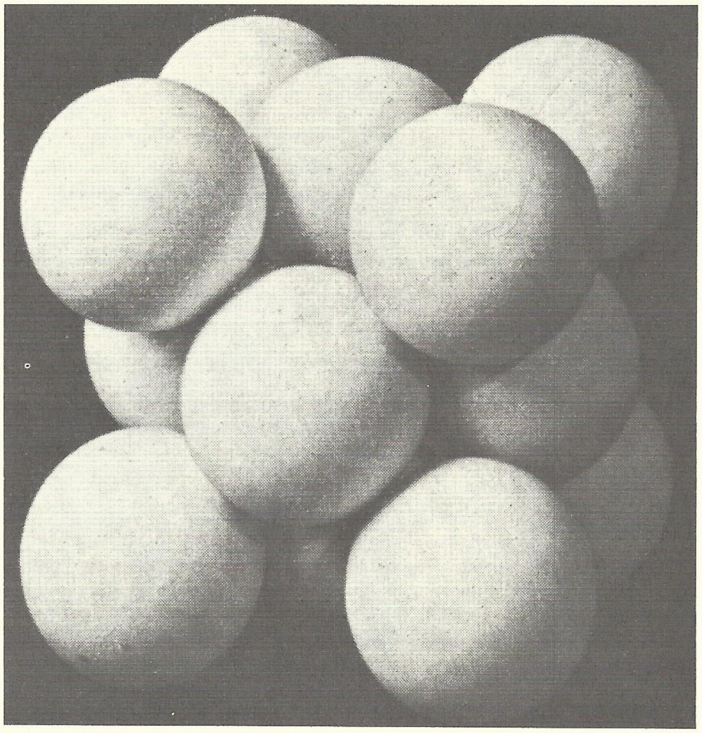

Figure 2 Cubic close-packed (fcc) crystal structure of the inert gases Ne, Ar, Kr, and Xe. The parameters of the cubic cells are 4.46, 5.31, 5.64, and 6.13 Å, respectively, at 4°K.

What holds an inert gas crystal together? We believe that the elect distribution in the crystal cannot be significantly distorted from the elect distribution around the free atoms, because the cohesive energy of an atom the crystal is only one percent or less of the ionization energy of an atom electron, from Table 2. Thus not much energy is available to distort the atom charge distributions. Part of this distortion is the van der Waals interac

Van der Waals-London Interaction

Consider two identical inert gas atoms at a separation R large in parison with any reasonable measure of the radii of the atoms. What actions exist between the two neutral atoms?

If the charge distributions on the atoms were rigid, the interaction bet atoms would be zero, because the electrostatic potential of a spherical bution of electronic charge is canceled outside a neutral atom by the ele static potential of the charge on the nucleus. Then the inert gas atoms show no cohesion and could not condense, contrary to experiment. It is that the time-average electric moments are all zero. But the electrons motion around the nucleus even in the lowest electronic state, and at any instant of time there is likely to be a nonvanishing electric dipole moment from this motion.[3] An instantaneous dipole moment of magnitude p_1 on one atom (Fig. 3) produces an electric field E of magnitude $2p_1/R^3$ at the center of the second atom distant R from the first atom. This field will induce an instantaneous dipole moment $p_2 = \alpha E = 2\alpha p_1/R^3$ on the second atom; here α is the electronic polarizability, defined in Eq. (13.31) as the dipole moment per unit electric field.

The standard result of electrostatics for the energy of interaction of two dipoles of moment $\mathbf{p}_1$ and $\mathbf{p}_2$ separated by $\mathbf{R}$ is

$$\text{(CGS)} \qquad U(R) = \frac{\mathbf{p}_1 \cdot \mathbf{p}_2}{R^3} - \frac{3(\mathbf{p}_1 \cdot \mathbf{R})(\mathbf{p}_2 \cdot \mathbf{R})}{R^5} \; . \tag{1a}$$

Because the induced moments in the van der Waals interaction are parallel, we have for the potential energy of the dipole moments

$$\text{(CGS)} \qquad U(R) \approx -\frac{2p_1p_2}{R^3} = -\frac{4\alpha p_1{}^2}{R^6} \; . \tag{1b}$$

The interaction is attractive. To obtain (1) in SI, multiply the right-hand side by $1/4\pi\epsilon_0$.

The coefficient $\alpha p_1{}^2$ may be estimated as follows: Electronic polarizabilities have dimensions [length]^3 as we see from the relation $p_2 = 2\alpha p_1/R^3$ above; and the relevant length is an atomic radius, denoted by r_0. Dipole moments have dimensions [charge] × [length] and have magnitudes of the order of er_0. Thus

$$\text{(CGS)} \quad U(R) \approx -\frac{4e^2r_0{}^5}{R^6} \approx -\frac{4(5 \times 10^{-10})^2(1 \times 10^{-8})^5}{R^6} \approx -\frac{10^{-58}}{R^6} \; , \tag{2}$$

in ergs for R in cm. We have taken $r_0 \approx 10^{-8}$ cm.

We write the interaction as

$$U(R) = -\frac{C}{R^6} \; . \tag{3}$$

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[3] The semiclassical model leads to the correct result, but the language is not to be taken entirely literally. A simple quantum-mechanical model (two harmonic oscillators) is developed in Advanced Topic B.

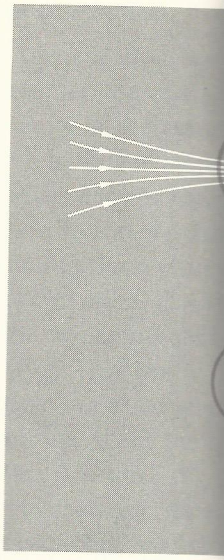

Figure 3 Origin of the
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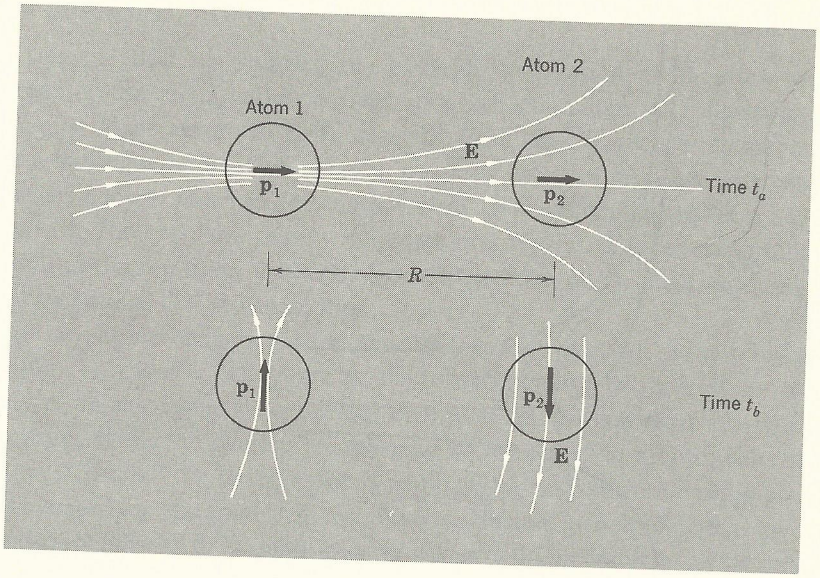

Figure 3 Origin of the van der Waals interaction, according to a classical argument. At one instant of time there is a dipole moment p_1 on atom 1. This produces an electric field E at atom 2, which acquires an induced dipole moment p_2. Diagrams are shown for two times, t_a and t_b. The interaction is always attractive: the closer the atoms, the tighter the binding.

his is known variously as the **van der Waals interaction,**[4] the London inter-
tion, or the induced dipole-dipole interaction. It is the principal attractive
teraction in crystals of inert gases and also in crystals of many organic mole-
les. Taking $C \approx 10^{-58}$ erg-cm^6, the interaction[5] at a separation $R = 4$ Å as
krypton has the value $U \approx 2 \times 10^{-14}$ erg, whence in temperature units
$/k_B \approx 100$°K, of the order of magnitude of the melting temperature of inert
s crystals.

Because of the R^{-6} dependence the interaction increases rapidly at shorter
tances. For example, at the interatomic separation of metallic copper, 2.55 Å,
van der Waals interaction between the Cu$^+$ ion cores is $\approx 2 \times 10^{-13}$ ergs
the above value of C. A better value of C may be as much as ten times
ater, which would account for a substantial part of the high cohesive energy
copper (Table 1).

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[4] The quantum-mechanical theory is discussed by H. Margenau, Revs. Mod. Phys. **11**, 1 (1939);
lso *Advances in chemical physics* **12**: *Intermolecular forces*, J. O. Hirschfelder, ed., Interscience,
, and S. Doniach, Phil. Mag. 8, 129 (1963).

[5] It is easier to grasp the magnitude of an interaction energy U if it is expressed in terms of an
tive temperature which we define by the relation $k_BT = U$, where k_B is the Boltzmann constant.

Advanced Topic B

DERIVATION OF THE VAN DER WAALS INTERACTION

We consider two identical linear harmonic oscillators 1 and 2 separated by R. Each oscillator bears charges $\pm e$ with separations x_1 and x_2, as in Fig. 1. The particles oscillate along the x axis. Let p_1 and p_2 denote the momenta $m(dx_1/dt)$ and $m(dx_2/dt)$. Then the hamiltonian of the unperturbed system is

$$\mathcal{H}_0 = \frac{1}{2m}p_1^2 + \tfrac{1}{2}\beta x_1^2 + \frac{1}{2m}p_2^2 + \tfrac{1}{2}\beta x_2^2 \ . \tag{1}$$

The uncoupled oscillators each have the resonance frequency

$$\omega_0 = \left(\frac{\beta}{m}\right)^{\frac{1}{2}} \tag{2}$$

appropriate to a simple harmonic oscillator.

Let $\mathcal{H}_1$ be the interaction energy of the two oscillators. The geometry is shown in the figure. The internuclear coordinate is R. Then

$$\mathcal{H}_1 = \frac{e^2}{R} + \frac{e^2}{R + x_1 - x_2} - \frac{e^2}{R + x_1} - \frac{e^2}{R - x_2} \ ; \tag{3a}$$

in the approximation $|x_1|, |x_2| \ll R$ we have

$$\mathcal{H}_1 \cong -\frac{2e^2x_1x_2}{R^3} \ . \tag{3b}$$

The total hamiltonian with the approximate form (3b) for $\mathcal{H}_1$ can be diagonalized by the normal mode transformation

$$x_s \equiv \frac{1}{\sqrt{2}}(x_1 + x_2) \ ; \qquad x_a \equiv \frac{1}{\sqrt{2}}(x_1 - x_2) \ , \tag{4}$$

or, on solving for x_1 and x_2,

$$x_1 = \frac{1}{\sqrt{2}}(x_s + x_a) \ ; \qquad x_2 = \frac{1}{\sqrt{2}}(x_s - x_a) \ . \tag{5}$$

The subscript s and a denote symmetric and antisymmetric modes of motion. Further, we have the momenta p_s, p_a associated with the two modes:

$$p_1 \equiv \frac{1}{\sqrt{2}}(p_s + p_a) \ ; \qquad p_2 \equiv \frac{1}{\sqrt{2}}(p_s - p_a) \ . \tag{6}$$

The total hamiltonia

$\mathcal{H} = \Big[\frac{1}{2m}p_s^2 + \frac{1}{2}\Big($

The two frequencies of t
to be

$\omega = \Big[\Big(\beta \pm \frac{2e^2}{R^3}\Big)\Big/m$

with ω_0 given by (2). In
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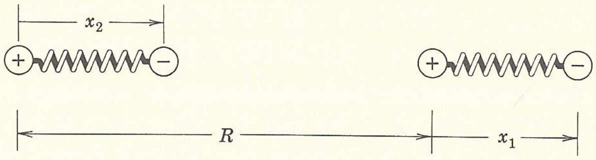

Figure 1 Coordinates of the two oscillators.

The total hamiltonian $\mathcal{H}_0 + \mathcal{H}_1$ after the transformations (5) and (6) is

$$\mathcal{H} = \left[\frac{1}{2m}p_s^2 + \frac{1}{2}\left(\beta - \frac{2e^2}{R^3}\right)x_s^2\right] + \left[\frac{1}{2m}p_a^2 + \frac{1}{2}\left(\beta + \frac{2e^2}{R^3}\right)x_a^2\right] . \quad (7)$$

The two frequencies of the coupled oscillators are found by inspection of (7) to be

$$\omega = \left[\left(\beta \pm \frac{2e^2}{R^3}\right)\Big/ m\right]^{\frac{1}{2}} \cong \omega_0\left[1 \pm \frac{1}{2}\left(\frac{2e^2}{\beta R^3}\right) - \frac{1}{8}\left(\frac{2e^2}{\beta R^3}\right)^2 + \cdots\right] , \quad (8)$$

with ω_0 given by (2). In (8) we have expanded the square root.

The zero point energy of the system is $\frac{1}{2}\hbar(\omega_s + \omega_a)$; the sum is lowered because of the interaction by the amount

$$\Delta U = \tfrac{1}{2}\hbar(\Delta\omega_s + \Delta\omega_a) = -\hbar\omega_0 \cdot \frac{1}{8}\left(\frac{2e^2}{\beta R^3}\right)^2 . \quad (9)$$

This is an attractive interaction which varies as the minus sixth power of the separation of the two oscillators.

The polarizability of an oscillator is

$$\alpha \equiv \frac{\text{electric dipole moment}}{\text{electric field intensity}} = \frac{e^2}{\beta} , \quad (10)$$

by the argument of Chap. 13. Thus

$$\Delta U = -\hbar\omega_0 \frac{\alpha^2}{2R^6} = -\frac{C}{R^6} , \quad (11)$$

where $C \equiv \hbar\omega_0\alpha^2$. This is the **van der Waals interaction** of Eq. (3.3). The interaction is a quantum effect, in the sense that $\Delta U \to 0$ as $\hbar \to 0$. To summarize: the zero point energy of the system is lowered by the dipole-dipole coupling $\mathcal{H}_1 = -2e^2x_1x_2/R^3$ of Eq. (3), even though the dipole moment $-ex_1$ averaged over an isolated atom is zero.

There is even an attractive van der Waals interaction between the plates of a parallel plate capacitor. The theory for this geometry is simple and elegant: it is due to Casimir.[1] The interaction of parallel plates has been measured directly by Derjaguin.[2]

Calculations of the van der Waals interaction between two H atoms are given in the text by Pauling and Wilson.[3] Retardation effects change the form of the interaction at very large distances: an account of the corrections is given by Casimir and Polder.[4]

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[1] H. G. B. Casimir, Proceedings of the Amsterdam Academy of Sciences **51**, 793 (1948).

[2] B. Derjaguin, Scientific American, July 1960, pp. 47–53.

[3] L. Pauling and E. B. Wison, *Introduction to quantum mechanics*, McGraw-Hill, 1935, Sec. 47.

[4] H. B. G. Casimir and D. Polder, Physical Review 73, 360 (1948).

From the result (6

we see that there is a si
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