

Substituting dV from (S.4.34.2) and dV' from (S.4.34.3) into (S.4.34.1), we have

$$\tau = c_v (\tau' - \tau) + (P - P') \frac{\tau'}{P'} \quad (\text{S.4.34.4})$$

So,

$$\begin{aligned} \tau' &= \frac{(1 + c_v) \tau}{c_v + P/P' - 1} = \frac{c_p \tau}{c_v + P/P' - 1} \quad (\text{S.4.34.5}) \\ &= \frac{C_P \tau}{C_V + (P/P' - 1) N_A} \end{aligned}$$

When $P = P'$, (S.4.34.5) becomes

$$\tau_1 = \frac{C_P}{C_V} \tau \quad (\text{S.4.34.6})$$

Ideal Gas and Classical Statistics

4.35 Poisson Distribution in Ideal Gas (Colorado)

The probability ω_1 of finding a particular molecule in a volume V is

$$\omega_1 = \frac{V}{\tilde{V}}$$

The probability ω_N of finding N marked molecules in a volume V is

$$\omega_N = \left(\frac{V}{\tilde{V}} \right)^N \quad (\text{S.4.35.1})$$

Similarly, the probability of finding one particular molecule outside of the volume V is

$$\bar{\omega}_1 = \frac{\tilde{V} - V}{\tilde{V}}$$

and for $\tilde{N} - N$ particular molecules outside V ,

$$\bar{\omega}_{\tilde{N}-N} = \left(\frac{\tilde{V} - V}{\tilde{V}} \right)^{\tilde{N}-N} \quad (\text{S.4.35.2})$$

Therefore, the probability P_N of finding any N molecules in a volume V is the product of the two probabilities (S.4.35.1) and (S.4.35.2) weighted by the number of combinations for such a configuration:

$$P_N = \frac{\tilde{N}!}{N! (\tilde{N} - N)!} \left(\frac{V}{\tilde{V}} \right)^N \left(1 - \frac{V}{\tilde{V}} \right)^{\tilde{N}-N} \quad (\text{S.4.35.3})$$

The condition $V \ll \tilde{V}$ also implies that $N \ll \tilde{N}$. Then we may approximate

$$\begin{aligned}\tilde{N}! &\approx (\tilde{N} - N)! \tilde{N}^N \\ \tilde{N} - N &\approx \tilde{N}\end{aligned}\tag{S.4.35.4}$$

So, (S.4.35.3) becomes

$$\begin{aligned}P_N &= \frac{(\tilde{N} - N)! \tilde{N}^N}{N! (\tilde{N} - N)!} \left(\frac{V}{\tilde{V}}\right)^N \left(1 - \frac{V}{\tilde{V}}\right)^{\tilde{N}} \\ &= \frac{1}{N!} \left(\frac{\tilde{N}V}{\tilde{V}}\right)^N \left(1 - \frac{V}{\tilde{V}}\right)^{\tilde{N}} \\ &= \frac{\langle N \rangle^N}{N!} \left(1 - \frac{\langle N \rangle}{\tilde{N}}\right)^{\tilde{N}}\end{aligned}\tag{S.4.35.5}$$

where we used the average number of molecules in V :

$$\langle N \rangle = \frac{\tilde{N}}{\tilde{V}} V$$

Noticing that, for large \tilde{N} ,

$$\left(1 - \frac{x}{\tilde{N}}\right)^{\tilde{N}} \approx e^{-x}$$

we obtain

$$P_N = \frac{\langle N \rangle^N}{N!} e^{-\langle N \rangle}\tag{S.4.35.6}$$

where we used

$$\frac{\langle N \rangle}{\tilde{N}} \ll 1 \quad \tilde{N} \gg 1$$

(S.4.35.6) can be applied to find the mean square fluctuation in an ideal gas (see Problem 4.94) when the fluctuations are not necessarily small (i.e., it is possible to have $(N - \langle N \rangle) / \langle N \rangle \sim 1$, although N is always much smaller than the total number of particles in the gas \tilde{N}).

4.36 Polarization of Ideal Gas (Moscow Phys-Tech)

The potential energy of a dipole in an electric field \mathbf{E} is

$$U = -\mathbf{p} \cdot \mathbf{E} = -pE \cos \theta$$

where the angle θ is between the direction of the electric field (which we choose to be along the $\hat{\mathbf{z}}$ axis) and the direction of a the dipole moment. The center of the spherical coordinate system is placed at the center of the dipole. The probability $d\omega$ that the direction of the dipole is within a solid angle $d\omega = \sin \theta d\varphi d\theta$ is

$$d\omega = Ae^{-U/\tau} d\Omega = \frac{e^{pE \cos \theta/\tau} \sin \theta d\varphi d\theta}{\int_0^{2\pi} \int_0^\pi e^{pE \cos \theta/\tau} \sin \theta d\varphi d\theta} \quad (\text{S.4.36.1})$$

The total electric dipole moment per unit volume of the gas is

$$\begin{aligned} P &= N \langle p \rangle = N \langle p_z \rangle = N \int p \cos \theta d\Omega \quad (\text{S.4.36.2}) \\ &= \frac{N \int_0^{2\pi} \int_0^\pi p \cos \theta e^{pE \cos \theta/\tau} \sin \theta d\varphi d\theta}{\int_0^{2\pi} \int_0^\pi e^{pE \cos \theta/\tau} \sin \theta d\varphi d\theta} \end{aligned}$$

Introducing a new variable $x \equiv \cos \theta$ and denoting $\alpha \equiv pE/\tau$, we obtain

$$\begin{aligned} P &= \frac{Np \int_{-1}^1 x e^{\alpha x} dx}{\int_{-1}^1 e^{\alpha x} dx} = Np \frac{d}{d\alpha} \ln \left[\int_{-1}^1 e^{\alpha x} dx \right] \\ &= Np \frac{d}{d\alpha} \ln \left(\frac{2 \sinh \alpha}{\alpha} \right) \\ &= Np \left[\frac{\alpha}{\sinh \alpha} \left(\frac{\cosh \alpha}{\alpha} - \frac{\sinh \alpha}{\alpha^2} \right) \right] \quad (\text{S.4.36.3}) \\ &= Np \left(\coth \alpha - \frac{1}{\alpha} \right) = Np \left[\coth \frac{pE}{\tau} - \frac{\tau}{pE} \right] \\ &= Np \mathcal{L} \left(\frac{pE}{\tau} \right) \end{aligned}$$

where $\mathcal{L}(pE/\tau)$ is the Langevin function. For $pE \ll \tau$ ($\alpha \ll 1$), we can expand (S.4.36.3) to obtain

$$P = \frac{p^2 N}{3\tau} E \quad (\text{S.4.36.4})$$

Since $\mathbf{D} = \epsilon \mathbf{E}$ and

$$\mathbf{D} = \mathbf{E} + 4\pi \mathbf{P} = \mathbf{E} \left(1 + 4\pi \frac{p^2 N}{3\tau} \right)$$

we have for the dielectric constant

$$\epsilon = 1 + \frac{4\pi p^2 N}{3\tau} \quad (\text{S.4.36.5})$$

4.37 Two-Dipole Interaction (Princeton)

Introduce spherical coordinates with the $\hat{\mathbf{z}}$ axis along the line of the separation between the dipoles. Then the partition function reads

$$Z = \int \int d\Omega_1 d\Omega_2 e^{-U/\tau} \quad (\text{S.4.37.1})$$

The potential energy of the interaction can be rewritten in the form

$$\begin{aligned} U &= \frac{\mu_{1x}\mu_{2x} + \mu_{1y}\mu_{2y} + \mu_{1z}\mu_{2z}}{r^3} - 3 \frac{\mu_{1z}\mu_{2z}}{r^3} \quad (\text{S.4.37.2}) \\ &= \frac{\mu_{1x}\mu_{2x} + \mu_{1y}\mu_{2y} - 2\mu_{1z}\mu_{2z}}{r^3} \end{aligned}$$

Since

$$\begin{aligned} \mu_{ix} &= \mu_i \sin \theta_i \cos \varphi_i \\ \mu_{iy} &= \mu_i \sin \theta_i \sin \varphi_i \\ \mu_{iz} &= \mu_i \cos \theta_i \end{aligned} \quad (\text{S.4.37.3})$$

(S.4.37.2) becomes

$$\begin{aligned} U &= \frac{\mu_1 \mu_2}{r^3} [\sin \theta_1 \sin \theta_2 \cos(\varphi_1 - \varphi_2) - 2 \cos \theta_1 \cos \theta_2] \quad (\text{S.4.37.4}) \\ &= \frac{\mu_1 \mu_2}{r^3} f(\theta_1, \theta_2) \end{aligned}$$

and

$$Z = \int_0^\pi \int_0^{2\pi} \int_0^\pi \int_0^{2\pi} \sin \theta_1 \, d\theta_1 \, d\varphi_1 \, \sin \theta_2 \, d\theta_2 \, d\varphi_2 \quad (\text{S.4.37.5})$$

$$\cdot \exp \left[-\frac{\mu_1 \mu_2}{\tau r^3} f(\theta_1, \theta_2) \right]$$

We can expand the exponential at high temperatures $\mu_1 \mu_2 / \tau r^3 \ll 1$ so that

$$\exp \left[-\frac{\mu_1 \mu_2}{\tau r^3} f(\theta_1, \theta_2) \right] \quad (\text{S.4.37.6})$$

$$\approx 1 - \frac{\mu_1 \mu_2}{\tau r^3} f(\theta_1, \theta_2) + \frac{1}{2!} A f^2(\theta_1, \theta_2) + \dots$$

where $A \equiv \mu_1^2 \mu_2^2 / \tau^2 r^6$. The first-order terms are all zero upon integration, and we have

$$Z = (4\pi)^2 + \frac{A}{2!} \int_0^\pi \int_0^{2\pi} \int_0^\pi \int_0^{2\pi} d \cos \theta_1 \, d \cos \theta_2 \, d\varphi_1 \, d\varphi_2 \quad (\text{S.4.37.7})$$

$$\cdot [\sin^2 \theta_1 \, \sin^2 \theta_2 \, \cos^2(\varphi_2 - \varphi_1) + 4 \cos^2 \theta_1 \, \cos^2 \theta_2]$$

where the cross term also vanishes, and we find

$$Z = (4\pi)^2 + 2\pi^2 A \int_0^\pi \int_0^\pi d \cos \theta_1 \, d \cos \theta_2$$

$$\cdot \left(\frac{1}{2} \sin^2 \theta_1 \, \sin^2 \theta_2 + 4 \cos^2 \theta_1 \, \cos^2 \theta_2 \right)$$

$$= (4\pi)^2 + 2\pi^2 A \int_{-1}^1 \int_{-1}^1 dz_1 \, dz_2 \left[\frac{1}{2} (1 - z_1^2) (1 - z_2^2) + 4z_1^2 z_2^2 \right]$$

$$= (4\pi)^2 + 2\pi^2 A \int_{-1}^1 \int_{-1}^1 dz_1 \, dz_2 \left[\frac{1}{2} - \frac{1}{2} (z_1^2 + z_2^2) + \frac{9}{2} z_1^2 z_2^2 \right] \quad (\text{S.4.37.8})$$

$$= (4\pi)^2 + 2\pi^2 A \left[2 - \frac{1}{2} \cdot 2 \cdot \frac{4}{3} + \frac{9}{2} \cdot \frac{4}{9} \right]$$

$$= (4\pi)^2 + \frac{(4\pi)^2}{3} \frac{\mu_1^2 \mu_2^2}{\tau^2 r^6} = (4\pi)^2 \left(1 + \frac{\mu_1^2 \mu_2^2}{3\tau^2 r^6} \right)$$

The average force is given by

$$\langle \mathbf{f} \rangle = - \left\langle \frac{\partial U}{\partial \mathbf{r}} \right\rangle = - \left(\frac{\partial F}{\partial \mathbf{r}} \right)_{\tau, V}$$

where F is the free energy. So,

$$\langle \mathbf{f} \rangle = \tau \frac{\partial \ln Z}{\partial \mathbf{r}} \approx -2 \frac{\mu_1^2 \mu_2^2}{\tau r^7} \frac{\mathbf{r}}{r} \quad (\text{S.4.37.9})$$

The minus sign indicates an average attraction between the dipoles.

4.38 Entropy of Ideal Gas (Princeton)

a) For an ideal gas the partition function factors; however, we must take the sum of N identical molecules divided by the number of interchanges $N!$ to account for the fact that one microscopic quantum state corresponds to a number of different points in phase space. So

$$Z = \frac{1}{N!} \left(\sum_k e^{-E_k/\tau} \right)^N \quad (\text{S.4.38.1})$$

Now, the Helmholtz free energy, F , is given by

$$\begin{aligned} F &= -\tau \ln Z = -\tau \ln \frac{1}{N!} \left(\sum_k e^{-E_k/\tau} \right)^N \\ &= -N\tau \ln \left(\sum_k e^{-E_k/\tau} \right) + \tau \ln N! \end{aligned} \quad (\text{S.4.38.2})$$

Using Stirling's formula, $\ln N! \approx \int_1^N \ln x \cdot dx \approx N \ln(N/e)$, we obtain

$$F = -N\tau \ln \sum_k e^{-E_k/\tau} + N\tau \ln \frac{N}{e} = -N\tau \ln \left[\frac{e}{N} \sum_k e^{-E_k/\tau} \right] \quad (\text{S.4.38.3})$$

Using the explicit expression for the molecular energy E_k , we can rewrite (S.4.38.3) in the form

$$F = -N\tau \ln \left[\frac{e}{N} \int_0^\infty \int_{-\infty}^\infty \int_{-\infty}^\infty \int_{-\infty}^\infty \frac{dp_x dp_y dp_z dV}{(2\pi\hbar)^3} \right]$$

$$\begin{aligned}
& \cdot e^{-(p_x^2+p_y^2+p_z^2)/2m\tau} \sum_k e^{-\varepsilon_k/\tau} \Big] & (S.4.38.4) \\
& = -N\tau \ln \left[\frac{eV_1}{N} \left(\frac{m\tau}{2\pi\hbar^2} \right)^{3/2} \sum_k e^{-\varepsilon_k/\tau} \right] \\
& = -N\tau \ln \frac{eV_1}{N} + Nf(\tau)
\end{aligned}$$

Here we used the fact that the sum depends only on temperature, so we can define $f(\tau)$:

$$f(\tau) \equiv -\tau \ln \left[\left(\frac{m\tau}{2\pi\hbar^2} \right)^{3/2} \sum_k e^{-\varepsilon_k/\tau} \right] \quad (S.4.38.5)$$

b) Now we can calculate the total entropy S of the two gases (it is important that the gases be identical so that $f(\tau)$ is the same for both vessels):

$$S = - \left(\frac{\partial F}{\partial \tau} \right)_V \quad (S.4.38.6)$$

where F is defined by (S.4.38.4).

$$S_1 = N \ln \frac{eV_1}{N} - Nf'(\tau) \quad (S.4.38.7)$$

$$S_2 = N \ln \frac{eV_2}{N} - Nf'(\tau)$$

We have for total entropy

$$\begin{aligned}
S & = S_1 + S_2 = N \ln \frac{eV_1}{N} - Nf'(\tau) + N \ln \frac{eV_2}{N} - Nf'(\tau) \quad (S.4.38.8) \\
& = N \ln \frac{\tau}{P_1} + N \ln \frac{\tau}{P_2} - 2Nf'(\tau) = -N \ln P_1 P_2 + 2N \ln \tau - 2Nf'(\tau)
\end{aligned}$$

c) After the vessels are connected their volume becomes $V = V_1 + V_2$, the number of particles becomes $2N$, and the temperature remains the same (no work is done in mixing the two gases). So now

$$\begin{aligned}
\tilde{S} & = 2N \ln \frac{e(V_1 + V_2)}{2N} - 2Nf'(\tau) \quad (S.4.38.9) \\
& = -2N \ln P + 2N \ln \tau - 2Nf'(\tau)
\end{aligned}$$

It can be easily seen that the pressure becomes $\tilde{P} = 2P_1P_2/(P_1 + P_2)$, so

$$\begin{aligned}\tilde{S} &= -2N \ln \frac{2P_1P_2}{P_1 + P_2} + 2N \ln \tau - 2N f'(\tau) \quad (\text{S.4.38.10}) \\ &= -N \ln \left(\frac{2P_1P_2}{P_1 + P_2} \right)^2 + 2N \ln \tau - 2N f'(\tau)\end{aligned}$$

and

$$\Delta S = \tilde{S} - S = -N \ln \frac{4P_1P_2}{(P_1 + P_2)^2} = N \ln \frac{(P_1 + P_2)^2}{4P_1P_2} \quad (\text{S.4.38.11})$$

Let us show that ΔS is always nonnegative. This is equivalent to the condition

$$\frac{(P_1 + P_2)^2}{4P_1P_2} \geq 1 \quad (P_1 - P_2)^2 \geq 0 \quad (\text{S.4.38.12})$$

which is always true. At $P_1 = P_2$ ($V_1 = V_2$), $\Delta S = 0$, which makes perfect sense.

4.39 Chemical Potential of Ideal Gas (Stony Brook)

The expression for the Helmholtz free energy was derived in Problem 4.38:

$$F = -N\tau \ln \left[\frac{eV}{N} \left(\frac{m\tau}{2\pi\hbar^2} \right)^{3/2} \sum_k e^{-\varepsilon_k/\tau} \right] \quad (\text{S.4.39.1})$$

Since all the molecules are in the ground state, the sum only includes one term, which we can take as an energy zero, $\varepsilon_0 = 0$. Then (S.4.39.1) becomes

$$F = -N\tau \ln \left[\frac{eV}{N} \left(\frac{m\tau}{2\pi\hbar^2} \right)^{3/2} g \right] \quad (\text{S.4.39.2})$$

where we took into account a degeneracy of the ground state g . The Gibbs free energy G is then

$$\begin{aligned}G = F + PV &= -N\tau \ln \left[\frac{eV}{N} \left(\frac{m\tau}{2\pi\hbar^2} \right)^{3/2} g \right] + PV \\ &= -N\tau \ln \left[\frac{eV}{N} \left(\frac{m\tau}{2\pi\hbar^2} \right)^{3/2} g \right] + N\tau \quad (\text{S.4.39.3}) \\ &= -N\tau \ln \left[\frac{gV}{N} \left(\frac{m\tau}{2\pi\hbar^2} \right)^{3/2} \right] = -N\tau \ln \left[\frac{g\tau}{P} \left(\frac{m\tau}{2\pi\hbar^2} \right)^{3/2} \right]\end{aligned}$$

where we have expressed G as a function of τ, P . The chemical potential $\mu = G/N$, so we obtain, from (S.4.39.3),

$$\begin{aligned}\mu &= \tau \ln \left[\frac{g\tau^{5/2}}{P} \left(\frac{m}{2\pi\hbar^2} \right)^{3/2} \right] \\ &= \tau \ln \left[\frac{P}{g\tau^{5/2}} \left(\frac{2\pi\hbar^2}{m} \right)^{3/2} \right] = \tau \ln \left[\frac{N}{gV} \left(\frac{2\pi\hbar^2}{m\tau} \right)^{3/2} \right]\end{aligned}\quad (\text{S.4.39.4})$$

This approximation is valid when the temperature is much lower than the energy difference ΔE between the electronic ground state and the first excited state; since this ΔE is comparable to the ionization energy ε_{ion} , this condition is equivalent to $\tau \ll \varepsilon_{\text{ion}}$. However, even at temperatures $\tau \sim \varepsilon_{\text{ion}}$, the gas is almost completely ionized (see Landau and Lifshitz, *Statistical Physics*, Sect. 106). Therefore (S.4.39.4) is always valid for a nonionized gas.

4.40 Gas in Harmonic Well (Boston)

a) The partition function is given by a standard integral (compare with 4.38, where the molecules are indistinguishable):

$$\begin{aligned}Z &= \int e^{-\varepsilon/\tau} \frac{d^3p \, d^3x}{(2\pi\hbar)^3} \\ &= \frac{1}{(2\pi\hbar)^3} \int_0^\infty e^{-p^2/2m\tau} 4\pi p^2 \, dp \int_{-\infty}^\infty e^{-(x^2+y^2+z^2)/2V^{2/3}\tau} \, dx \, dy \, dz \\ &= \frac{1}{2\pi^2\hbar^3} \frac{\sqrt{\pi}}{4} (2m\tau)^{3/2} 2^{3/2} V \tau^{3/2} \pi^{3/2} \\ &= \frac{\tau^3 m^{3/2} V}{\hbar^3}\end{aligned}\quad (\text{S.4.40.1})$$

The Helmholtz free energy F follows directly from the partition function:

$$\begin{aligned}F &= -N\tau \ln Z = -N\tau \ln V - 3N\tau \ln \tau - N\tau \ln \frac{m^{3/2}}{\hbar^3} \\ &= -N\tau \ln V + Nf(\tau)\end{aligned}\quad (\text{S.4.40.2})$$

b) We may find the force from F :

$$\dot{P} = - \left(\frac{\partial F}{\partial V} \right)_\tau = \frac{N\tau}{V}\quad (\text{S.4.40.3})$$

The equation of state is therefore analogous to the gas in a container with rigid walls, where

$$\tilde{P}V = N\tau$$

c) The entropy, energy, and heat capacity all follow in quick succession from F :

$$S = - \left(\frac{\partial F}{\partial \tau} \right)_V = N \ln V + 3N \ln \tau + 3N + N \ln \frac{m^{3/2}}{\hbar^3} \quad (\text{S.4.40.4})$$

$$E = F + \tau S = 3N\tau \quad (\text{S.4.40.5})$$

$$C_V = \left(\frac{\partial E}{\partial \tau} \right)_V = 3N \quad (\text{S.4.40.6})$$

4.41 Ideal Gas in One-Dimensional Potential (Rutgers)

a) The coordinate- and momentum-dependent parts of the partition function can be separated. The coordinate-dependent part of the partition function

$$Z_q = \int_0^{\infty} e^{-U(x)/\tau} dx \quad (\text{S.4.41.1})$$

For the potential in this case we have

$$\begin{aligned} Z_q &= \int_0^{\infty} e^{-Ax^n/\tau} dx = \frac{1}{n} \left(\frac{\tau}{A} \right)^{1/n} \int_0^{\infty} e^{-z} z^{1/n-1} dz \quad (\text{S.4.41.2}) \\ &= \frac{\tau^{1/n}}{nA^{1/n}} \Gamma \left(\frac{1}{n} \right) \end{aligned}$$

where we substituted

$$x = \left(\frac{\tau}{A} \right)^{1/n} z^{1/n}$$

$$dx = \frac{1}{n} \left(\frac{\tau}{A} \right)^{1/n} z^{1/n-1} dz$$

and

$$\int_0^{\infty} z^{1/n-1} e^{-z} dz \equiv \Gamma \left(\frac{1}{n} \right)$$

The free energy associated with the coordinate-dependent part of the partition function is

$$F_q = -\tau \ln Z = -\tau \frac{1}{n} \ln \tau - \tau \ln \left[\frac{\Gamma(1/n)}{nA^{1/n}} \right] \quad (\text{S.4.41.3})$$

The average potential energy is given by

$$\langle U \rangle = F_q - \tau \left(\frac{\partial F_q}{\partial \tau} \right)_{\nu} = -\tau^2 \left[\frac{\partial}{\partial \tau} \left(\frac{F_q}{\tau} \right) \right] = \frac{\tau}{n} \quad (\text{S.4.41.4})$$

For $n = 2$ we have a harmonic oscillator, and in agreement with the equipartition theorem (see Problem 4.42)

$$\langle U \rangle = \langle T \rangle = \frac{\tau}{2}$$

b) For $n = 1$, $U = mgx$, and the average potential energy per particle

$$\langle U \rangle = \tau$$

which also agrees with the generalized equipartition theorem.

4.42 Equipartition Theorem (Columbia, Boston)

a) For both of these averages the method is identical, since the Hamiltonian depends on the same power of either p or q . Compose the first average as follows:

$$\frac{\langle p_i^2 \rangle}{2m_i} = \frac{\int (p_i^2/2m_i) e^{-p_i^2/2m_i\tau} dp_i \int e^{-E'/\tau} dq_1 \cdots dp_N}{\int e^{-p_i^2/2m_i\tau} dp_i \int e^{-E'/\tau} dq_1 \cdots dp_N} \quad (\text{S.4.42.1})$$

where the energy is broken into the p_i -dependent term and E' , the rest of the sum. The second integrals in the numerator and denominator cancel, so the remaining expression may be written

$$\frac{\langle p_i^2 \rangle}{2m_i} = -\frac{\partial}{\partial \beta} \ln \int_{-\infty}^{\infty} e^{-\beta p_i^2/2m_i} dp_i \quad (\text{S.4.42.2})$$

where, as usual, $\beta \equiv 1/\tau$. A change of variables produces a piece dependent on β and an integral that is not:

$$p_i \equiv y \sqrt{2m_i/\beta}$$

$$\begin{aligned} \frac{\langle p_i^2 \rangle}{2m_i} &= -\frac{\partial}{\partial \beta} \ln \left[\sqrt{\frac{2m_i}{\beta}} \int_{-\infty}^{\infty} e^{-y^2} dy \right] \\ &= -\frac{\partial}{\partial \beta} \ln \sqrt{\beta} = \frac{1}{2\beta} = \frac{\tau}{2} \end{aligned} \quad (\text{S.4.42.3})$$

The $(k_i/2)\langle q_i^2 \rangle$ average proceeds in precisely the same way, yielding

$$\frac{k_i}{2} \langle q_i^2 \rangle = \frac{\tau}{2} \quad (\text{S.4.42.4})$$

b) The heat capacity, C_V , at constant volume is equal to $\partial E/\partial \tau$. From part (a), we have

$$E = \langle H \rangle = \left\langle \sum_{i=1}^{3N} \frac{p_i^2}{2m_i} + \sum_{i=1}^{3N} \frac{k_i}{2} q_i^2 \right\rangle = 3N \frac{\tau}{2} + 3N \frac{\tau}{2} = 3N\tau \quad (\text{S.4.42.5})$$

where we now sum over the 3-space and momentum degrees of freedom per atom. The heat capacity,

$$C_V = \frac{\partial E}{\partial \tau} = 3N \quad (\text{S.4.42.6})$$

is the law of Dulong and Petit.

c) Now take the average:

$$\begin{aligned} \left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle &= \frac{\int e^{-E/\tau} x_i (\partial H / \partial x_j) \prod_k dx_k}{\int e^{-E/\tau} \prod_k dx_k} \\ &= \frac{-\int \tau (\partial e^{-E/\tau} / \partial x_j) x_i \prod_k dx_k}{\int e^{-E/\tau} \prod_k dx_k} \end{aligned} \quad (\text{S.4.42.7})$$

Integration by parts yields

$$= \frac{-\tau \int (e^{-E/\tau} x_i) \Big|_{x_j=-\infty}^{\infty} \prod'_k dx_k + \tau \int e^{-E/\tau} (\partial x_i / \partial x_j) \prod_k dx_k}{\int e^{-E/\tau} \prod_k dx_k} \quad (\text{S.4.42.8})$$

where the prime on the product sign in the first term indicates that we integrate over all x_i except $i = j$. If $i \neq j$, then the first term in the

numerator equals zero. If x_j is one of the q 's, then by the assumption of U infinite, the term still equals zero. Finally, if $i = j > N$, then by l'Hôpital's rule the first term again gives zero. In the second term, $\partial x_i / \partial x_j = \delta_{ij}$, so the expression reduces to

$$\frac{\tau \int e^{-E/\tau} \delta_{ij} \prod_k dx_k}{\int e^{-E/\tau} \prod_k dx_k} \quad (\text{S.4.42.9})$$

Finally,

$$\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = \tau \delta_{ij} \quad (\text{S.4.42.10})$$

d) By definition,

$$\begin{aligned} \left\langle q \frac{\partial \varepsilon(q)}{\partial q} \right\rangle &= \frac{\int_{-\infty}^{\infty} q \frac{\partial \varepsilon(q)}{\partial q} e^{-\varepsilon(q)/\tau} dq}{\int_{-\infty}^{\infty} e^{-\varepsilon(q)/\tau} dq} \\ &= \frac{-\tau \int_{-\infty}^{\infty} q \frac{\partial}{\partial q} e^{-\varepsilon(q)/\tau} dq}{\int_{-\infty}^{\infty} e^{-\varepsilon(q)/\tau} dq} \quad (\text{S.4.42.11}) \\ &= -\tau \frac{q e^{-\varepsilon(q)/\tau} \Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} e^{-\varepsilon(q)/\tau} dq}{\int_{-\infty}^{\infty} e^{-\varepsilon(q)/\tau} dq} = \tau \end{aligned}$$

Given a polynomial dependence of the energy on the generalized coordinate:

$$\varepsilon(q) = \alpha q^n \quad (\text{S.4.42.12})$$

(S.4.42.11) yields

$$\begin{aligned} \left\langle q \frac{\partial \varepsilon(q)}{\partial q} \right\rangle &= \langle n \alpha q^n \rangle = n \langle \alpha q^n \rangle \quad (\text{S.4.42.13}) \\ &= n \langle \varepsilon(q) \rangle = \tau \end{aligned}$$

To satisfy the equipartition theorem:

$$\langle \varepsilon(q) \rangle = \frac{\tau}{n} = \frac{\tau}{2} \quad (\text{S.4.42.14})$$

Thus, we should have $n = 2$.

4.43 Diatomic Molecules in Two Dimensions (Columbia)

a) The partition function Z_{rot} may be calculated in the usual way by multiplying the individual Boltzmann factors by their degeneracies and summing:

$$Z_{\text{rot}} = 1 + 2 \sum_{J=1}^{\infty} e^{-hcBJ^2/\tau} = 2 \sum_{J=0}^{\infty} e^{-hcBJ^2/\tau} - 1 \quad (\text{S.4.43.1})$$

This is difficult to sum, but we may consider the integral instead, given the assumption that $\tau \gg hcB$:

$$Z_{\text{rot}} = 2 \int_0^{\infty} e^{-hcBx^2/\tau} dx - 1 = \sqrt{\frac{\pi\tau}{hcB}} - 1 \quad (\text{S.4.43.2})$$

b) The energy and heat capacity of the set of diatomic molecules described above may be determined from the partition function for the set:

$$Z = \frac{1}{N!} (Z_{\text{rot}})^N = \frac{1}{N!} \left(\sqrt{\frac{\pi\tau}{hcB}} - 1 \right)^N \approx \frac{1}{N!} \left(\frac{\pi\tau}{hcB} \right)^{N/2} \quad (\text{S.4.43.3})$$

where the N -fold product has been divided by the number of permutations of the N indistinguishable molecules. Recall that

$$E = \tau^2 \frac{\partial}{\partial \tau} \ln Z$$

We then find that

$$E = \tau^{3/2} \frac{N}{2} \sqrt{\frac{\pi}{hcB}} \frac{1}{\sqrt{\pi\tau/hcB} - 1} \approx \frac{N\tau}{2} \quad (\text{S.4.43.4})$$

Again, for $\tau \gg hcB$, the heat capacity is

$$C_V = \frac{\partial E}{\partial \tau} \approx \frac{N}{2} \quad (\text{S.4.43.5})$$

A diatomic rotor in three dimensions would have contributions to the energy of $(1/2)\tau$ per degree of freedom. Three degrees of translation and two degrees of rotation (assuming negligible inertia perpendicular to its length) gives for one molecule

$$E = \frac{5}{2} \tau \quad (\text{S.4.43.6})$$

$$E = \frac{5}{2} N\tau \quad (\text{S.4.43.7})$$

A diatomic rotor confined to a plane would have three degrees of freedom, two translational and one rotational. Hence,

$$E = \frac{3}{2} \tau \quad (\text{S.4.43.8})$$

$$c_v = \frac{3}{2} \quad (\text{S.4.43.9})$$

The quantization of energy is not apparent since we have assumed $\tau \gg hcB$.

4.44 Diatomic Molecules in Three Dimensions (Stony Brook, Michigan State)

a) We first transform the expression of the kinetic energy ε_k :

$$\varepsilon_k = \frac{1}{2} \sum_{i=1}^2 m_i (\dot{x}_i^2 + \dot{y}_i^2 + \dot{z}_i^2) \quad (\text{S.4.44.1})$$

where x_i, y_i, z_i are the Cartesian coordinates of the molecule in the frame with the c.m. at the origin to spherical coordinates:

$$\begin{aligned} x_i &= r_i \sin \theta_i \cos \varphi_i \\ y_i &= r_i \sin \theta_i \sin \varphi_i \\ z_i &= r_i \cos \theta_i \end{aligned} \quad (\text{S.4.44.2})$$

For the rigid diatom,

$$\begin{aligned} \theta_1 &= \pi - \theta_2 \equiv \theta \\ \varphi_1 &= \pi + \varphi_2 \equiv \varphi \end{aligned}$$

We may substitute (S.4.44.2) into (S.4.44.1), obtaining

$$\varepsilon_k = \frac{1}{2} (m_1 r_1^2 + m_2 r_2^2) (\dot{\theta}^2 + \sin^2 \theta \dot{\varphi}^2) \quad (\text{S.4.44.3})$$

Using the definition of c.m., we may write

$$\begin{aligned} m_1 r_1 &= m_2 r_2 \\ |r_1| + |r_2| &= a \end{aligned} \quad (\text{S.4.44.4})$$

yielding

$$\begin{aligned} r_1 &= \frac{m_2}{m_1 + m_2} a \\ r_2 &= \frac{m_1}{m_1 + m_2} a \end{aligned} \quad (\text{S.4.44.5})$$

Then (S.4.44.3) becomes

$$\varepsilon_k = \frac{1}{2} \frac{m_1 m_2}{m_1 + m_2} a^2 (\dot{\theta}^2 + \sin^2 \theta \dot{\varphi}^2) = \frac{1}{2} I (\dot{\theta}^2 + \sin^2 \theta \dot{\varphi}^2) \quad (\text{S.4.44.6})$$

with

$$I = \frac{m_1 m_2}{m_1 + m_2} a^2$$

b) In order to find the conjugate momenta p_θ , p_φ , we must compute the Lagrangian \mathcal{L} :

$$\begin{aligned} \mathcal{L} &= \varepsilon_k - V = \varepsilon_k = \frac{1}{2} I (\dot{\theta}^2 + \sin^2 \theta \dot{\varphi}^2) \\ p_\varphi &= \frac{\partial \mathcal{L}}{\partial \dot{\varphi}} = I \sin^2 \theta \dot{\varphi} \\ p_\theta &= \frac{\partial \mathcal{L}}{\partial \dot{\theta}} = I \dot{\theta} \end{aligned} \quad (\text{S.4.44.7})$$

Expressing $\dot{\varphi}$, $\dot{\theta}$ through p_φ , p_θ ,

$$\dot{\theta} = \frac{p_\theta}{I} \quad \dot{\varphi} = \frac{p_\varphi}{I \sin^2 \theta}$$

we may rewrite the Hamiltonian as

$$H = \frac{1}{2} I \left(\frac{p_\theta^2}{I^2} + \frac{p_\varphi^2}{I^2 \sin^2 \theta} \right) = \frac{p_\theta^2}{2I} + \frac{p_\varphi^2}{2I \sin^2 \theta} \quad (\text{S.4.44.8})$$

c) The single-diatom partition function may be computed as follows:

$$\begin{aligned} Z_{cl} &= \frac{1}{\hbar^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_0^{2\pi} \int_0^\pi e^{-H/\tau} d\theta d\varphi dp_\theta dp_\varphi \\ &= \frac{2\pi}{\hbar^2} \int_{-\infty}^{\infty} dp_\theta e^{-p_\theta^2/2I\tau} \int_0^\pi d\theta \int_{-\infty}^{\infty} dp_\varphi e^{-p_\varphi^2/2I \sin^2 \theta} \\ &= \frac{2\pi}{\hbar^2} \sqrt{2I\tau\pi} \int_0^\pi d\theta \sqrt{2I\tau\pi} \sin \theta = \frac{4\pi^2 I \tau}{\hbar^2} \int_0^\pi d\theta \sin \theta = \frac{8\pi^2 I}{\hbar^2} \tau \end{aligned} \quad (\text{S.4.44.9})$$

Now the free energy F for N such classical molecules may be found from

$$F = -N\tau \ln Z = -N\tau \ln \frac{8\pi^2 I\tau}{\hbar^2} \quad (\text{S.4.44.10})$$

The entropy S is then

$$S = -\frac{\partial F}{\partial \tau} = N \ln \frac{8\pi^2 I\tau}{\hbar^2} + N \quad (\text{S.4.44.11})$$

and the energy E and heat capacity C are

$$\begin{aligned} E = F + \tau S &= -N\tau \ln \frac{8\pi^2 I\tau}{\hbar^2} + N\tau \ln \frac{8\pi^2 I\tau}{\hbar^2} + N\tau = N\tau \\ C = \frac{\partial E}{\partial \tau} &= N \end{aligned} \quad (\text{S.4.44.12})$$

d) For the quantum case the Schrödinger equation for a rigid rotator

$$E\psi = \frac{J^2}{2I}\psi = -\frac{\hbar^2}{2I} \frac{1}{\sin^2\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} + \frac{\partial^2}{\partial\varphi^2} \right) \psi \quad (\text{S.4.44.13})$$

admits the standard solution

$$\begin{aligned} \psi_{jm} &= e^{im\varphi} Y_{jm}(\theta) \\ E_{jm} &= \frac{\hbar^2}{2I} j(j+1) \end{aligned} \quad (\text{S.4.44.14})$$

where each of the energy states is $(2j+1)$ -degenerate. The partition function Z_q is given by

$$Z_q = \sum_{j=0}^{\infty} (2j+1) e^{-\hbar^2 j(j+1)/2I\tau} \quad (\text{S.4.44.15})$$

For low temperatures we may neglect high-order terms and write

$$Z_q \approx 1 + 3e^{-\hbar^2/I\tau}$$

where we left only terms with $j=0$ and $j=1$. For N molecules we find for the free energy that

$$F = -N\tau \ln Z_q = -N\tau \ln \left(1 + 3e^{-\hbar^2/I\tau} \right) \approx -3N\tau e^{-\hbar^2/I\tau} \quad (\text{S.4.44.16})$$

The energy E and heat capacity C are then

$$E = -\tau^2 \frac{\partial}{\partial \tau} \left(\frac{F}{\tau} \right) = \frac{3N\tau^2 \hbar^2}{I\tau^2} e^{-\hbar^2/I\tau} = \frac{3N\hbar^2}{I} e^{-\hbar^2/I\tau} \quad (\text{S.4.44.17})$$

$$C = \frac{\partial E}{\partial \tau} = \frac{3N\hbar^2}{I} \frac{\hbar^2}{I\tau^2} e^{-\hbar^2/I\tau} = \frac{3N\hbar^4}{I^2\tau^2} e^{-\hbar^2/I\tau}$$

So, at low temperatures the heat capacity corresponding to the rotational degrees of freedom is exponentially small. This implies that there would be no difference, in this limit, between the heat capacity for monatomic and diatomic molecules. In the opposite case, at high temperatures, $\hbar^2/2I \ll \tau$, the sum may be replaced by an integral:

$$Z_q = \sum_{j=0}^{\infty} (2j+1) e^{-\alpha j(j+1)} \quad (\text{S.4.44.18})$$

where $\alpha \equiv \hbar^2/2I\tau$. Proceeding from (S.4.44.18), we have

$$\begin{aligned} Z_q &= 2 \sum_{j=0}^{\infty} \left(j + \frac{1}{2} \right) e^{-\alpha[(j+1/2)^2 - 1/4]} \\ &= 2e^{\alpha/4} \sum_{j=0}^{\infty} \left(j + \frac{1}{2} \right) e^{-\alpha(j+1/2)^2} \end{aligned} \quad (\text{S.4.44.19})$$

Replacing the sum by an integral, we obtain

$$\begin{aligned} Z_q &\approx 2e^{\alpha/4} \int_{1/2}^{\infty} dx x e^{-\alpha x^2} = e^{\alpha/4} \int_{1/4}^{\infty} dx^2 e^{-\alpha x^2} \\ &= \frac{1}{\alpha} = \frac{2I\tau}{\hbar^2} \end{aligned} \quad (\text{S.4.44.20})$$

Therefore, in the classical limit (high temperatures),

$$F = -N\tau \ln Z_q \approx -N\tau \ln \frac{2I\tau}{\hbar^2} \quad (\text{S.4.44.21})$$

The energy E and heat capacity C are given by

$$\begin{aligned} E &= -\tau^2 \frac{\partial}{\partial \tau} \left(\frac{F}{\tau} \right) = \tau^2 N \frac{1}{\tau} = N\tau \\ C &= \frac{\partial E}{\partial \tau} \approx N \end{aligned} \quad (\text{S.4.44.22})$$

We see that this is the same as found in (S.4.44.12). Since we expect a heat capacity per degree of freedom of $1/2$, we see that there are two degrees of freedom for each molecule since

$$c = \frac{C}{N} = 1$$

They correspond to the two rotational degrees of freedom of a classical rod. (There are no spatial degrees of freedom since the molecule is considered fixed.)

4.45 Two-Level System (Princeton)

a) There is nothing to prevent giving each atom its larger energy ϵ ; hence, $\eta = E/N\epsilon$ has a maximum of 1 with $E/N = \epsilon$. Clearly, the system would not be in thermal equilibrium. To compute the problem in equilibrium, we need to determine the partition function, Z . For distinguishable non-interacting particles, the partition function factors, so for identical energy spectra

$$Z = Z_1^N = \left(1 + e^{-\epsilon/\tau}\right)^N \quad (\text{S.4.45.1})$$

The free energy would be

$$F = -\tau \ln Z = -N\tau \ln Z_1 = -N\tau \ln(1 + e^{-\epsilon/\tau}) \quad (\text{S.4.45.2})$$

The energy is then

$$\begin{aligned} E = F + \tau S &= F - \tau \frac{\partial F}{\partial \tau} \\ &= -N\tau \ln Z_1 + N\tau^2 \frac{\partial}{\partial \tau} \ln Z_1 + N\tau \ln Z_1 \\ &= N\tau^2 \frac{\partial}{\partial \tau} \ln Z_1 \end{aligned} \quad (\text{S.4.45.3})$$

or

$$\begin{aligned} \frac{E}{N} &= \tau^2 \frac{\partial}{\partial \tau} \ln Z_1 = \tau^2 \frac{\partial}{\partial \tau} \ln \left(1 + e^{-\epsilon/\tau}\right) \\ &= \frac{\epsilon e^{-\epsilon/\tau}}{1 + e^{-\epsilon/\tau}} = \epsilon \frac{x}{1 + x} = \epsilon f(x) \end{aligned} \quad (\text{S.4.45.4})$$

where $x = e^{-\epsilon/\tau}$. Obviously, since both ϵ and τ are positive, x cannot be larger than 1. On the other hand, $x/(1+x)$ is a monotonic function which

goes to $1/2$ when τ goes to infinity; hence, $\max\{E/N\varepsilon\} = f(1) = 1/2$ at $\tau \rightarrow \infty$.

b) The entropy S may be found from (S.4.45.2)–(S.4.45.4):

$$S = \frac{E - F}{\tau} = \frac{E}{\tau} - \frac{F}{\tau} = \frac{N}{\tau} \frac{\varepsilon x}{1+x} + N \ln(1+x) \quad (\text{S.4.45.5})$$

The entropy per particle, $s = S/N$, is given by

$$s = \frac{\varepsilon}{\tau} \frac{x}{1+x} + \ln(1+x) \quad (\text{S.4.45.6})$$

Writing

$$\begin{aligned} \eta &\equiv \frac{x}{1+x} & x &= \frac{\eta}{1-\eta} & 1+x &= \frac{1}{1-\eta} \\ s &= \frac{\varepsilon}{\tau} \eta - \ln(1-\eta) & & & & (\text{S.4.45.7}) \\ &= \eta[\ln(1-\eta) - \ln \eta] - \ln(1-\eta) = -[\eta \ln \eta + (1-\eta) \ln(1-\eta)] \end{aligned}$$

We can check that

$$s \rightarrow \begin{cases} 0 & \text{as } \tau \rightarrow 0, \eta \rightarrow 0 \\ \ln 2 & \text{as } \tau \rightarrow \infty, \eta \rightarrow 1/2 \end{cases} \quad (\text{S.4.45.8})$$

as it should.

4.46 Zipper (Boston)

a) A partition function may be written as

$$Z = \sum_{n=0}^N e^{-n\varepsilon/\tau} \quad (\text{S.4.46.1})$$

where we have used the fact that a state with n open links has an energy $\varepsilon_n = n\varepsilon$. So

$$Z = \sum_{n=0}^N \eta^n = \frac{1 - \eta^{N+1}}{1 - \eta} \quad (\text{S.4.46.2})$$

where $\eta \equiv e^{-\varepsilon/\tau}$.

b) The average number of open links $\langle n \rangle$ is given by

$$\begin{aligned} \langle n \rangle &= \frac{\sum_{n=0}^N n e^{-n\epsilon/\tau}}{Z} = \frac{\sum_{n=0}^N n \eta^n}{\sum_{n=0}^N \eta^n} \\ &= \eta \frac{\partial}{\partial \eta} \ln Z = \eta \frac{\partial}{\partial \eta} \ln \left(\frac{1 - \eta^{N+1}}{1 - \eta} \right) \quad (\text{S.4.46.3}) \\ &= \frac{\eta}{1 - \eta} - \frac{(N+1)\eta^{N+1}}{1 - \eta^{N+1}} \end{aligned}$$

If $\tau \ll \epsilon$ then $\eta \ll 1$ and

$$\langle n \rangle \approx \eta = e^{-\epsilon/\tau}$$

which does not depend on N . It is also zipped up tight!

4.47 Hanging Chain (Boston)

a) Let the number of links with major axis vertical be n ; the number of horizontal major axis links will then be $N - n$. The total length of the chain is then

$$L(n) = (l + a)n + (l - a)(N - n) \quad (\text{S.4.47.1})$$

The energy of the system, is also a function of n since

$$\begin{aligned} E(n) &= -MgL(n) = -Mg(l + a)n - Mg(l - a)(N - n) \quad (\text{S.4.47.2}) \\ &= -E_1 n - E_2(N - n) \end{aligned}$$

where we let $E_{1,2} = Mg(l \pm a)$. The partition function

$$\begin{aligned} Z &= \sum_n g_n e^{-E_n/\tau} = \sum_{n=0}^N \frac{N!}{n!(N-n)!} e^{E_1 n/\tau + E_2(N-n)/\tau} \quad (\text{S.4.47.3}) \\ &= \left(e^{E_1/\tau} + e^{E_2/\tau} \right)^N \end{aligned}$$

where $g_n = N!/[n!(N-n)!]$ is the number of possible configurations with n major axis vertical links.

b) The average energy can be found from (S.4.47.3):

$$\langle E \rangle = \tau^2 \frac{\partial \ln Z}{\partial \tau} = -\frac{\partial}{\partial \beta} (\ln Z) = -N \frac{\partial}{\partial \beta} \ln (e^{\beta E_1} + e^{\beta E_2}) \quad (\text{S.4.47.4})$$

where $\beta = 1/\tau$. Therefore,

$$\begin{aligned}
 \langle E \rangle &= -N \frac{E_1 e^{\beta E_1} + E_2 e^{\beta E_2}}{e^{\beta E_1} + e^{\beta E_2}} \\
 &= -NMg \frac{(l+a)e^{\beta Mg(l+a)} + (l-a)e^{\beta Mg(l-a)}}{e^{\beta Mg(l+a)} + e^{\beta Mg(l-a)}} \quad (\text{S.4.47.5}) \\
 &= -NMg \frac{l(e^{\beta Mga} + e^{-\beta Mga}) + a(e^{\beta Mga} - e^{-\beta Mga})}{e^{\beta Mga} + e^{-\beta Mga}} \\
 &= -NMg [l + a \tanh(\beta Mga)]
 \end{aligned}$$

The average length is

$$\langle L \rangle = -\frac{\langle E \rangle}{Mg} \quad (\text{S.4.47.6})$$

We can check that, if $M = 0$,

$$\langle L \rangle = Nl = L_0$$

At $\tau \rightarrow 0$, $\langle L \rangle \rightarrow N(l+a)$ (lowest energy state). At $\tau \rightarrow \infty$, $\langle L \rangle \rightarrow Nl + N\beta Mga^2 = L_0 + N\beta Mga^2$.

4.48 Molecular Chain (MIT, Princeton, Colorado)

a) Consider one link of the chain in its two configurations: α and β . The energy of the link is

$$E_\alpha = \varepsilon_\alpha - fa \quad E_\beta = \varepsilon_\beta - fb \quad (\text{S.4.48.1})$$

The partition function for the entire chain is given by

$$Z = \left(\sum_{\alpha, \beta} e^{-E_{\alpha, \beta}} \right)^N = \left(e^{(fa - \varepsilon_\alpha)/\tau} + e^{(fb - \varepsilon_\beta)/\tau} \right)^N \quad (\text{S.4.48.2})$$

b) The average length of the chain may be found from the partition function:

$$\langle L \rangle = \tau \left(\frac{\partial \ln Z}{\partial f} \right)_{\tau, N} = \frac{N (ae^{(fa - \varepsilon_\alpha)/\tau} + be^{(fb - \varepsilon_\beta)/\tau})}{e^{(fa - \varepsilon_\alpha)/\tau} + e^{(fb - \varepsilon_\beta)/\tau}} \quad (\text{S.4.48.3})$$

c) If $f = 0$, (S.4.48.3) becomes

$$\begin{aligned}
 \langle L \rangle &= N \frac{ae^{-\varepsilon_\alpha/\tau} + be^{-\varepsilon_\beta/\tau}}{e^{-\varepsilon_\alpha/\tau} + e^{-\varepsilon_\beta/\tau}} \quad (\text{S.4.48.4}) \\
 &= N \frac{a + be^{(\varepsilon_\alpha - \varepsilon_\beta)/\tau}}{1 + e^{(\varepsilon_\alpha - \varepsilon_\beta)/\tau}}
 \end{aligned}$$

If $\varepsilon_{\alpha,\beta} \ll \tau$, high temperature,

$$\langle L \rangle \approx N \frac{a+b}{2} \quad (\text{S.4.48.5})$$

If $\varepsilon_{\alpha,\beta} \gg \tau$,

$$\langle L \rangle \approx N(ae^{-\delta} + b) \quad (\text{S.4.48.6})$$

where we let $\delta = (\varepsilon_{\alpha} - \varepsilon_{\beta})/\tau$. The changeover temperature is obviously $\varepsilon_{\alpha} - \varepsilon_{\beta}$.

d) From (S.4.48.3),

$$\begin{aligned} \langle L \rangle &= N \frac{ae^{fa/\tau} + be^{fb/\tau+\delta}}{e^{fa/\tau} + e^{fb/\tau+\delta}} \quad (\text{S.4.48.7}) \\ &= N \frac{a + be^{f(b-a)/\tau+\delta}}{1 + e^{f(b-a)/\tau+\delta}} \end{aligned}$$

At small f , (S.4.48.7) becomes

$$\begin{aligned} \langle L \rangle &\approx N \frac{a + be^{\delta} + bf(b-a)/\tau \cdot e^{\delta}}{1 + e^{\delta} + f(b-a)/\tau \cdot e^{\delta}} \\ &\approx N \left[\frac{a + be^{\delta}}{1 + e^{\delta}} + \frac{bf(b-a)/\tau \cdot e^{\delta}}{1 + e^{\delta}} - \frac{(a + be^{\delta})f(b-a)/\tau \cdot e^{\delta}}{(1 + e^{\delta})^2} \right] \\ &= N \frac{a + be^{\delta}}{1 + e^{\delta}} + \frac{Nfe^{\delta}(b-a)}{\tau(1 + e^{\delta})} \left[b - \frac{a + be^{\delta}}{1 + e^{\delta}} \right] \quad (\text{S.4.48.8}) \\ &= N \frac{a + be^{\delta}}{1 + e^{\delta}} + \frac{Nfe^{\delta}(b-a)^2}{\tau(1 + e^{\delta})^2} \end{aligned}$$

Therefore,

$$\left. \frac{\partial \langle L \rangle}{\partial f} \right|_{f=0} = \frac{Ne^{\delta}}{\tau} \left(\frac{b-a}{1+e^{\delta}} \right)^2 > 0 \quad (\text{S.4.48.9})$$

as it should, since (for the specified direction of the tensile force f) it corresponds to a thermodynamic inequality for a system at equilibrium:

$$-\left(\frac{\partial V}{\partial P} \right) > 0$$