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Problem Sheet 3
Lectures 7–9

Learning Outcomes

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Jargon

   Translational, rotational and vibrational degrees of freedom, van der Waals force, ionic and covalent bonds, van der Waals equation of state, mean free path.
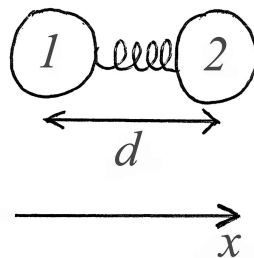
Concepts

   Degrees of freedom for a diatomic molecule; how quantum effects modify the number of degrees of freedom of real gases, and how the number varies as the temperature is raised for a diatomic gas; the Lennard-Jones 6-12 potential; the origin of the coefficients a and b in the van der Waals equation of state; understand qualitatively why the internal energy of a van der Waals gas differs from an ideal gas with the same N, V and T; the form of the van der Waals isotherms on a P-V diagram; derivation of an expression for the mean free path, assuming rigid spherical particles, only one of which is moving.

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Problems

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1. Show that $< v_x^2 >= \dfrac{k_B T}{m}$.

2. A diatomic molecule can be regarded as two identical particles joined by a spring. At any instant the x coordinates (defining the x direction as shown) of the centres of the two particles are $x_1 = x - d/2$ and $x_2 = x + d/2$, where x is the x coordinate of the centre of mass of the molecule and d is the separation of the particles. By writing $d = d_0 + \xi$, where d_0 is the equilibrium separation and ξ is the displacement from equilibrium, show that the kinetic energy associated with the x component of the two particles' velocities is $\dfrac{1}{2}mv_x^2 + \dfrac{1}{2}\left(\dfrac{m}{4}\right)\nu^2$ where m is the mass of the whole molecule, $v_x = \dfrac{\mathrm{d}x}{\mathrm{d}t} = x$ component of the centre of mass velocity, and $\nu = \dfrac{\mathrm{d}\xi}{\mathrm{d}t}$.

3. The Lennard-Jones 6-12 potential has the form $U(r) = \dfrac{A}{r^{12}} - \dfrac{B}{r^6}$.

    (a) Calculate the equilibrium separation r_0 in terms of A and B.

    (b) Calculate the value of the potential at equilibrium $U(r_0)$

    (c) Given that the binding energy equals $-\epsilon$ (i.e. $U(r_0) = -\epsilon$) show that the Lennard-Jones potential can be rewritten in the form, $U(r) = \epsilon\left\{ \left(\dfrac{r_0}{r}\right)^{12} - 2\left(\dfrac{r_0}{r}\right)^6 \right\}$

    (d) The angular frequency of oscillations of a particle in a van der Waal lattice about its equilbrium position is given by $\omega_E = \left(\dfrac{2}{m}\dfrac{\mathrm{d}^2 U(r)}{\mathrm{d}r^2}\right)^{1/2}$ for $r = r_0$. (Remember the 2 comes from the fact that their are two bonds in any one direction). Calculate this frequency, and find the phase velocity of these oscillations for a wavelength $\lambda = r_0$, in terms of r_0 and ϵ. (This is the speed of sound in a VW solid.)

4.   (a) We can generalize the Lennard-Jones 6-12 potential by assuming an attractive potential $\propto -r^{-n}$, while keeping the repulsive potential $\propto r^{-12}$. The potential energy of the interaction can be written $U = \dfrac{A}{x^{12}} - \dfrac{B}{x^n}$ where A and B are constants, $x = r/r_0$ and r_0 is the equilibrium separation. Show that $B = 12A/n$, and, hence, that the magnitude of the binding energy is given by $\epsilon = A\left(\dfrac{12}{n} - 1\right)$.

    (b) The van der Waals force corresponds to $n = 6$, while the Coulomb force responsible for ionic boning corresponds to $n = 1$. Assuming that the repulsive force (i.e., the value of A) is the same in both cases, compare the depths of the van der Waals and ionic potential wells. What does this suggest about the relative strengths of van der Waals and ionic bonds?

5. A simple model of a gas treats the molecules as hard spheres of radius a, which only interact through collisions (i.e. there is no attractive force between them). Consider one molecule to be moving, and the others stationary. The moving molecule's path is deflected at each collision, but if we straighten it out we could imagine the molecule sweeping out a cylinder of cross-sectional area σ such that a collision will occur whenever the centre of one of the stationary molecules falls within the cylinder.

    (a) Write down an expression for σ in terms of a.

    (b) Show that the average number of collisions experienced by the moving molecule in travelling a distance l is $4\pi n l a^2$, where n is the density of molecules.

    (c) Hence show that the average distance travelled before experiencing a collision (the mean free path) is given by $\lambda_m = \dfrac{1}{4\pi n a^2}$.

(d) When the motion of the other molecules is taken into account the value of λ_m is reduced by a factor of $\sqrt{2}$. Assuming the ideal gas equation of state show that the mean free path can be written $\lambda_m = \dfrac{k_B T}{4\sqrt{2}\pi a^2 P}$.

(e) Calculate λ_m for an oxygen molecule in air at 20°C and a pressure of 1 atmosphere ($= 1.01 \times 10^5$ N m^{-2}). Assume the molecule is a sphere of radius 2.0×10^{-10} m.

(f) In Problem Sheet 2, we found that the average speed of an oxygen molecule at 20° C was 440 m s^{-1}. Calculate the average time between collisions.

6. Show that the constant volume heat capacity of a van der Waals gas is the same as that of a monatomic ideal gas containing the same number of molecules.

7. Assuming that Oxygen molecules are spheres of radius 2.0×10^{-10} m, estimate the pressure at which the finite size of the molecules causes a 1% departure from ideal gas behaviour at 20°C. (Ignore the attractive force between molecules.)

8. In Section 8.1 of Lecture 8 we saw that the low temperature isotherms of the van der Waals gas on a $P-V$ diagram have a maximum and a minimum, while the high temperature ones don't. The dividing line between these two types is an isotherm along which there is a point (called the *critical point*) at which $\left(\dfrac{\partial P}{\partial V}\right)_T = 0$ and $\left(\dfrac{\partial^2 P}{\partial V^2}\right)_T = 0$. The temperature of this isotherm is called the *critical temperature, T_c*. Show that $V_c = 3Nb$ and $T_c = \dfrac{8a}{27k_B b}$, where V_c is the volume at the critical point, and a and b are the constants in the van der Waals equation of state.

Numerical Answers

4. (b) Ionic potential well is 11 × deeper.

5. (e) 5.63×10^{-8} m,

   (f) 1.28×10^{-10} s.

7. About 3 atmospheres.