

kinetic theory of liquids

J. Frenkel

KINETIC THEORY OF LIQUIDS

BY
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PREFACE

THE recent development of the theory of the liquid state, which distinguishes this theory from the older views based on the analogy between the liquid and the gaseous state, is characterized by the reapproximation of the liquid state—at temperatures not too far removed from the crystallization point—to the solid (crystalline) state.

The apparent opposition between these two states has been removed by the disclosure of elements of rigidity and order in liquid bodies on the one hand, and of elements of fluidity and disorder in solid (crystalline) bodies on the other.

The kinetic theory of liquids must accordingly be developed as a generalization and extension of the kinetic theory of solid bodies. As a matter of fact, it would be more correct to unify them under the title of 'condensed bodies'.

In the present book the main stress is laid upon the liquid state; the solid state is considered (in the first two chapters) from the point of view of the amendments which must be introduced in the classical theory of ideal crystal lattices in order to bridge the gap between the solid and liquid states.

I was led to a revision of this classical theory in 1924, in connexion with a study of such processes as the evaporation, diffusion, and conduction of electricity in solid bodies at elevated temperatures.

The introduction into the kinetic theory of real crystals of the conception of a partial dissociation of the crystal lattice (Joffé), of interstitial atoms and movable holes, of the heat motion as an alternation of small vibrations about fixed equilibrium positions with a jerk-like displacement of these positions, has paved the way to a correct understanding of the character of the heat motion of molecules in liquid bodies as a motion of a vibration-diffusion type, with a much more pronounced diffusion component than in the case of solids, i.e. with a much more rapid displacement of the equilibrium positions, in conjunction with the absence of regularity in their spatial distribution.

This conception forms the molecular-kinetic basis for that phenomenological unification of the solid and liquid states of matter from the point of view of their mechanical ('visco-elastic') properties, which was proposed long ago by Maxwell with respect to *amorphous* bodies.

It was believed, however, until the pioneer work of Stewart (1928) on the X-ray analysis of the structure of liquid bodies, that these

differ sharply from solid bodies in the thermodynamically stable (crystalline) state by the absence of any regularity in the arrangement and orientation of the atoms or molecules constituting them.

This difference has proved to be rather in the *degree* of order than a qualitative difference, since liquid bodies have been shown to display at low temperatures, lying in the vicinity of the crystallization point, a high degree of local (short-range) order in the relative distribution and orientation of their molecules, of the same type as that characteristic of the corresponding solids.

While the fundamental principles of the kinetic theory of liquids can be regarded as more or less settled, the quantitative development of various general questions of this theory is still in an embryonic stage. This refers, in particular, to such questions as the theory of fusion and the equation of state of liquid bodies. It has further been hardly possible to obtain a satisfactory quantitative theory of various types of liquids, corresponding to different special types of molecular structure and molecular forces, in spite of the considerable number of studies of this subject that have been published in the course of the last few years.

In these conditions the publication of a book on the kinetic theory of liquids may be thought premature. I feel justified, however, in having written it for three reasons. In the first place, because I myself have been interested in this theory for the last twenty years and have made a number of contributions to it (many of which have been published in Russian journals only and have remained unknown to foreign readers). In the second place, because an understanding of the principles of the kinetic theory of liquids seems to have been restricted thus far to a somewhat narrow circle of physicists and chemists, whereas it is of vital importance to all those who have to deal with matter in the condensed state. Finally, a presentation of this new theory, even in a very crude and incomplete form, may serve to attract the attention of other scientists to this subject and accelerate its further development.

The choice of the material incorporated in this book has been determined partly by the author's personal interests and partly by the limitations imposed by its size. Certain topics are treated at a greater length than they may appear to deserve, while other very interesting topics are wholly omitted. I have limited myself to the consideration of ordinary liquids, whose properties can be understood on the basis of classical mechanics and statistical theory, leaving wholly aside a number of interesting questions referring to 'quantum liquids', such as liquid

helium II, the free electrons in metals, and the proton-neutron liquid in complex atomic nuclei.

I have written this book at a time ill suited to the pursuit of purely academic tasks. I may be excused for this by the consideration that, when victory had become certain, it seemed advisable to revert to topics of pre-war and post-war interest. In recalling the state of mind and the conditions in which this work has been carried through, I wish to express my debt of deepest gratitude to the men and women of my country who, in the ranks of the Russian Red Army, have heroically and victoriously struggled for the salvation of our life and civilization against the ruthless forces of the Nazi barbarians.

J. F.

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July 1943

NOTE

The publication of this book, which was written at Kazan in 1942 under rather difficult conditions, has been delayed owing to mailing difficulties connected with the war. I wish to express my warmest thanks to Professor N. F. Mott and to Dr. R. Sack, who undertook the arduous task of reading the proofs and corrected a number of mistakes which had slipped in owing to the impossibility of reading them myself.

J. F.

LENINGRAD, PHYSICO-TECHNICAL INSTITUTE
March 1946

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REAL CRYSTALS AT ELEVATED TEMPERATURES

1. Evaporation of Crystalline Bodies

CRYSTALLINE bodies are usually described as possessing a perfectly regular structure. The only deviation from perfect regularity which is taken into account consists in the vibration of the atoms about their equilibrium positions, which are assumed to constitute an ideal three-dimensional crystal lattice (with a correction for the thermal expansion).

From this point of view, however, such processes as the evaporation of a crystal, its dissolution in a liquid medium, or the mutual diffusion of two different crystalline substances would be utterly unintelligible.

The simplest of these processes—the evaporation of a solid body—obviously consists in the separation of a fraction of the superficial atoms from the rest and their escape into the surrounding space. The possibility—more than that, the necessity—of such an escape directly follows from the general principles of statistical mechanics, in particular from Maxwell's law specifying the velocity distribution (which at elevated temperatures is the same in the solid and liquid as in the gaseous state). If v_x , the component of the velocity of a superficial atom along an axis x normal to the surface of the crystal, is directed outwards and is sufficiently large, the attractive force acting on this atom will not be able to prevent it from escaping into the surrounding space. The minimum value of v_x is determined by the equation

$$\frac{1}{2}mv_x^2_{\min} = U_0,$$

where m is the mass of an atom and U_0 is the work necessary to remove it from its (superficial) equilibrium position to infinity, i.e. the evaporation energy referred to a single atom.

Now according to Maxwell's law the relative number of atoms whose velocity in the x -direction lies between v_x and $v_x + dv_x$ is equal to

$$f(v_x)dv_x = \sqrt{\left(\frac{m}{2\pi kT}\right)} e^{-mv_x^2/2kT} dv_x, \quad (1)$$

where T is the absolute temperature of the body.

The number of superficial atoms which during a time dt pass through the respective equilibrium positions in the outward direction with a velocity in the range between v_x and $v_x + dv_x$ referred to unit area of the surface is equal to $n f(v_x) dv_x v_x dt$, where n is the average number of atoms in unit volume of the body. All those atoms for which $v_x \geq v_{x\min}$

do not return to their equilibrium positions but escape, i.e. are evaporated. Their number referred to unit time is thus equal to

$$G = n \int_{v_x \min}^{\infty} v_x f(v_x) dv_x,$$

that is,
$$G = n \sqrt{\left(\frac{m}{2\pi kT}\right)} \frac{1}{m} \int_{\frac{1}{2}mv_x^2 = U_0}^{\infty} e^{-mv_x^2/2kT} d\left(\frac{mv_x^2}{2}\right),$$

or
$$G = n \sqrt{\left(\frac{kT}{2\pi m}\right)} e^{-U_0/kT}. \quad (2)$$

This expression is a measure of the rate of evaporation of a solid body as a function of the temperature. So long as $kT \ll U_0$, the rate of evaporation is practically negligible; it must rapidly increase, however, as kT approaches the value U_0 .

The preceding result can be obtained, without recourse to Maxwell's velocity distribution law, by using Boltzmann's law for the distribution of molecules in space under the influence of given external forces. According to this law the probability that an atom will be found in a position corresponding to a potential energy U is proportional to the expression $e^{-U/kT}$ irrespective of the direction and magnitude of its velocity.

Let us consider a definite atom and let us compare the probability P' of its being bound to a certain equilibrium position on the surface of the body with the probability P'' that it will be found in a free state, i.e. in the gas phase.

For the sake of simplicity we shall assume, to begin with, that the potential energy of the atom preserves over the whole surface S of the body up to a certain distance $x = \delta$ (of the order of the interatomic distance) the constant value zero, while for $x > \delta$ it assumes a constant positive value U_0 .

If V denotes the volume of the gas phase, we get

$$\frac{P''}{P'} = \frac{e^{-U_0/kT} V}{S\delta}. \quad (3)$$

Now, the ratio of the probabilities P''/P' must obviously be equal to the ratio between the number N'' of atoms in the gas phase and the number N' of atoms situated on the surface S of the body (i.e. forming its superficial layer). Hence it follows that

$$\frac{N''}{V} = \frac{N'}{S\delta} e^{-U_0/kT},$$

i.e.
$$n'' = \frac{n'}{\delta} e^{-U_0/kT}, \quad (4)$$

where n'' is the number of atoms in unit volume of the gas phase and n' is the number of atoms per unit area of the surface of the solid body.

Since n' is practically independent of the temperature, the temperature dependence of the density (concentration) of the saturated vapour is characterized by the Boltzmann factor $e^{-U_0/kT}$.

In order to obtain the equation (2) let us consider the inverse process to the evaporation of a solid, i.e. the condensation of a saturated vapour, and let us take into account the fact that in a state of statistical equilibrium the number of atoms which are evaporated per unit time and area must be equal (on the average) to the number of atoms which are condensed on the same area in unit time. Let us further assume that each atom of the vapour striking the surface of the solid remains attached to the latter (whereas in reality a fraction of the atoms striking the surface are reflected from it, as assumed in the elementary kinetic theory of gases). Under such conditions we get

$$G = n'' \bar{v}_x, \quad (5)$$

where \bar{v}_x is the average velocity of the atoms of the vapour moving towards the surface of the solid body.

Using Maxwell's law we get for it the expression

$$\bar{v}_x = \int_0^{\infty} f(v_x) v_x dv_x = \sqrt{\left(\frac{m}{2kT\pi}\right)} \frac{1}{m} \int_0^{\infty} e^{-mv_x^2/2kT} d\left(\frac{mv_x^2}{2}\right),$$

$$\text{i.e.} \quad \bar{v}_x = \sqrt{\left(\frac{kT}{2\pi m}\right)}. \quad (5a)$$

Hence, according to (5) and (4),

$$G = \frac{n'}{\delta} \sqrt{\left(\frac{kT}{2\pi m}\right)} e^{-U_0/kT}. \quad (6)$$

This formula is identical with (2) if the number of atoms per unit area of the surface layer n' is identified with the product $n\delta$, which fully corresponds to the physical meaning of the quantity δ , namely the thickness of the surface layer.

In reality, of course, the latter has no definite thickness, and a better approximation to the actual conditions, referring to the superficial atoms, is obtained if the potential energy of one of them is represented as a function of its distance x from the surface by a curve of the type shown in Fig. 1. This curve is characterized by a horizontal asymptote $U = U_0$ for $x = \infty$, a vertical asymptote for $x = 0$ (which corresponds to the impenetrability of the following atomic layer), and

a minimum $U = 0$ at a point $x = x_0$ corresponding to the equilibrium position.

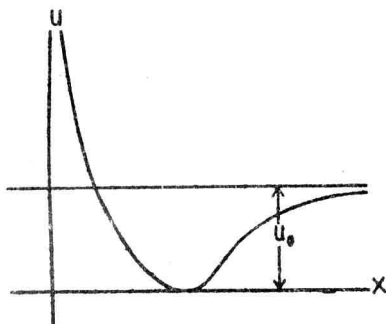


FIG. 1

For small values of the displacement $x - x_0 = \xi$ the potential energy can be represented approximately in the form

$$U(x) = U(x_0) + \frac{1}{2}U''(x_0)\xi^2 = \frac{1}{2}f\xi^2, \quad (7)$$

where f , the value of d^2U/dx^2 at the point $x = x_0$, is an essentially positive quantity.

This approximate expression for the potential energy can be used for the description of an atom in a bound state (on the surface of the body), whereas the potential energy of a free atom (in the gas phase) is equal to U_0 , as before.

Under such conditions equation (3) must be replaced by the following equation:

$$\frac{P''}{P'} = \frac{Ve^{-U_0/kT}}{S \int e^{-f\xi^2/2kT} d\xi},$$

where the integration with respect to ξ can be extended from $-\infty$ to $+\infty$ (because of the rapid decrease of the function $e^{-f\xi^2/2kT}$).

We thus come back to the previous equations (4) and (6) with the following expression for the 'effective thickness' of the surface layer:

$$\delta = \sqrt{\left(\frac{2\pi kT}{f}\right)}. \quad (8)$$

Substituting in (6) we get

$$G = n' \frac{1}{2\pi} \sqrt{\left(\frac{f}{m}\right)} e^{-U_0/kT}. \quad (9)$$

Now the quantity

$$\nu_0 = \frac{1}{2\pi} \sqrt{\left(\frac{f}{m}\right)}$$

is the frequency of free vibrations performed by the surface atom in the bound state about its equilibrium position (so long as the amplitude of these vibrations is sufficiently small). We thus have

$$G = n' \nu_0 e^{-U_0/kT}. \quad (9a)$$

From the definition of the quantity G it follows that the factor

$$\alpha = \nu_0 e^{-U_0/kT} \quad (10)$$

can be defined as the probability of the evaporation of a superficial atom in unit time. This means that the reciprocal quantity

$$\tau = \tau_0 e^{U_0/kT}, \quad (10a)$$

where $\tau_0 = 1/\nu_0$ is the period of free vibrations, is equal to the mean life of the superficial atom in the bound state reckoned from any given instant up to the instant of its evaporation. The exponential factor $e^{U_0/kT}$ is thus equal to the average number of oscillations about a given equilibrium position performed by a superficial atom before it is torn away from it and escapes into the gas phase.

The actual length of time the atom remains attached to the surface of the body can of course be either greater or smaller than the mean life τ . We meet here the same situation as in the theory of atomic collisions in a gas. According to Clausius's formula the probability that a molecule of a gas will not suffer any collisions along a path with a length exceeding x is equal to $e^{-x/\lambda}$, where λ is the mean free path. In a similar way it can be shown that the probability of a superficial atom remaining attached during a time exceeding t is equal to

$$p(t) = e^{-t/\tau}. \quad (11)$$

The preceding theory† is not, of course, quite exact: it does not take into account the forces acting on the atom in a direction parallel to the surface and preventing it from moving freely along the latter; further it does not take into account the fact that different superficial atoms are, in general, characterized by different values of U_0 , the latent heat of evaporation per atom being equal to the average value of U_0 .

Along with the ordinary evaporation, which corresponds to a complete removal of a (superficial) atom from the crystal aggregate constituted by the remaining atoms, we must consider the other types of processes, which can be denoted by the term *incomplete evaporation*.

One of them consists in a transition of a superficial atom from a

† Cf. J. Frenkel, *Z. f. Phys.* 26, 117 (1924); see also Dushman and Langmuir, *Phys. Rev.* 20, 113 (1922).

regular position in the outermost layer into a regular position *on the top* of the latter, which can be considered as the starting-point for the formation of the next layer of the surface on the one hand, and of a vacant site or 'hole' in the crystal lattice on the other. The second process consists in the transition of a superficial atom from a regular lattice site into an adjacent interstitial position ('inner evaporation'), thus leading to the formation of a hole in the surface layer, which is the starting-point for the 'self-solution' of the external layers of the crystal in its interior. A similar process can, finally, take place not only on the surface of the crystal but equally well inside it; one of the inner atoms jumping from its regular position in a lattice site into an adjacent interstitial position lying between the neighbouring atoms. This type of 'inner evaporation', resulting in the appearance of a dislocated interstitial atom and of a vacant lattice site or hole, will be designated in the sequel as a *dissociation* of the crystal lattice.

These types of 'incomplete' or 'inner' evaporation must play an important role in the behaviour of a real crystal at elevated temperatures; we shall see later on that they are responsible for the processes of self-diffusion (i.e. mixing up of the atoms in a chemically homogeneous crystal) and mutual diffusion in solid solutions. An understanding of these processes can be obtained only if we abandon the idealized picture of the heat motion in a crystal as constituted by small vibrations of the atoms about fixed equilibrium positions, and complete this type of motion by larger displacements of an irreversible character. Just as in the case of an ordinary evaporation, these irreversible displacements are connected with an escape from the original equilibrium position, with the difference that the escaping atom is immediately captured in a new equilibrium position—in a previously vacant lattice site or in an interstice.

The existence of such processes of incomplete and inner evaporation in a crystal at $T > 0$ is a direct corollary from the general principles of statistical mechanics (in conjunction with the character of inter-atomic forces), just as is the existence of the ordinary evaporation. Hence it follows that at any temperature different from the absolute zero the structure of a real crystal must differ from that described in the usual conception of an ideal crystal lattice by the presence of 'distortions' in the form of holes (vacant lattice sites) and of dislocated (interstitial) atoms, the number of such distortions increasing with the rise of the temperature according to a law of the same type as that determining the pressure (concentration) of a saturated vapour.

2. Mechanism of the Processes of Dissociation and Hole Formation in a Crystal

The dislocated atoms and holes can arise in a real crystal lattice in two essentially different ways, namely inside it and on its surface.

(1) In the first case one of the inner atoms escapes from the corresponding regular lattice site and is trapped in one of the adjacent interstitial positions, to which it remains attached for a limited length of time. This process, which was considered for the first time by Joffé in connexion with the electric conductivity of ionic crystals and has been described as a 'dissociation' of the crystal lattice,[†] is connected with the simultaneous appearance of a vacant site, i.e. of a 'hole'. It is thus quite similar to the dissociation of a diatomic molecule of a gas into two separate atoms, the interstitial atom playing the role of one partner and the hole that of the second partner. From this point of view a regularly located lattice atom corresponds to an undissociated diatomic molecule.[‡]

It must be noted that this dissociation process cannot be regarded as completed while the dislocated atom is situated in the vicinity of the hole left by it. A configuration of this kind might be described as a state of 'pre-dissociation', which can be followed either by a 'recombination' of the atom with the hole (i.e. by a return of the atom to its original place) or by a complete dissociation, if the dislocated atom quits its initial position and jumps into an interstice further removed from the vacant site, which thereby becomes an actual 'free' hole. This second step, connected with a transition from the pre-dissociated state into a truly dissociated one, requires additional energy, whereas all the subsequent wanderings of the dislocated atom and of the hole correspond to a constant value of the dissociation energy.

The transformation of a pre-dissociated pair into a fully dissociated one can also be realized, not by the dislocated atom, but by a transition of the hole into an adjacent lattice site (farther removed from the occupied interstice) as a result of the transition of an atom, which was initially situated at this site, into the initially vacated site. A dislocated atom and a hole left by it can thus be treated as fully dissociated, i.e. capable of moving through the lattice independently when their distance apart is larger than the lattice constant.

(2) Whereas *inside* the crystal the dislocated atoms and the holes can only arise simultaneously, through processes of pre-dissociation

[†] A. Joffé, *Ann. d. Phys.* 72, 461 (1923).

[‡] J. Frenkel, *Z. f. Phys.* 35, 652 (1926).

and dissociation considered above, on the *surface* of the crystal they can arise independently, penetrating afterwards inside the crystal (over interstitial positions or lattice sites). They can form two independent types of 'distortions' with entirely different concentrations (numbers per unit volume).

(a) As regards the holes, they can arise on the surface by means of a process which may be described as the dissolution in the crystal of the surrounding vacuum.† The initial preliminary step of this process, corresponding to the process of pre-dissociation, consists in the displacement of a superficial atom outwards, as in the case of an ordinary evaporation, the escaping atom being attached on the top of the original surface layer and starting the formation of a new, still more external, layer. As a result a hole is formed which can be regarded as *adsorbed* on the surface of the crystal.

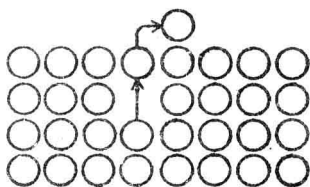


FIG. 2

The next and practically final step consists in the occupation of this superficial hole by an atom which was initially situated underneath it. The lattice site vacated by this atom (see Fig. 2, where

the displacements of the two atoms are indicated by arrows) may be treated as a hole *absorbed* by the crystal from the surrounding space.

Let us consider, for the sake of illustration, a simple cubic lattice built up of small cubical atoms, and let us assume that each atom interacts with its nearest neighbours only, with which it has common faces. The energy which is necessary for the separation of two such atoms will be denoted by U_1 . In this case the 'adsorption' of a hole is connected with an increase of the energy of the crystal by the amount $4U_1$ (for the atom 1 in its original position possessed five neighbours, and in the final position a single neighbour only); for the second step of the process, connected with the transformation of the adsorbed hole into an absorbed one, the additional energy U is required, and the third step proceeds without further increase of energy. In reality the relations are not so simple, but the simplified model gives a correct qualitative picture.

If the atoms displaced on the surface of the crystal by the absorbed holes make a regularly built layer (or several such layers), so that the effective volume of the crystal is increased without any essential change in the shape or structure of its surface, the increase of energy per hole

† Cf. W. Schottky, *Z. phys. Chem. B*, 29, 335 (1935).