Physics 127a: Class Notes

Lecture 19: Molecular Gases

Diatomic gases

Consider a molecule made up of two atoms A and B, and at temperatures much lower than an electronic excitation energy (typically around $10^4 K$).

First let's suppose that the temperature is high enough so that all the degrees of freedom can be treated classically. This is the case if $kT \gg \Delta\varepsilon$ where $\Delta\varepsilon$ is the spacing between the quantized energy levels. (We will see what these are below.) Of course the gas must not be at too high density or at too low temperature when the gas becomes degenerate—in practice not an issue in bulk gases. The Hamiltonian for a single molecule is

$$H(\mathbf{p}_A, \mathbf{p}_B, \mathbf{r}_A, \mathbf{r}_B) = \frac{p_A^2}{2m_A} + \frac{p_B^2}{2m_B} + V(|\mathbf{r}_A - \mathbf{r}_B|) \tag{1}$$

and the partition function for N molecules is $Q_N = Q_1^N/N!$ with

$$Q_1 = \frac{1}{h^6}\int d^3p_A \int d^3p_B \int d^3r_A \int d^3r_B \, e^{-\beta H}. \tag{2}$$

The momentum and the position integrals can, as is generally true in classical statistical mechanics, be evaluated separately

$$Q_1 = \frac{1}{h^6}\int d^3p_A \int d^3p_B \exp\left[-\beta\left(\frac{p_A^2}{2m_A} + \frac{p_B^2}{2m_B}\right)\right] \times \int d^3r_A \int d^3r_B \exp(-\beta V). \tag{3}$$

Since the momentum terms in the Hamiltonian are quadratic, equipartition tells us that the contribution to the internal energy per molecule is $6 \times \frac{1}{2}kT$ (6 quadratic terms). For the position integrals we go to centre of mass coordinate R and relative coordinate $\mathbf{r} = \mathbf{r}_A - \mathbf{r}_B$. There is no dependence of the Hamiltonian on the centre of mass coordinate, and this integral just contributes a factor of the volume to Q_1. If we expand the potential $V(r)$ about the minimum to quadratic order, we get an additional quadratic term in the Hamiltonian, and so by equipartition get an additional $\frac{1}{2}kT$ contribution to the internal energy. Thus, altogether in the classical limit

$$\frac{U}{N} = \frac{7}{2}kT. \tag{4}$$

(Note that we could evaluate the momentum integrals in terms of centre of mass momentum, two rotational momenta, and the momentum of the relative coordinate, again giving a contribution $3kT$ to the internal energy per molecule.)

For a quantum mechanical treatment we must first use the Hamiltonian to calculate the energy levels of the internal degrees of freedom, then calculate the internal canonical partition function $j(T)$ introduced in the previous lecture. From this we can calculate the contributions to the thermodynamic quantities, e.g.

$$\frac{U_{int}}{N} = kT^2 \frac{\partial \ln j(T)}{\partial T}. \tag{5}$$

To a reasonable approximation the energy levels can be accounted for in terms of vibration and rotation spectra

$$E_{n,l} \simeq (n + \frac{1}{2})\hbar\omega + l(l+1)\frac{\hbar^2}{2I}. \tag{6}$$

Typically the vibrational temperature $\theta_v = \hbar\omega/k$ is about $10^3 K$, and the rotational temperature $\theta_r = \hbar^2/2Ik$ is $1 - 100K$ (both are higher for lighter atoms). We will take I and ω to be constants for each molecule, although more accurately the rotation spectrum will depend slightly on the vibration state.

For the spectrum Eq. (6) the internal partition function separates into vibrational and rotational parts

$$j(T) = j_v(T) j_r(T). \tag{7}$$

The vibrational part is the partition function of a harmonic oscillator that we have looked at before

$$j_v(T) = \frac{1}{2\sinh(\hbar\omega/2kT)} \tag{8}$$

giving an extra contribution to the specific heat $\Delta C_V^{(v)}$ that is Nk at high temperatures (cf. equipartition, one kinetic one potential degree of freedom) and exponentially small for $T \ll \theta_r$.

The rotational part is

$$j_r(T) = \sum_{l=0}^{\infty} (2l+1) e^{-l(l+1)\theta_r/T} \tag{9}$$

since the degeneracy of the orbital angular momentum state l is $2l+1$. At low temperatures

$$j(T) \to 1 + 3e^{-\theta_r/T}, \qquad \Delta C_V^{(r)} = 12\left(\frac{\theta_r}{T}\right)^2 e^{-2\theta_r/T}. \tag{10}$$

At high temperatures we can use the *Euler-Maclaurin* series expansion (see, for example, *Handbook of Mathematical Functions* by *Abramowitz and Stegun* §3.6.28 or §25.4.7)

$$\sum_{n=0}^{\infty} f(n) = \int_0^{\infty} f(x)dx + \frac{1}{2}f(0) - \frac{1}{12}f'(0) + \frac{1}{720}f'''(0) + \cdots \tag{11}$$

with $f(x) = (2x+1)e^{-x(x+1)\theta_r/T}$. The integral gives the result

$$j_r(T) \to \frac{T}{\theta_r} = \frac{8\pi^2 I}{h^2} kT \tag{12}$$

giving the equipartition specific heat $\Delta C_V^{(r)} = NkT$ (two kinetic degrees of freedom). This can also be derived from the classical expression

$$j_r(T) \to \frac{1}{h^2}\int_{-\infty}^{\infty} dp_\theta \int_{-\infty}^{\infty} dp_\phi \int_0^{\pi} d\theta \int_0^{2\pi} d\phi \; e^{-\beta H_r} \tag{13}$$

with

$$H_r = \frac{1}{2I}\left(p_\theta^2 + \frac{p_\phi^2}{\sin^2\theta}\right). \tag{14}$$

Keeping further terms in the expansion (you actually need all the terms retained in Eq. (11)) gives the *high temperature expansion*

$$j_r(T) \to \frac{T}{\theta_r} + \frac{1}{3} + \frac{1}{15}\frac{\theta_r}{T} \cdots \tag{15}$$

$$\frac{\Delta C_V^{(r)}}{Nk} \to 1 + \frac{1}{45}\left(\frac{\theta_r}{T}\right)^2 + \cdots. \tag{16}$$

An interesting conclusion is that as the temperature is lowered the specific heat *increases* above Nk before beginning to decrease at low temperatures. You can plot the full expression by evaluating and plotting Eq. (9) with Mathematica etc.

The specific heat of the nondegenerate gas

$$C_V = \frac{3}{2}Nk + \Delta C_V^{(v)} + \Delta C_V^{(r)} \tag{17}$$

changes from $(3/2)Nk$ at low temperatures (only translational degrees of freedom excited) to $(5/2)Nk$ for $\theta_r \lesssim T \lesssim \theta_v$ as the rotational degrees of freedom are excited, to $(7/2)Nk$ at high temperatures when the vibrational modes are excited to equipartition. The specific heat ratio $\gamma = C_P/C_V = 1 + Nk/C_V$ is correspondingly temperature dependent. This is evident physically in the adiabatic gas law $PV^\gamma =$ const, the speed of sound in the gas, and other properties. So in this regards (internal degrees of freedom) the statistical mechanics of common gases show the effects of discrete quantum energy levels at room temperature and above.

Homonuclear molecules

Diatomic molecules of the type $A - A$ are particular interesting because the *nuclear spin* degrees of freedom become coupled to the *orbital* degrees of freedom through the *symmetry restriction* of the quantum wave function. This results in a rather pronounced peak in the specific heat (as the nuclear spins order and decrease the entropy with decreasing temperature) at temperatures *much* higher than any interaction energy of the nuclear spins.

The wavefunction of the nuclear coordinates is the product of orbital and spin parts

$$\psi_N = \psi_{N,r}\ \psi_{N,\mathrm{spin}}. \tag{18}$$

Here $\psi_{N,r}(\mathbf{r})$ is the rotation and vibration part of the molecular wave function.

Nuclear spin 0: The nuclei are *bosons*, and so ψ_N must be symmetric under particle exchange. There is no spin component, so this means $\psi_{N,r}$ must be symmetric under particle exchange. But a rotation of π has the effect of interchanging the nuclei. This multiplies the wave function by $(-1)^l$ with l the angular momentum quantum number. Thus we deduce l must be *even*. The rotational contribution to the partition function is then

$$j_r = \sum_{l \text{ even}} (2l+1)e^{-l(l+1)\theta_r/T}. \tag{19}$$

Compared with the results for $A - B$ molecules, the exponential dependence at low temperatures is stronger

$$j \simeq 1 + 5e^{-6\theta_r/T} + \cdots, \qquad T \to 0, \tag{20}$$

and the high temperature result is half as big

$$j_r \simeq \frac{1}{2}\frac{T}{\theta_r}, \qquad T \to \infty. \tag{21}$$

(The later result follows from the first term (the integral) in the Euler-Maclaurin series with $f(x) = (4x + 1)e^{-2x(2x+1)\theta_r/T}$. It can also be derived classically by noting that the coordinate integral should only go over a half sphere (a solid angle of 2π) since otherwise the states are double counted.) The internal energy remains the same in the high temperature limit.

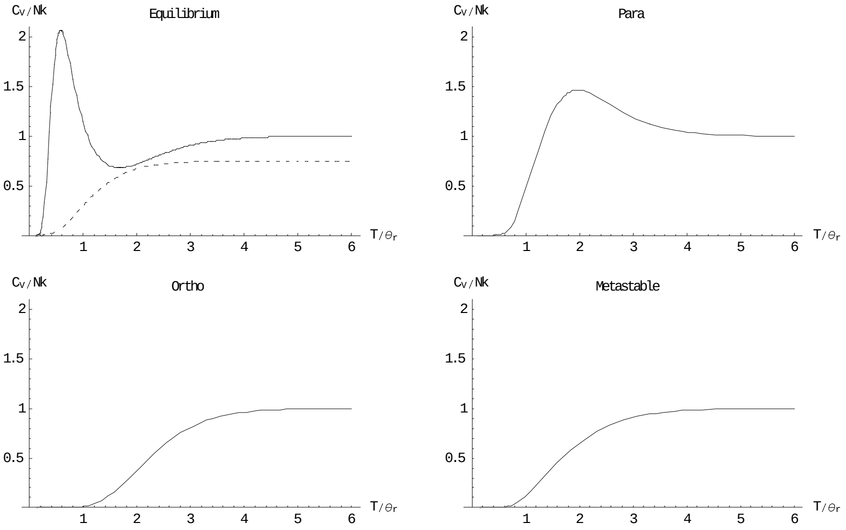

Figure 1: Specific heat C_V/Nk for *equilibrium*, *ortho*, *para*, and *metastable* (quenched from room temperature) hydrogen as a function of T/θ_r. The dashed line in the first panel is the fracttion of ortho hydrogen in the equilibrium state.

Nuclear spin $\frac{1}{2}$ (e.g. Hydrogen) The nuclei are *fermions* and ψ_N must be *antisymmetric*. To form an antisymmetric total wavefunction we can use: nuclear spin $I = 0$, $\psi_{N,\text{spin}} \propto \uparrow\downarrow - \downarrow\uparrow$ (antisymmetric), and a symmetric orbital wave function, i.e. l even; or nuclear spin $I = 1$, $\psi_{N,\text{spin}} \propto \uparrow\uparrow$, $\uparrow\downarrow + \downarrow\uparrow$, or $\downarrow\downarrow$ (symmetric, degeneracy factor 3), antisymmetric orbital wave function, i.e. l odd. The equilibrium rotational partition function is given by summing over all states

$$j_r = \sum_{\substack{\text{spin}\\\text{states}}} \sum_{\substack{\text{orbital}\\\text{states}}} e^{-l(l+1)\theta_r/T} = 3r_{\text{odd}} + r_{\text{even}} \tag{22}$$

with

$$r_{\substack{\text{odd}\\\text{even}}} = \sum_{\substack{l\ \text{odd}\\ l\ \text{even}}} (2l+1)e^{-l(l+1)\theta_r/T}. \tag{23}$$

From j_r the contribution to the internal energy, specific heat, etc. may be calculated. Note that the ratio of the probability of finding the nuclei in the $I = 1$ state relative to the probability of finding them in the $I = 0$ state is

$$\frac{P(I=1)}{P(I=0)} = \frac{3r_{\text{odd}}}{r_{\text{even}}} \tag{24}$$

which is 3 at high temperature but exponentially small $9e^{-2\theta_r/T}$ at low temperatures. This “ordering” of the nuclear spins decreases the entropy per particle by $k \ln 3$ as the temperature is lowered through about θ_r, and gives a quite large specific heat peak (see figure below).

The weakness of the nuclear spin interaction with other degrees of freedom results in a very long equilibration time for the gas to come to equilibrium—in fact days at low temperatures for hydrogen. If the gas is cooled over shorter periods, the nuclear spins remain in the original configuration. In fact the gas behaves as a mixture of two types: one component (called *ortho*) with $I = 1$ and thermodynamic properties given by r_{odd}, and one component (called *para*) with $I = 0$ and thermodynamic properties given by r_{even}. For example, if cooled from the 3 : 1 equilibrium ratio at room temperature the specific heat would be

$$C_{\text{quench}} = \frac{3}{4} C_{\text{ortho}} + \frac{1}{4} C_{\text{para}} \tag{25}$$

with

$$C_{\text{ortho}} = Nk \frac{\partial}{\partial T} \left(T^2 \frac{\partial}{\partial T} \ln r_{\text{odd}} \right), \tag{26a}$$

$$C_{\text{para}} = Nk \frac{\partial}{\partial T} \left(T^2 \frac{\partial}{\partial T} \ln r_{\text{even}} \right). \tag{26b}$$

Nuclear spin 1 **(e.g. Deuterium)** The nuclei are now Bosons so that the total wave function must be symmetric. The total nuclear spin $I = 0$ (1 state) and $I = 2$ (5 states) states are symmetric in the spin coordinates (see a quantum text book for adding angular momentum), and so must be correspond to even l rotational states. The 3 $I = 1$ states are antisymmetric in the spin coordinates, and so correspond to odd l rotational states. I'll leave you to work out the specific heats in various circumstances. An interesting application is to the equilibrium constant $K(T)$ for the reaction

$$H_2 + D_2 \rightleftharpoons HD. \tag{27}$$