

Pathria + Beale, Chapter 6

Problem 6.6

Let $f(u)$ be the velocity distribution, it can be normalized so that

$$\int_0^{\infty} du f(u) = 1$$

The Schwarz inequality implies

$$\begin{aligned} 1 &= \left[\int_0^{\infty} du f(u) \right]^2 = \left[\int_0^{\infty} du u \cdot \frac{1}{u} f(u) \right]^2 \\ &\leq \int_0^{\infty} du u f(u) \int_0^{\infty} du \frac{1}{u} f(u) = \langle u \rangle \langle \frac{1}{u} \rangle \end{aligned}$$

Thus $\langle u \rangle \langle \frac{1}{u} \rangle \geq 1$

The Maxwellian velocity distribution is

$$f(u) = \sqrt{\frac{2}{\pi}} \frac{1}{(kT)^{3/2}} u^2 \exp\left(-\frac{\frac{1}{2}mu^2}{kT}\right)$$

The average value of u and $1/u$ are

$$\langle u \rangle = \int_0^{\infty} du u f(u) = \sqrt{\frac{8kT}{\pi m}}$$

$$\langle \frac{1}{u} \rangle = \int_0^{\infty} du \frac{1}{u} f(u) = \sqrt{\frac{2m}{\pi kT}}$$

Their product is $\langle u \rangle \langle \frac{1}{u} \rangle = \frac{4}{\pi}$

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Problem 6.8

The Hamiltonian for a single particle is

$$H = \frac{1}{2m} (p_x^2 + p_y^2 + p_z^2) - mgz$$

If the cylinder has radius R , its area is $A = \pi R^2$.
The coordinates of the particle satisfy $x^2 + y^2 < R^2$
and $z > 0$.

The partition function of the canonical ensemble with temperature $T = 1/\beta$ for N noninteracting identical particles is

$$Z = \frac{1}{N!} Z_1^N$$

The partition function for one particle is

$$\begin{aligned} Z_1 &= \frac{1}{(2\pi\hbar)^3} \int_{x^2+y^2 < R} dx dy \int_0^\infty dz \int d^3p \exp\left(-\beta\left(\frac{1}{2m}\vec{p}^2 - mgz\right)\right) \\ &= \frac{1}{(2\pi\hbar)^3} A \int_0^\infty dz e^{-\beta mgz} \int_{-\infty}^\infty dp_x \int_{-\infty}^\infty dp_y \int_{-\infty}^\infty dp_z e^{-\beta(p_x^2 + p_y^2 + p_z^2)/2m} \\ &= \frac{1}{(2\pi\hbar)^3} A \frac{1}{\beta mg} \left(\sqrt{\frac{2\pi m}{\beta}}\right)^3 \\ &= \frac{AT}{mg} \left(\frac{mT}{2\pi\hbar^2}\right)^{3/2} \end{aligned}$$

The Helmholtz free energy F is

$$\begin{aligned}
 F &= -\frac{1}{\beta} \log Z \\
 &= -\frac{1}{\beta} \left[N \log Z_1 - \log(N!) \right] \\
 &= -T \left[N \left(\log \frac{AT}{mg} + \frac{3}{2} \log \frac{mT}{2\pi\hbar^2} \right) - (N \log N - N) \right]
 \end{aligned}$$

The thermodynamic relation for F is

$$dF = -SdT + \mu dN$$

The entropy is

$$\begin{aligned}
 S &= -\left(\frac{\partial F}{\partial T}\right)_N \\
 &= N \left[\log \frac{AT}{mg} + \frac{3}{2} \log \frac{mT}{2\pi\hbar^2} - \log N + 1 \right] + NT \left[\frac{1}{T} + \frac{3}{2} \frac{1}{T} \right] \\
 &= N \left[\log \frac{AT}{mg} + \frac{3}{2} \log \frac{mT}{2\pi\hbar^2} - \log N + \frac{7}{2} \right]
 \end{aligned}$$

The chemical potential is

$$\begin{aligned}
 \mu &= + \left(\frac{\partial F}{\partial N}\right)_T \\
 &= -T \left[\log \frac{AT}{mg} + \frac{3}{2} \log \frac{mT}{2\pi\hbar^2} - \log N + 1 \right] - TN \left[-\frac{1}{N} \right] \\
 &= -T \left[\log \frac{AT}{mg} + \frac{3}{2} \log \frac{mT}{2\pi\hbar^2} - \log N + 2 \right]
 \end{aligned}$$

The average energy is

$$U = F + ST$$

$$= -NT \left[\log \frac{\Delta T}{mg} + \frac{3}{2} \log \frac{mT}{2\pi k^2} - \log N + 1 \right]$$

$$+ NT \left[\log \frac{\Delta T}{mg} + \frac{3}{2} \log \frac{mT}{2\pi k^2} - \log N + \frac{7}{2} \right]$$

$$= \frac{5}{2} NT$$

The specific heat per particle is

$$c = \frac{1}{N} T \left(\frac{\partial S}{\partial T} \right)_N$$

$$= \frac{1}{N} N \left[\frac{1}{T} + \frac{3}{2} \frac{1}{T} \right]$$

$$= \frac{5}{2} T$$

The corresponding specific heat for a particle in a box is $c = \frac{3}{2} T$.

The specific heat is larger in the gravitational field because some of the heat goes into increasing the average height of the particles.

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Problem 6.14

(a) If the hole in the wall is in the xy -plane, the effusion rate R is the number density multiplied by the average value of $v_z = p_z/m$ from particles with $p_z > 0$:

$$R = n \left\langle \frac{p_z}{m} \right\rangle_{p_z > 0}$$

The average value of $\langle p_z \rangle$ from particles with $p_z > 0$ is

$$\begin{aligned} \langle p_z \rangle_{p_z > 0} &= \langle p \cos \theta \rangle_{\theta < \pi/2} \\ &= \frac{\int_0^\infty dp p^2 \int_0^{\pi/2} \sin \theta d\theta \int_0^{2\pi} d\phi p \cos \theta e^{-\beta p^2/2m}}{\int_0^\infty dp p^2 \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi \cdot e^{-\beta p^2/2m}} \\ &= \frac{\int_0^\infty dp p^3 e^{-\beta p^2/2m} \int_0^1 d \cos \theta \cos \theta}{\int_0^\infty dp p^2 e^{-\beta p^2/2m} \int_0^1 d \cos \theta} \\ &= \frac{\frac{1}{2} \left(\frac{2m}{\beta} \right)^2 \frac{1}{2}}{\frac{\sqrt{\pi}}{4} \left(\frac{2m}{\beta} \right)^{3/2} 2} \\ &= \frac{1}{2\sqrt{\pi}} \left(\frac{2m}{\beta} \right)^{1/2} \end{aligned}$$

The effusion rate can be expressed as

$$R = \frac{n}{m} \frac{1}{2\sqrt{\pi}} (2m kT)^{1/2} = \sqrt{\frac{kT}{2\pi m}} n$$

The average kinetic energy of the effusing particles is given by the following ratio of integrals:

$$\frac{\int_0^{\infty} dp p^2 \int_0^{\pi/2} \sin \theta d\theta \int_0^{2\pi} d\phi p \cos \theta \frac{p^2}{2m} e^{-\beta p^2/2m}}{\int_0^{\infty} dp p^2 \int_0^{\pi/2} \sin \theta d\theta \int_0^{2\pi} d\phi p \cos \theta e^{-\beta p^2/2m}}$$

$$= \frac{1}{2m} \frac{\int_0^{\infty} dp p^5 e^{-\beta p^2/2m}}{\int_0^{\infty} dp p^3 e^{-\beta p^2/2m}}$$

$$= \frac{1}{2m} \frac{\left(\frac{2m}{\beta}\right)^3}{\frac{1}{2} \left(\frac{2m}{\beta}\right)^2}$$

$$= \frac{1}{m} \frac{2m}{\beta} = 2kT$$

(b) If the system is in quasistatic equilibrium at temperature T , it obeys the ideal gas law

$$PV = NkT$$

and its average energy is

$$U = \frac{3}{2} NkT$$

The rate of decrease in the number of particles is

$$\frac{d}{dt} N = -RA = -A \sqrt{\frac{kT}{2\pi m}} \frac{N}{V}$$

The rate of decrease in the energy of the system is

$$\begin{aligned}\frac{d}{dt} U &= -RA(2kT) \\ &= -A \sqrt{\frac{kT}{2\pi m}} \frac{N}{V} \cdot 2kT\end{aligned}$$

The time dependence of T can be deduced from the time derivative of U/N

$$\begin{aligned}\frac{d}{dt} \frac{U}{N} &= \frac{1}{N} \frac{dU}{dt} - \frac{U}{N^2} \frac{dN}{dt} \\ &= \frac{1}{N} \left(-\frac{2A}{\sqrt{2\pi m}} \frac{N}{V} (kT)^{3/2} \right) - \frac{\frac{3}{2} N kT}{N^2} \left(-\frac{A}{\sqrt{2\pi m}} \frac{N}{V} (kT)^{1/2} \right) \\ &= -\frac{A/V}{2\sqrt{2\pi m}} (kT)^{3/2}\end{aligned}$$

This must be equal to the time derivative of $\frac{3}{2} kT$

$$\frac{3}{2} \frac{d}{dt} (kT) = -\frac{A/V}{2\sqrt{2\pi m}} (kT)^{3/2}$$

$$\frac{\frac{d}{dt} (kT)}{(kT)^{3/2}} = -\frac{A/V}{3\sqrt{2\pi m}}$$

$$\frac{d}{dt} \left(-2(kT)^{-1/2} \right) = -\frac{A/V}{3\sqrt{2\pi m}}$$

$$-2 \left[\frac{1}{\sqrt{kT(t)}} - \frac{1}{\sqrt{kT(0)}} \right] = -\frac{A/V}{3\sqrt{2\pi m}} t$$

$$kT(t) = \frac{1}{\left[\frac{1}{\sqrt{kT(0)}} + \frac{A/V}{6\sqrt{2\pi m}} t \right]^2}$$

We can now solve the equation for $\frac{dn}{dt}$ to obtain the time dependence of $n(t) = \frac{N(t)}{V}$:

$$\frac{1}{n} \frac{dn}{dt} = - \frac{A/V}{\sqrt{2\pi m}} \sqrt{kT}$$

$$d[\log n(t)] = - \frac{A/V}{\sqrt{2\pi m}} \sqrt{kT(t)}$$

$$\log n(t) - \log n(0) = - \frac{A/V}{\sqrt{2\pi m}} \int_0^t dt' \frac{1}{\frac{1}{\sqrt{kT(0)}} + \frac{A/V}{6\sqrt{2\pi m}} t'}$$

$$\log \frac{n(t)}{n(0)} = - \frac{A/V}{\sqrt{2\pi m}} \frac{6\sqrt{2\pi m}}{A/V} \log \frac{\frac{1}{\sqrt{kT(0)}} + \frac{A/V}{6\sqrt{2\pi m}} t}{\frac{1}{\sqrt{kT(0)}}$$

$$= -6 \log \left(1 + \frac{A/V}{6\sqrt{2\pi m}} \frac{t}{\sqrt{kT(0)}} \right)$$

$$n(t) = n(0) \left[1 + \frac{A/V}{6\sqrt{2\pi m}} \frac{t}{\sqrt{kT(0)}} \right]^{-6}$$

The time dependence of $P(t)$ can now be obtained from the ideal gas law:

$$P(t) = n(t) kT(t)$$

$$= n(0) \left[1 + \frac{A/V}{6\sqrt{2\pi m}} \frac{t}{\sqrt{kT(0)}} \right]^{-6} kT(0) \left[1 + \frac{A/V}{6\sqrt{2\pi m}} \frac{t}{\sqrt{kT(0)}} \right]^{-2}$$

$$= P(0) \left[1 + \frac{A/V}{6\sqrt{2\pi m}} \frac{t}{\sqrt{kT(0)}} \right]^{-8}$$

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Problem 6.21

The partition function for N diatomic molecules HD at temperature T high enough to allow the classical approximation for rotational motion but low enough that vibrations can be ignored has the form

$$Z = \frac{1}{N!} \left[\frac{V}{\lambda_{th}^3} (2S_H+1)(2S_D+1) \frac{2IkT}{h^2} \right]^N$$

The nuclear spins are $S_H = \frac{1}{2}$, $S_D = 1$. The thermal length and the moment of inertia are

$$\lambda_{th} = \sqrt{\frac{2\pi\hbar^2}{(m_H+m_D)kT}}$$

$$I = \frac{m_H m_D}{m_H + m_D} r_0^2$$

where r_0 is the radius of the minimum in the interatomic potential (which is the same for HD, H₂ and D₂).

The chemical potential can be expressed as

$$\mu_{HD} = -kT \frac{\partial}{\partial N} \log Z$$

$$= -kT \left[\log \frac{V}{\lambda_{th}^3} + \log Z_{spin} + \log Z_{rot} - \log N + 1 \right]$$

where the partition functions for nuclear spins and rotation

$$Z_{\text{spin}} = (2S_H + 1)(2S_D + 1)$$

$$Z_{\text{rot}} = \frac{2IkT}{h^2}$$

The chemical potential of an HD molecule in a system of N_{HD} HD molecules is

$$\begin{aligned} \mu_{\text{HD}} = -kT & \left[\log \left(V \left(\frac{(m_H + m_D)kT}{2\pi h^2} \right)^{3/2} \right) + \log(2S_H + 1) + \log(2S_D + 1) \right. \\ & \left. + \log \left(\frac{m_H m_D}{m_H + m_D} \cdot \frac{2r_0^2 kT}{h^2} \right) - \log N_{\text{HD}} + 1 \right] \end{aligned}$$

The chemical potential for an H_2 molecule in a system of N_{H_2} H_2 molecules is obtained by setting $m_D = m_H$, $S_D = S_H$, and dividing Z_{rot} by 2 because the two H nuclei are identical fermions:

$$\begin{aligned} \mu_{\text{H}_2} = -kT & \left[\log \left(V \left(\frac{(2m_H)kT}{2\pi h^2} \right)^{3/2} \right) + 2 \log(2S_H + 1) \right. \\ & \left. + \log \left(\frac{1}{2} \left(\frac{m_H}{2} \right) \frac{2r_0^2 kT}{h^2} \right) - \log N_{\text{H}_2} + 1 \right] \end{aligned}$$

The chemical potential for a D_2 molecule in a system of N_{D_2} D_2 molecules is obtained by setting $m_H = m_D$, $S_H = S_D$, and dividing Z_{rot} by 2 because the two D nuclei are identical bosons:

$$\mu_{D_2} = -kT \left[\log \left(V \left(\frac{(2m_D)kT}{2\pi\hbar^2} \right)^{3/2} \right) + 2 \log(2S_D + 1) \right. \\ \left. + \log \left(\frac{1}{2} \left(\frac{m_D}{2} \right) \frac{2r_0^2 kT}{\hbar^2} \right) - \log N_{D_2} + 1 \right]$$

The condition for chemical equilibrium from the reaction $H_2 + D_2 \leftrightarrow 2 HD$ is

$$\mu_{H_2} + \mu_{D_2} = 2\mu_{HD}$$

If we subtract the left side from the right side, the only terms that do not cancel are those that depend on masses and molecule numbers:

$$0 = \frac{3}{2} \log \frac{(m_H + m_D)^2}{(2m_H)(2m_D)} + \log \frac{\left(\frac{m_H m_D}{m_H + m_D} \right)^2}{\frac{1}{2} \left(\frac{m_H}{2} \right) \frac{1}{2} \left(\frac{m_D}{2} \right)} - \log \frac{N_{HD}^2}{N_{H_2} N_{D_2}}$$

$$\log \frac{N_{HD}^2}{N_{H_2} N_{D_2}} = \frac{3}{2} \log \frac{(m_H + m_D)^2}{4m_H m_D} + \log \frac{16m_H m_D}{(m_H + m_D)^2}$$

Setting $m_D = 2m_H$, this reduces to

$$\log \frac{N_{HD}^2}{N_{H_2} N_{D_2}} = \frac{3}{2} \log \frac{9}{8} + \log \frac{32}{9}$$

Exponentiating, we get

$$\frac{N_{HD}^2}{N_{H_2} N_{D_2}} = 3\sqrt{2}$$

This equilibrium constant is independent of T , and it does not have the expected value 4.

The value 4 can be obtained by including also the high-temperature limit of the vibrational contributions. This is unphysical, since the nonharmonic corrections and the couplings between rotations and vibrations are also important at such high temperature.

The partition function for vibration in the HD molecule

$$Z_{\text{vib}} = \frac{1}{2 \sinh(\beta \hbar \omega_{\text{HD}}/2)}$$

where the angular frequency is given by

$$\omega_{\text{HD}} = \sqrt{V''(r_0) / \frac{m_{\text{H}} m_{\text{D}}}{m_{\text{H}} + m_{\text{D}}}}$$

The interatomic potential $V(r)$ does not depend on the masses

The high-temperature limit of $\log Z_{\text{vib}}$ is

$$\log Z_{\text{vib}} = -\log(\beta \hbar \omega_{\text{HD}})$$

The additional contribution to the logarithm of the equilibrium constant is

$$-\log \frac{\omega_{\text{HD}}^2}{\omega_{\text{H}_2} \omega_{\text{D}_2}} = +\log \sqrt{\frac{4 m_{\text{H}} m_{\text{D}}}{(m_{\text{H}} + m_{\text{D}})^2}} = +\log \sqrt{\frac{2}{3}}$$

It gives an additional factor in the equilibrium constant of $\frac{2\sqrt{2}}{3}$.

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Problem 6.23

The Morse potential is

$$V(r) = V_0 \left[e^{-2(r-r_0)/a} - 2e^{-(r-r_0)/a} \right]$$

Its first and second derivatives are

$$V'(r) = V_0 \left[\left(-\frac{2}{a}\right) e^{-2(r-r_0)/a} - 2 \cdot \left(-\frac{1}{a}\right) e^{-(r-r_0)/a} \right]$$

$$V''(r) = V_0 \left[\left(-\frac{2}{a}\right)^2 e^{-2(r-r_0)/a} - 2 \left(-\frac{1}{a}\right)^2 e^{-(r-r_0)/a} \right]$$

Its minimum, which satisfies $V'(r_0) = 0$, is at $r_0 = a$.

The second derivative at the minimum is

$$V''(a) = V_0 \left[\left(-\frac{2}{a}\right)^2 - 2 \left(-\frac{1}{a}\right)^2 \right] = 3 \frac{V_0}{a^2}$$

The vibrational quantum of energy is $\hbar\omega$, where ω satisfies $V''(a) = \left(\frac{1}{2}m\right)\omega^2$, where m is the mass of a hydrogen atom:

$$\hbar\omega = \hbar \sqrt{\frac{V''(a)}{m/2}} = \sqrt{6 \frac{\hbar^2}{ma^2} V_0}$$

The given parameters of the potential are

$$V_0 = 7 \times 10^{-12} \text{ erg} = 7 \times 10^{-12} \frac{\text{g} \cdot \text{cm}^2}{\text{s}^2}$$

$$a = 5 \times 10^{-9} \text{ cm}$$

$$r_0 = 8 \times 10^{-9} \text{ cm}$$

The mass of the hydrogen atom is $m = 1.008 \text{ amu}$
 The vibrational quantum is therefore

$$h\nu = 3.34 \times 10^{-12} \text{ erg} = 2.09 \text{ eV}$$

The corresponding temperature is

$$\frac{h\nu}{k_B} = 2.42 \times 10^4 \text{ K}$$

The vibrational quantum is

$$\frac{h^2}{2I} = \frac{h^2}{2mr_0^2} = 5.19 \times 10^{-15} \text{ erg} = 0.00324 \text{ eV}$$

The corresponding temperature is

$$\frac{h^2/2I}{k_B} = 37.6 \text{ K}$$

Rotational modes should begin contributing to the specific heat at a temperature around 40K

Vibrational modes should begin contributing to the specific heat at a temperature around 20,000K.

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Problem 6.25

The differences between the energies of the energy levels ϵ_J for $J=0,1,2$ are

$$\epsilon_1 - \epsilon_0 = 68.0 \text{ cm}^{-1}$$

$$\epsilon_2 - \epsilon_0 = 226.5 \text{ cm}^{-1}$$

The conversion factor from cm^{-1} to K

$$hc/k_B = 2\pi^2 hc/k_B = 1.44 \text{ cm K}$$

The partition function for the 3 energy levels is

$$\begin{aligned} Z &= \sum_{l=0}^2 (2l+1) e^{-\epsilon_l/kT} \\ &= e^{-\epsilon_0/kT} + 3e^{-\epsilon_1/kT} + 5e^{-\epsilon_2/kT} \end{aligned}$$

The probabilities are

$$P_l = (2l+1) e^{-\epsilon_l/kT} / Z$$

Their numerical values are $P_0 = 0.050$, $P_1 = 0.208$, $P_2 = 0.74$

The relative fractions are $\frac{P_1}{P_0} = 4.16$, $\frac{P_2}{P_0} = 14.82$