillators at the same frequency, the expression is

$$F = NkT \ln (1 - e^{-\epsilon/kT})$$

6.42b

Applying the partial derivative relation between entropy and Helmholtz free energy,

$$\begin{aligned} S &= - \left(\frac{\partial F}{\partial T} \right)_{N,V} = - \left(Nk \ln (1 - e^{-\epsilon/kT}) - NkT \frac{1}{1 - e^{-\epsilon/kT}} \frac{\epsilon e^{-\epsilon/kT}}{kT^2} \right) \\ &= N \left(\frac{\epsilon}{T e^{\epsilon/kT} - T} - k \ln (1 - e^{-\epsilon/kT}) \right) \end{aligned}$$

6.49

The volume of the gas is, by the ideal gas law,

$$V = \frac{nRT}{P} = \frac{(1 \text{ mol})(8.31 \text{ J/mol} \cdot \text{K})(300 \text{ K})}{1 \times 10^5 \text{ Pa}} = 0.025 \text{ m}^3$$

We have

$$U = U_{int} + \frac{3}{2}nRT$$

In our case, kT is higher than ϵ by roughly a factor of 100, so the high temperature limit may be used to calculate U_{int} . The average rotational energy calculation at high temperature performed in the book yields for identical atoms kT per molecule, implying the total internal energy in the gas is nRT . We then have

$$U = \frac{5}{2}nRT = \frac{5}{2}(1 \text{ mol})(8.31 \text{ J/mol} \cdot \text{K})(300 \text{ K}) = 6.23 \text{ kJ}$$

The enthalpy is

$$H = U + PV = \frac{7}{2}nRT = 8.73 \text{ kJ}$$

The internal partition function for one molecule is, since kT is higher than ϵ by roughly a factor of 100 and vibrational modes are frozen out,

$$Z_{rot} \approx \frac{kT}{2\epsilon} = \frac{(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})}{2(0.00025 \text{ eV})(1.6 \times 10^{-19} \text{ J/eV})} = 51.75$$

The quantum volume is, since the mass of a nitrogen molecule is $28 \text{ amu} = 4.6 \times 10^{-26} \text{ kg}$,

$$v_Q = \left(\frac{h}{\sqrt{2\pi mkT}} \right)^3 = \left(\frac{6.67 \times 10^{-34} \text{ J} \cdot \text{s}}{\sqrt{2\pi(4.6 \times 10^{-26} \text{ kg})(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})}} \right)^3 = 7.17 \times 10^{-33} \text{ m}^3$$

These quantities enable us to calculate the entropy of the gas using the result of 6.48a:

$$\begin{aligned} S &= nR \left[\ln \left(\frac{VZ_{rot}}{(nR/k)v_Q} \right) + \frac{7}{2} \right] \\ &= (1 \text{ mol})(8.31 \text{ J/mol} \cdot \text{K}) \left[\ln \left(\frac{(0.025 \text{ m}^3)(1)(51.75)}{[(1 \text{ mol})(8.31 \text{ J/mol} \cdot \text{K})/(1.38 \times 10^{-23} \text{ J/K})](7.17 \times 10^{-33} \text{ m}^3)} \right) + \frac{7}{2} \right] \\ &= 191 \text{ J/K} \end{aligned}$$

From this, we can get the Helmholtz and Gibbs free energies

$$F = U - TS = 6.23 \text{ kJ} - (300 \text{ K})(191 \text{ J/K}) = -51 \text{ kJ}$$

and

$$G = H - TS = 8.73 \text{ kJ} - (300 \text{ K})(191 \text{ J/K}) = -49 \text{ kJ}$$

The chemical potential is the Gibbs free energy per particle, so

$$\mu = G/N_A = \frac{-49 \text{ kJ}}{6.02 \times 10^{23}} = -8.07 \times 10^{-20} \text{ J} = -0.5 \text{ eV}$$

6.52

From the de Broglie relation, $p_n = \frac{hn}{2L}$. Applying the relativistic energy, we have a translational kinetic energy of

$$E_n = \frac{hcn}{2L}$$

The partition function is then

$$Z_{1d} = \sum_n e^{-E_n/kT} = \sum_n e^{-hcn/2kLT} \approx \int_0^\infty e^{-hcn/2kLT} dn = -\frac{2kLT}{hc} e^{-hcn/2kLT} \Big|_0^\infty = \frac{2kLT}{hc}$$