

STUDENT

PROS

LIQUIDS AND SOLIDS

M.T. SPRACKLING

LIQUIDS AND SOLIDS

Michael Sprackling took his PhD at Bristol University and was Assistant Master at King Edward VI School, Stourbridge, before taking up an Assistant Lectureship at Queen Elizabeth College, University of London. He is currently Senior Lecturer in Physics at King's College, University of London, and is the author of *The Mechanical Properties of Matter* (1970) and *The Plastic Deformation of Simple Ionic Crystals* (1976).

STUDENT PHYSICS SERIES

Series Editor:

Professor R.J. Blin-Stoyle, FRS

Professor of Theoretical Physics, University of Sussex

Advisory Editors:

Professor E.R. Dobbs, *University of London*

Dr J. Goddard, *City of London Polytechnic*

The aim of the *Student Physics Series* is to cover the material required for a first degree course in physics in a series of concise, clear and readable texts. Each volume will cover one of the usual sections of the physics degree course and will concentrate on covering the essential features of the subject. The texts will thus provide a core course in physics that all students should be expected to acquire, and to which more advanced work can be related according to ability. By concentrating on the essentials, the texts should also allow a valuable perspective and accessibility not normally attainable through the more usual textbooks.

'At a time when many undergraduate textbooks illustrate inflation in poundage, both in weight and cost, an interesting countertrend is established by the introduction from Routledge of a series of small carefully written paperbacks devoted to key areas of physics. The enterprising authors are E.R. Dobbs (*Electricity and Magnetism*), B.P. Cowan (*Classical Mechanics*), R.E. Turner (*Relativity Physics*) and Paul Davies (*Quantum Mechanics*). The student is offered an account of a key area of physics summarised within an attractive small paperback, and the lecturer is given the opportunity to develop a lecture treatment around this core.' – Daphne Jackson and David Hurd, *New Scientist*

Already published

Quantum Mechanics, *P.C.W. Davies*

Electricity and Magnetism, *E.R. Dobbs*

Classical Mechanics, *B.P. Cowan*

Relativity Physics, *R.E. Turner*

Electromagnetic Waves, *E.R. Dobbs*

LIQUIDS AND SOLIDS

M.T. Sprackling

*Senior Lecturer in Physics,
King's College,
University of London*



ROUTLEDGE & KEGAN PAUL
London, Boston, Melbourne and Henley

First published in 1985

by Routledge & Kegan Paul plc

14 Leicester Square, London WC2H 7PH, England

9 Park Street, Boston, Mass. 02108, USA

*464 St Kilda Road, Melbourne,
Victoria 3004, Australia and*

*Broadway House, Newtown Road,
Henley on Thames, Oxon RG9 1EN, England*

Set in IBM Press Roman

*by Hope Services, Abingdon, Oxon
and*

*by Cox & Wyman Ltd
Reading, Berkshire*

© *M. T. Sprackling 1985*

*No part of this book may be reproduced in
any form without permission from the publisher,
except for the quotation of brief passages
in criticism*

Library of Congress Cataloging in Publication Data

Sprackling, M. T. (Michael Thomas)

Liquids and solids.

(Student physics series)

Includes index.

1. Liquids. 2. Solids. I. Title. II. Series.

QC145.2.S67 1985 530.4 84-27740

ISBN 978-0-7102-0484-4

ISBN 978-94-011-6093-3 (eBook)

DOI 10.1007/978-94-011-6093-3

Contents

Preface	ix
Chapter 1 <i>Condensed phases</i>	1
1.1 Introduction	1
1.2 The three phases of matter	2
1.3 Intermolecular forces	7
1.4 Solids	15
1.5 Liquids	20
Chapter 2 <i>The elastic properties of matter</i>	24
2.1 Forces and equilibrium in a finite body	24
2.2 Elasticity	26
2.3 Stress	27
2.4 Strain	31
2.5 Infinitesimal strain	34
2.6 The relationship between stress and strain	36
2.7 Moduli of elasticity	37
2.8 The theorem of superposition	38
2.9 The linear, isotropic, elastic solid	39
2.10 Elastic moduli and intermolecular forces	48
2.11 Strain energy	50
2.12 The torsion of a right circular cylinder	52
2.13 Elastic limit and yield stress	55
2.14 The elasticity of liquids	56

Chapter 3	<i>The deformation and fracture of simple crystals</i>	57
3.1	Introduction	57
3.2	Plastic deformation	59
3.3	Plastic deformation by slip	64
3.4	The theoretical critical resolved shear stress	66
3.5	Dislocations	68
3.6	The critical resolved shear stress and work hardening	72
3.7	Brittle fracture	73
3.8	The theoretical brittle strength	74
3.9	Ductile fracture	79
3.10	The plastic deformation of brittle solids	80
Chapter 4	<i>The liquid phase</i>	81
4.1	Introduction	81
4.2	The tensile strength of liquids	82
4.3	Liquid flow	83
4.4	Coefficient of viscosity	86
4.5	Critical velocity	89
4.6	Fluidity and solidity	90
4.7	Models of simple liquids	92
4.8	Melting	96
4.9	Liquid helium	97
4.10	The two-fluid model of HeII	100
Chapter 5	<i>Ideal liquids</i>	102
5.1	Introduction	102
5.2	Some large-scale properties of liquids	102
5.3	Real and ideal liquids	106
5.4	The acceleration of a liquid particle	106
5.5	Euler's equations of motion	109
5.6	The equation of continuity	111
5.7	Solutions of Euler's equations	115
5.8	Applications of the Bernoulli equation	123
5.9	Irrotational flow	126
5.10	The stream function	131
5.11	Circulation and vorticity	133
5.12	The Navier–Stokes equation	137

Chapter 6 <i>The slow viscous flow of liquids</i>	140
6.1 Introduction	140
6.2 Creeping viscous flow in a semi-infinite channel	140
6.3 Poiseuille flow in tubes of circular cross-section	144
6.4 Motion of a Newtonian liquid between two coaxial cylinders	148
6.5 Bodies in liquids	151
6.6 Liquid flow and intermolecular forces	154
6.7 Non-Newtonian liquids	157
6.8 Viscometers	160
Chapter 7 <i>Surface effects</i>	163
7.1 Introduction	163
7.2 Excess surface free energy and surface tension of liquids	163
7.3 The total surface energy of liquids	167
7.4 Surface tension and intermolecular forces	168
7.5 Solid surfaces	171
7.6 Specific surface free energy and the intermolecular potential	172
7.7 Liquid surfaces and the Laplace-Young equation	174
7.8 Liquid spreading	178
7.9 Young's relation	181
7.10 Capillary effects	184
7.11 The sessile drop	187
7.12 Vapour pressure and liquid-surface curvature	189
7.13 The measurement of surface free energies	191
Chapter 8 <i>High polymers and liquid crystals</i>	197
8.1 Introduction	197
8.2 High polymers	197
8.3 The mechanisms of polymerisation	198
8.4 The size and shape of polymer molecules	199
8.5 The structure of solid polymers	201
8.6 The glass transition temperature	203
8.7 Young's modulus of solid polymers	205
8.8 Stress-strain curves of polymers	206
8.9 Viscous flow in polymers	209
8.10 Liquid crystals	212

Appendix 1 <i>Exercises</i>	216
Appendix 2 <i>Answers to exercises</i>	229
Index	233

Preface

Most of the matter in the world is in a condition described as solid or liquid. In both of these conditions adjacent constituent particles – ions, atoms or molecules – are so close together that they may be described as being in contact.

The aim of this book is to give an elementary account of the properties of solids and liquids and, in particular, of their response to applied forces. Their behaviour is examined on the large scale, that is, in terms of quantities that are measured in the laboratory, and also from the atomic standpoint. An attempt is made to show how the bulk properties are related to what the constituent particles are doing, that is, to the properties of a large assembly of strongly interacting particles. (The properties of gases, kinetic theory, and a more detailed treatment of atoms, molecules and interatomic forces, are discussed in a separate volume in this series.)

The treatment is essentially rough and ready and tries to bring out the essential features by a simple-minded approach. Further, the treatment is largely restricted to the properties of solids and liquids consisting of small molecules, though there is a brief introduction to the behaviour of high polymers and liquid crystals.

The text contains a number of worked examples and also exercises for the reader. Many of the quantities discussed have directional properties, but vector notation is used only where it is considered helpful or where vector algebra is used.

Chapter 1

Condensed phases

1.1 Introduction

The three phases of matter — solid, liquid and gas — are the result of competition between the internal energy and the intermolecular forces of a large assembly of molecules. It is this competition which determines whether a given substance, under given conditions, is a solid, liquid or gas.

This book gives an account of the bulk properties of solids and liquids (and, particularly, their response to external forces) and an attempt is made to show how many of these properties can be explained in terms of the intermolecular forces and the internal energy. In this chapter a simple account is given of the most important properties of solids and liquids in terms of intermolecular forces. No detailed account of the origin of these forces is given, but the basic features are described and characterised.

The idea that matter is composed of very small, discrete basic particles is the essence of the kinetic theory of matter. This idea is a very old one but was only put on a quantitative basis early in the nineteenth century, when such a view was seen to give a ready explanation of the laws of chemical combination. These laws suggest that each unit mass of a given chemical element is proportional to the mass of some basic particle of that element, and that chemical reactions involve the joining together of these basic particles in definite and reproducible small numbers.

The basic postulates of Dalton's theory (1803) are that:

1. the chemical elements consist of discrete particles called atoms, which cannot be subdivided by any known chemical process and which preserve their identity in chemical changes;

2. all atoms of the same element are identical in all respects; different elements are distinguished by having atoms of different mass;
3. chemical compounds are formed by the joining of atoms of different elements in simple numerical proportions.

The distinction between the smallest particle that can take part in a chemical reaction (the atom) and that which can exist in the free state (the molecule) was made by Avogadro in 1811. Studies of the electrolysis of matter, largely performed by Faraday in the years immediately before 1833, showed that atoms may exist in a charged condition, when they are called ions.

Since the early nineteenth century it has become clear that however the particular properties of atoms may be modified in the light of new discoveries and ideas the concept that matter is composed of discrete entities is an essential feature of (classical) physical theory.

1.2 The three phases of matter

One way of classifying substances in bulk is according to their condition of aggregation, or phase. Three phases are usually recognised: solid, liquid and gas. Traditional descriptions of these three phases are as follows. A solid is an aggregation of matter that occupies a definite volume at a given temperature and pressure and, in the absence of external forces, has a definite shape. A liquid has a definite volume at a given temperature and pressure, but its shape is determined by that of the containing vessel, except in the case of very small drops. In contrast, a gas fills completely all the space made available to it and necessarily takes the shape of the boundaries of the space. The term phase is also used to describe different modifications of the arrangement of the constituent particles of a given solid.

All materials are gaseous at sufficiently high temperatures and all condense into liquids as the temperature is lowered. In addition, all except helium form solids under their own vapour pressure as the temperature is lowered still further. Condensation indicates that there must be attractive forces between the basic particles to make them cohere, though this force must become

repulsive at very short interparticle distances, otherwise all matter would coalesce.

For some substances the change from one phase to another as, say, the temperature is changed at constant pressure, is not very distinct, but for a simple pure substance, i.e. one consisting of a single chemical species, a clear distinction can usually be made between the solid, liquid and gaseous phases. Consider a given mass of such a substance contained in a cylinder by means of a frictionless piston. Any equilibrium condition, or state, of this substance is specified by a certain set of values of the pressure p , volume V and temperature T . The totality of equilibrium states for a given mass of a particular chemical species is represented by a continuous surface in p - V - T space. Since the surface is usually of a complicated shape, it is often more useful to project sections of the p - V - T surface on to one of the principal planes. The two most useful projections are shown in Fig. 1.1. In the p - V projection (Fig. 1.1(a)) the full lines shown join states having a common temperature, giving a pattern of isotherms, while the dotted lines indicate where phase boundaries occur. This plot shows clearly the states of mixed phase equilibrium. The lines shown in the p - T projection (Fig. 1.1(b)) are the phase boundaries, since in the p - T plane the regions of mixed phases project into lines.

From these two projections it can be seen that for all temperatures above T_c , known as the critical temperature, the substance remains in the gaseous phase, whatever the value of the applied pressure.

At temperatures T_c and below it is always possible to produce a liquid or a solid phase of the substance by the application of pressure. The production of liquid or solid from the gaseous phase is called condensation, and liquids and solids are referred to as condensed phases. When the temperature of the substance is the triple-point temperature T_t , condensation from the gaseous phase produces both liquid and solid so that, along the horizontal portion of the T_t isotherm in the p - V plot, solid, liquid and gas coexist in equilibrium. For temperatures in the range $T_t < T \leq T_c$ condensation from the vapour phase is to the liquid phase and the application of sufficient pressure in this temperature range results in

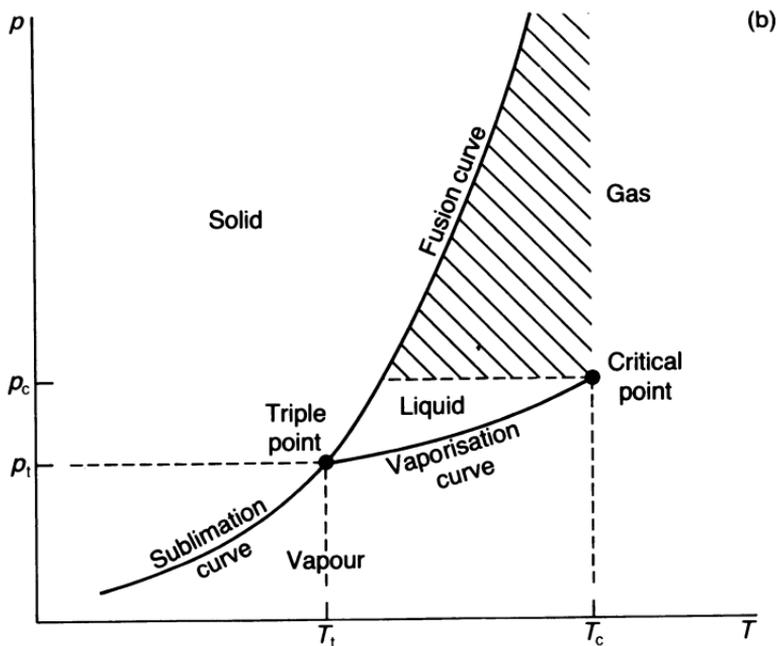
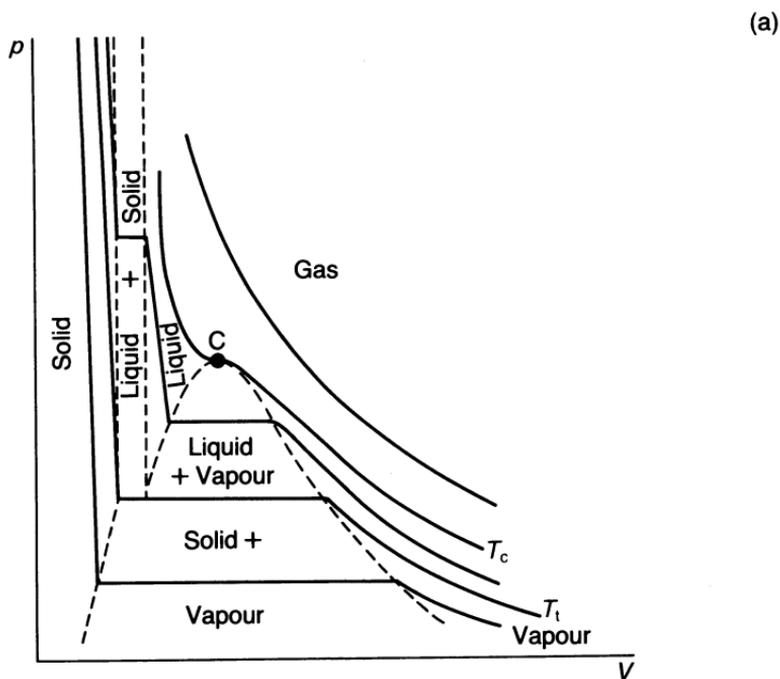


Fig. 1.1

the conversion of the liquid phase to the solid phase. When the temperature is below T_t the gaseous phase condenses directly to the solid phase. (It is convenient to refer to the gaseous phase as a gas when $T > T_c$ and as a vapour when $T \leq T_c$; a vapour can always be condensed by the application of pressure at constant temperature.)

Quantitative studies show that solids usually expand slightly on melting whereas liquids always expand considerably on becoming gaseous. In general, the density of the solid phase at the melting point is hardly greater than that of the liquid phase at the same temperature; both phases are almost incompressible and both show cohesion. This implies that the atoms, ions or molecules comprising the substance are hardly more closely packed in the solid than in the liquid: in both solids and liquids the basic constituent particles are effectively in contact. This is the physical basis for the classification of solids and liquids as condensed phases.

A major difference between solids and liquids is that solids show rigidity whereas liquids do not; in solids the basic particles maintain their positions relative to each other while in liquids they are free to move relative to each other. Further, some samples of simple solids show very regular external surfaces and split or cleave in a regular geometrical way. These properties suggest that the particles making up the solid are arranged in a regular three-dimensional pattern, a result confirmed by X-ray diffraction, even in cases where regular external surfaces are not obtained.

The mobility of the particles in a liquid prevents a regular three-dimensional arrangement from being set up, and yet the density and compressibility requirements indicate that the environment of any particle cannot be very different whether it be in the solid or liquid phase. These considerations suggest that a liquid may be pictured as an assembly of small clusters of particles that are randomly oriented with respect to each other. Crudely, a liquid may be pictured as a very broken-up solid, and X-ray diffraction patterns from simple liquids do show the same essential features as those obtained from finely powdered solids, but are more blurred, a consequence of the smallness of the solid-like clusters and their transient nature.

In gases, in contrast, the constituent particles move about quite freely, only constrained by the wall of the container, the pressure arising from the bombardment of the wall by the gas particles.

A simple calculation shows that, for a model gas made up of point particles, each of mass m and exerting zero attractive forces on the other particles (known as an ideal gas), the pressure p exerted by the gas is given by:

$$p = \frac{1}{3} n m \bar{c}^2 \quad [1.1]$$

where n is the number of particles per unit volume and \bar{c}^2 is the mean value of the squares of the speeds of the particles.

If N_A is the Avogadro constant and V_m is the volume occupied by 1 mole of molecules, equation [1.1] may be written:

$$pV_m = \frac{1}{3} m N_A \bar{c}^2. \quad [1.2]$$

It may be shown that the equation of state of an ideal gas is:

$$pV_m = RT \quad [1.3]$$

where R is the gas constant and T is the thermodynamic temperature. Equations [1.2] and [1.3] are consistent if:

$$RT = \frac{1}{3} m N_A \bar{c}^2$$

which may be written as

$$RT = \frac{2}{3} \cdot \frac{1}{2} m \bar{c}^2$$

or, putting $R/N_A = k$, the Boltzmann constant:

$$kT = \frac{2}{3} \cdot \frac{1}{2} m \bar{c}^2. \quad [1.4]$$

Therefore, for ideal gases, the temperature is proportional to the mean kinetic energy per particle or, alternatively, the mean kinetic energy per particle of an ideal gas at a temperature T is $\frac{3}{2}kT$.

It is not difficult to extend this model to give a discussion of the properties of gases with particles of finite size. Estimates of the diameter of gas particles (assumed spherical) can then be obtained from, for example, the flow properties of the gas. In

this way values for the particle diameter of about 10^{-10} m are obtained.

Liquids are formed by supplying energy to solids to produce melting, and the further sufficient supply of energy will convert the liquid to the gaseous phase. For ideal gases all the energy of the particles is kinetic energy, but in real substances the interactions between the particles means that the energy of an assembly of particles is partly kinetic and partly potential. It is reasonable to infer that the total energy of a given collection of matter macroscopically at rest (the internal energy of the sample) increases as the temperature increases, though not necessarily proportionally as in the case of the ideal gas.

Introducing the concept of internal energy modifies the models of solids and liquids in the following way. The particles in a solid are arranged in a regular pattern, but the particles vibrate about mean positions. In a liquid the vibrations are sufficient to break up the extended regular pattern of particles, but the attractive forces are still able to hold the particles together, though not able to prevent them from wandering slowly from point to point. When the motion of the particles is so violent that they can break away completely from the attractive forces of neighbouring particles the gaseous phase is formed.

The different phases arise from the competition between the interparticle forces, which try to produce a regular arrangement of the particles, and the internal energy, which tries to destroy such an arrangement. Applied pressures affect the role played by the interparticle forces so that the phase in which a particular substance exists depends on both the temperature and pressure.

1.3 Intermolecular forces

The actual nature of the force between the constituent particles of matter depends on the electronic structures of the interacting particles, i.e. on whether they are atoms, ions or molecules. For example, the ionic interaction arises when electrons are transferred from atoms of one type to those of a second type, so that the material is composed of positive and negative ions, giving a force that is central and unsaturated (i.e., one positive ion can attract

several negative ions around it and the force exerted by the positive ion on each negative ion is not affected by the presence of the other ions). In the covalent interaction valence electrons are shared between two atoms to an appreciable extent, giving an interaction that is saturated and has marked directional properties. The van der Waals interaction is a weak electrostatic interaction which occurs even in atoms and molecules showing no permanent dipole moment. It arises from the fluctuating dipole moment associated with the instantaneous positions of the electrons in the atom. In many materials one type of interaction predominates so that, for example, a certain solid may be referred to as an ionic solid. In other cases the nature of the interaction may be less clear-cut.

Despite the differences in the nature of the interactions between the constituent particles, most simple materials show similar properties of aggregation as the temperature is changed, and similar responses to balanced applied forces. Therefore, qualitatively, the form of the interaction between the constituent particles in condensed matter must be the same in all cases. In view of this, the precise nature of the particles is unimportant for the purposes of this book and the constituent particles will generally be referred to as molecules, even though they are frequently ions or atoms. Distinctions will be made in particular cases where necessary.

Figure 1.1(a) shows that to produce even a small reduction in volume of the solid and liquid phases needs a very large increase in the applied pressure. This implies that, for small molecular separations, the intermolecular forces are repulsive and that they increase rapidly as the separation is reduced.

Solids (and under certain conditions liquids) can also resist extension up to some limiting value at which rupture occurs. Therefore, for larger molecular separations the intermolecular forces are attractive. The attractive force must increase with molecular separation for small changes in separation, since the force needed to extend a solid increases with the extension, at least for a small range of increase. However, at still larger molecular separations the attractive force must fall off rapidly, since gases obey Boyle's law reasonably well under conditions in which

the density is not very different from that of the liquid, yet Boyle's law can be deduced using the kinetic theory of gases only if the attractive intermolecular force is zero.

These simple observations concerning intermolecular forces can be represented in the following way. Consider the interaction between two molecules. If one of the molecules is taken as the origin of coordinates, repulsive intermolecular forces will be in the direction of increasing separation and will be counted positive; attractive intermolecular forces will be counted negative. Then, for simple substances generally, the variation of intermolecular force F with intermolecular distance r for a molecule and a single neighbour will take the form shown in Fig. 1.2(a). The force is repulsive for small intermolecular distances, becoming stronger as this distance decreases, and is attractive at larger distances, reaching a maximum and then falling practically to zero when the separation is a few molecular diameters. At some value r_0 of the intermolecular distance the value of F is zero. This is the equilibrium separation of the two molecules, provided that neither has any kinetic energy. For identical molecules r_0 is equal to the molecular diameter. The equilibrium is stable since, if the value of r is reduced, the molecules repel each other while if it is increased they attract. Therefore, if the molecules have a small amount of kinetic energy they will vibrate, with r_0 as the mean separation. The amplitude of this vibration will increase with temperature.

It is generally more rewarding to discuss interactions in terms of energies rather than forces. The potential energy of a pair of molecules is defined as the work done by forces external to the two molecules in changing their relative positions from some standard configuration to the given one. This standard configuration then constitutes a zero which must be stated when potential energy values are quoted. With two molecules an obvious standard configuration is when they are an infinite distance apart, so that their interaction is negligible. Then, if F_e is the external force needed to maintain the intermolecular distance at a value x , the work dw done by this force when one molecule moves so that the separation increases by dx along the line of centres is (assuming central forces):

$$dw = F_e dx$$

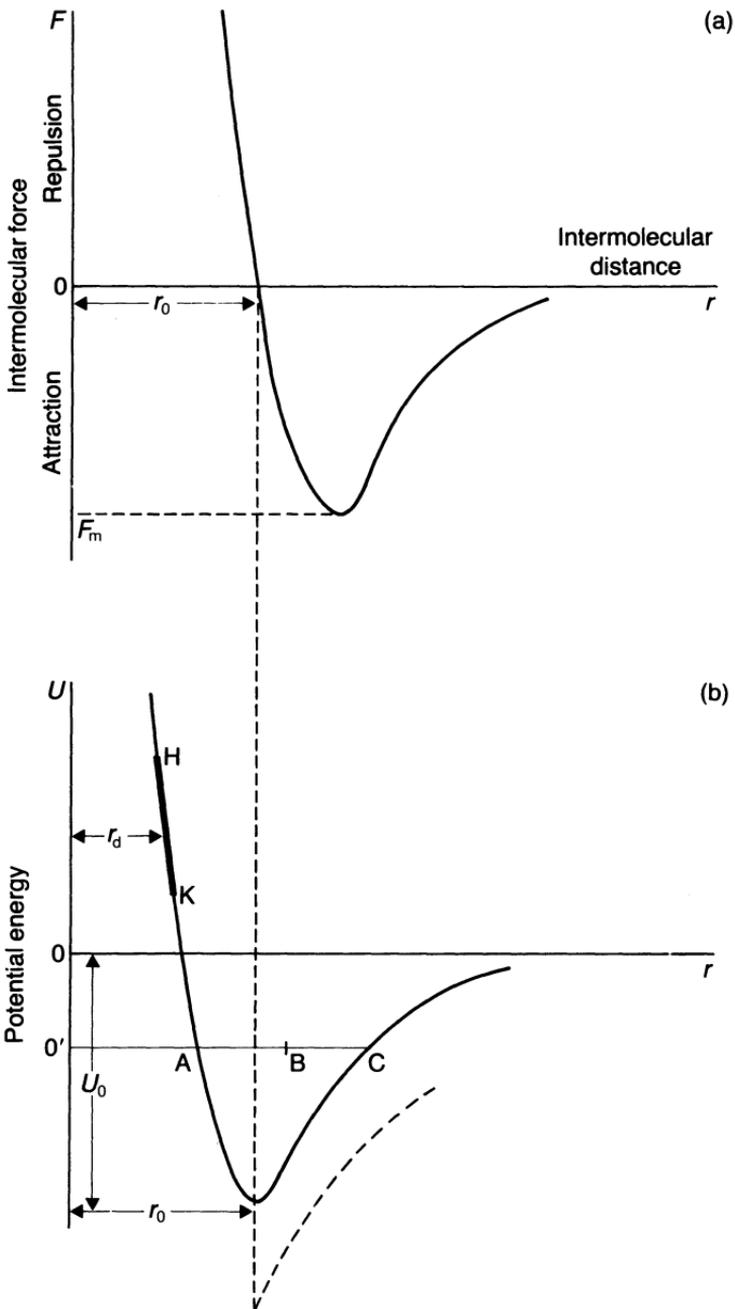


Fig. 1.2