Type of interaction		Interaction energy $w(r)$
Covalent, metallic	H_2, H_2O	Complicated, short range
Charge–charge	$Q_1 \quad r \quad Q_2$	$Q_1 Q_2 / 4\pi\varepsilon_0 r$ (Coulomb energy)
Charge–dipole	Fixed dipole	$-Qu\cos\theta / 4\pi\varepsilon_0 r^2$
	Freely rotating	$-Q^2 u^2 / 6(4\pi\varepsilon_0)^2 kT r^4$
Dipole–dipole	Fixed	$-u_1 u_2 [2\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2\cos\phi]/4\pi\varepsilon_0 r^3$
	Freely rotating	$-u_1^2 u_2^2 / 3(4\pi\varepsilon_0)^2 kT r^6$ (Keesom energy)
Charge–non-polar	$Q \quad r \quad \alpha$	$-Q^2\alpha / 2(4\pi\varepsilon_0)^2 r^4$
Dipole–non-dipolar	Fixed	$-u^2\alpha(1 + 3\cos^2\theta)/2(4\pi\varepsilon_0)^2 r^6$
	Rotating	$-u^2\alpha/(4\pi\varepsilon_0)^2 r^6$ (Debye energy)
Two non-polar molecules	$\alpha \quad r \quad \alpha$	$\dfrac{3}{4}\dfrac{h\nu\alpha^2}{(4\pi\varepsilon_0)^2 r^6}$ (London dispersion energy)
Hydrogen bond		Complicated, short range, energy roughly proportional to $-1/r^2$

Fig. 2.2. Common types of interactions between atoms, ions and molecules in vacuum. $w(r)$ is the interaction free energy (in J); Q, electric charge (C); u, electric dipole moment (C m); α, electric polarizability ($C^2 m^2 J^{-1}$); r, distance between interacting atoms or molecules (m); k, Boltzmann constant (1.381×10^{-23} J K^{-1}); T, absolute temperature (K); h, Planck's constant (6.626×10^{-34} J s); ν, electronic absorption (ionization) frequency (s^{-1}); ε_0, dielectric permittivity of free space (8.854×10^{-12} $C^2 J^{-1} m^{-1}$). The force is obtained by differentiating the energy $w(r)$ with respect to distance r.

a solvent medium involve polarization effects. Third, there are forces that are *quantum mechanical* in nature. Such forces give rise to *covalent* or *chemical bonding* (including charge-transfer interactions) and to the repulsive *steric* or *exchange interactions* (due to the Pauli exclusion principle) that balance the attractive forces at very short distances.

These three categories should be considered as neither rigid nor exhaustive: for certain types of forces, e.g., van der Waals forces, an unambiguous classification is not possible, while some intermolecular interactions (e.g., magnetic forces) will not even be mentioned, since for the systems we shall consider, they are always very weak. A commonly encountered and even more artificial classification of forces into short-range forces and long-range forces will not be adhered to here except in an intuitive sense whereby short-range forces refer to those interactions occurring at or very near atomic or molecular contacts.

Falling into the above categories are a number of fairly distinct interactions whose pair potentials in vacuum are given in Fig. 2.2. In the following chapters these will be considered in turn, and in the process we shall introduce important conceptual aspects of intermolecular forces especially for interactions occurring in a medium: in a condensed medium, whether liquid or solid, the force between two molecules depends on whether they are immobilized or free to rotate (see Fig. 2.2) and is rarely given by simply dividing the vacuum interaction by the medium's dielectric constant, ε.

PROBLEMS AND DISCUSSION TOPICS

2.1 For molecules constrained to interact on a surface (as occurs on adsorption and in surface monolayers) there is a 'two-dimensional' van der Waals equation of state, analogous to the three-dimensional one (Eq. (2.21)) This may be written as

$$(\Pi + a/A^2)(A - b) = kT, \qquad (2.29)$$

where Π is the externally applied surface pressure (in units of N m^{-1}), A the mean area occupied per molecule, and a and b are constants. Derive this equation for molecules of diameter σ interacting with a van der Waals-type interaction pair potential given by $w(r) = -C/r^6$, and find the relation between the constants a, b and C, σ.

Can this approach, which predicts the existence of a gas–liquid transition be extended to one-dimension? (*Hint*: carefully check the initial assumption of this approach.)