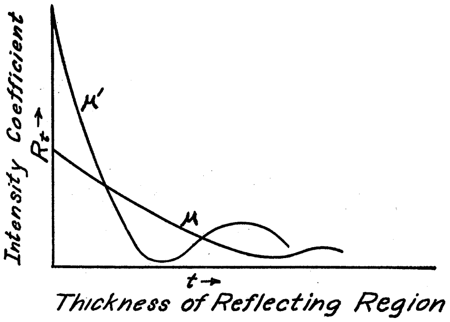

FIG. 1. The variation of the intensity coefficient with layer thickness for two sets of values of ϵ_1 and ϵ_2. The index of refraction $\mu=(\epsilon_2/\epsilon_1)^{\frac{1}{2}}$ is nearer unity than μ'.

$(n+1)/(\mu+n)$ in Eq. (16) increases for smaller values of μ. Also from the value of dR_t^2/dt it may be seen that R_t^2 decreases less rapidly for values of μ nearer unity.

The result on an exaggerated scale is illustrated in Fig. 1. Thus, although the reflection is much greater for truly sharp boundaries if μ differs considerably from one, the rate of decrease is also much greater. Hence, the Fresnel coefficient ($t=0$) becomes a better approximation for a given thickness if the value of μ is closer to one. In order to obtain information as to the exact way in which R_t decreases with t, it is necessary to make some assumptions as to the value of ϵ in the lower and upper regions and regarding the manner in which it changes in the transition layer (i.e., the nature of $F(x)$ of Eq. (8). These calculations will be published later.

The formulas developed here are applicable to the reflection of radio waves from different air masses in the troposphere. It is known from experiment that such reflections take place.[2]

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[2] R. C. Colwell and A. W. Friend, Nature **137**, 782 (1936).

DECEMBER 15, 1939 PHYSICAL REVIEW VOLUME 56

On the Interpretation of Atomic Distribution Curves for Liquids

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(Received July 24, 1939)

It is shown that if we approximate to a liquid by an Einstein model, in which each atom has a restricted region of motion, wherein it moves independently of its neighbors, and is surrounded by coordination shells of other atoms; and if we denote the density distribution of the atoms by $\rho(r)$, where r is the radial distance from any given atom; then the contribution to $\rho(r)$ made by any coordination shell, e.g., the ith is a function $\rho_i(r)$ for which $r\rho_i(r)$ is symmetrical about its corresponding maximum value. The complete distribution curve, $r\rho(r)$ against r, is the sum of peaks of equal width and similar shape. A semi-empirical application of this theory to liquid sodium (a reapplication of C. N. Wall's theory) gives a latent heat of melting in fair agreement with experiment. The model suggests a change of structure on melting, since agreement with the experimental distribution curve is impossible if the number of atoms in the first coordination shell is that of solid sodium. It is also shown that if the parameters in a partition function developed in this way are chosen to give agreement with any one physical property, then it is incorrect to add to the partition function terms representing "communal entropy."

§1. INTRODUCTION

SEVERAL experimental papers have appeared recently publishing atomic distribution curves for liquids.[1] These curves, found from Fourier analyses of the intensity distributions in x-ray scattering photographs, show $\rho(r)$, or $4\pi r^2\rho(r)$, as a function of r. $4\pi r^2\rho(r)dr$ is proportional to the probability that two unspecified atoms of the liquid are distant r to $r+dr$ apart.

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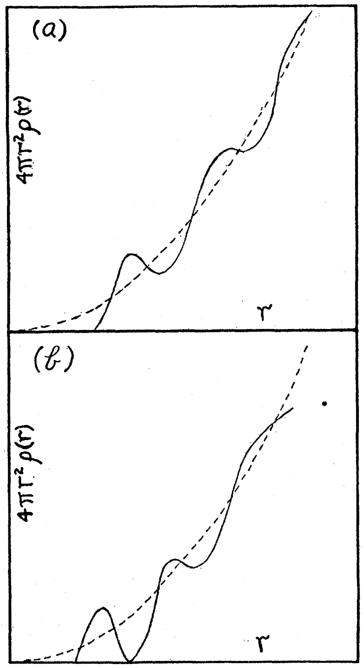
[1] (a) F. H. Trimble and N. S. Gingrich, Phys. Rev. **53**, 278 (1938); (b) C. D. Thomas and N. S. Gingrich, J. Chem. Phys. **6**, 411 (1938); (c) C. D. Thomas and N. S. Gingrich, J. Chem. Phys. **6**, 659 (1938); (d) J. Morgan and B. E. Warren, J. Chem. Phys. **6**, 666 (1938).



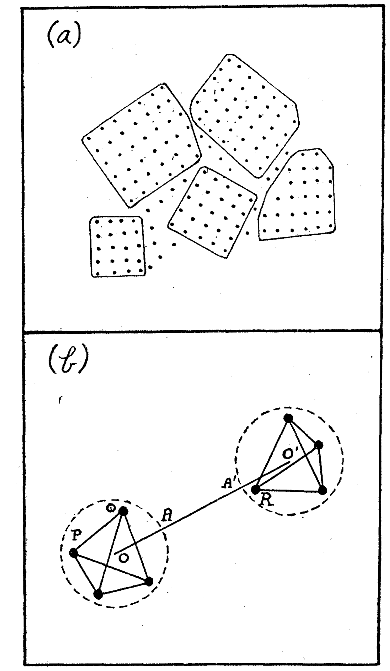


FIG. 1. (Left) Typical distribution curves for a liquid. (a) No structural units present. (b) With structural units.

FIG. 2. (Right) (a) Cybotactic groups in a liquid. (b) Structural units in liquid yellow phosphorus. From the experimental value of the density (found from the parabolas in Figs. 4 and 5 of Thomas and Gingrich's paper), i.e., $\rho_0^{-1}=29.1\ A^3$ at 48°C, and $=31.4\ A^3$ at 226°C, we can calculate an average distance apart for the centroids of two neighboring P_4 units. Since the data of Thomas and Gingrich suggest that each unit has a coordination of about 10, we have taken the mean of the results, which differ by only about 2 percent, found on the assumptions of body-centered and face-centered cubic packing. Thus the length OO′ is found to be 5.42A at 48°C, and 5.55A at 226°C. It is then clear that the first, second and third peaks in the figures of Thomas and Gingrich refer to the mean values of PQ, QR and PR. On account of valence saturation the atoms Q and R try to get as far apart as possible; this is why the distances AA', which are the shortest possible geometrically, do not occur in appreciable numbers.

In each case curves appropriate to various temperatures are given.

It is important to consider with what other experimentally determinable properties of the liquid we can correlate these curves; we may use either the shape of a single curve, the effect of a change of temperature on the curve, or relations between distribution curves for a family of substances such as the alkali metals. And the properties we deal with may be physical ones, e.g., density, viscosity, electrical resistance; or thermodynamic ones, e.g., entropy, vapor pressure, specific heat.

In this note we shall discuss the bearing of atomic distribution curves on the geometry of the atomic structure of a liquid, particularly in the neighborhood of the melting point, and the relation of this structure to the latent heat of melting ($L=T\Delta S$) which occurs at the phase change; incidentally this entails enquiry into the circumstances in which it is *relevant* to introduce the phrase "communal entropy." We shall be concerned mainly with the case of liquid sodium, for which C. N. Wall[2] has already given a theoretical discussion; indeed one object of this note is to reconsider Wall's application of his theory, for it seems to us that this can be done in a more satisfactory way.

§2. THE MEANING OF PEAKS IN A DISTRIBUTION CURVE

A typical distribution curve for a liquid, $4\pi r^2\rho(r)$ plotted against r, has peaks as shown in

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[2] C. N. Wall, Phys. Rev. **54**, 1062 (1938).

Fig. 1(a). The question arises whether these peaks have any meaning as far as the geometry of the structure of the liquid is concerned.

At temperatures just above the melting point the peaks are sufficiently sharp and characteristically shaped for it to be generally agreed that liquids have some sort of semi-crystalline structure.[3] In particular two types of atomic arrangement have been proposed; one being characterized by molecular homogeneity, i.e., all atoms are thought to be equivalent in the structure of the liquid,[4] and the other by the presence of cybotactic groups,[3] i.e., it is supposed that there are groups of atoms, probably of varying sizes and shapes, which have a more definite crystalline structure within them than the liquid has as a whole.

It is not, however, possible to decide, either from a single distribution curve, or from several curves for different temperatures, whether a liquid is molecularly homogeneous or consists mainly of small cybotactic groups, each containing less than, say, 2000 atoms: Fig. 2(a). For in the latter case the x-ray diffraction lines will be very much blurred by edge effects at the boundaries of the groups, irregularly spaced atoms between the groups and the unequalness of the spacings within the groups, due to their small linear dimensions. This blurring will make the distribution curve indistinguishable from that to be expected with a molecularly homogeneous liquid.

On the other hand, we could see from a distribution curve whether there were only large cybotactic structures, each containing more than about 2000 atoms;[5] for then the peaks would be quite sharp and separate from each other, approaching the lines we should get if we analyzed the intensity distribution in a powder photograph. We can also tell whether the atoms of the liquid form smaller groups, which we may call structural units, as, for example, with liquid yellow phosphorus in which the atoms are grouped, both in the liquid and in the vapor, as P_4 molecules. In this case the fact that the first peak is detached, $\rho(r)$ vanishing, or sensibly vanishing, between the first and second peaks, shows that there are structural units comparatively far apart from each other; Figs. 1(b) and 2(b). We shall indeed have valence saturation in each structural unit and therefore repulsion of any atom not in the same unit; see note under Fig. 2(b). The breadth of the first peak will be due to fluctuations in the atomic distances within the P_4 groups, as a result of vibrations, rotations and occasional collisions. If only a small fraction of the atoms are grouped in structural units, then the detached peak due to them will be masked and not separate from the rest of the atomic distribution curve.

On the assumption of molecular homogeneity the function $4\pi r^2\rho(r)$, which gives the distribution of interatomic distances in the liquid, will give the distribution of the distances of the atoms from any one particular atom. If, for clarity, we suppose that there are no small structural units, then according to Bernal[4] we can define round any atom first, second . . . coordination shells as in a crystalline solid except that now the atoms in these are distributed, somewhat randomly, about mean distances from the central atom. For the shells to be properly defined a suitable probability function for the distribution of the radial distances about the mean radii of the coordination shells ought to be prescribed. Bernal, following earlier work of Prins,[6] assumes a Gaussian distribution, so that in a shell of mean radius R_i, $\rho_i(r)\alpha \times\exp[-\lambda(r-R_i)^2]$. On the other hand, Wall finds that, to his approximation,[2] $r\rho_i(r)$ and not $\rho_i(r)$ or even $r^2\rho_i(r)$ is, for each shell, symmetrical about the mean radius. There seems to us to be insufficient experimental data for deciding between these three possibilities; we shall, however, show theoretically in the following paragraph that for any Einstein model of a liquid, $r\rho_i(r)$ for a single shell, is symmetrical about the mean radius of that shell. Wall's theory, which we are going to reapply to liquid sodium, is based on a particularly simple Einstein model.

An Einstein model is characterized by the assumption that each of the atoms of a substance

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[3] (a) P. Debye and H. Menke, Ergebnisse d. Tech. Röntgenkunde II, 1 (1931); (b) N. F. Mott and R. W. Gurney, *Reports on Progress in Physics* (Physical Society of London) **5**, 46 (1938).

[4] J. D. Bernal, Trans. Faraday Soc. **33**, 27 (1937).

[5] It is interesting in this connection that Riley, Chemistry and Industry **58**, 391 (1939) has been able to determine by use of x-rays the mean size of small graphite crystallites, which have about this limiting size.

[6] J. A. Prins, Physica **3**, 147 (1936).

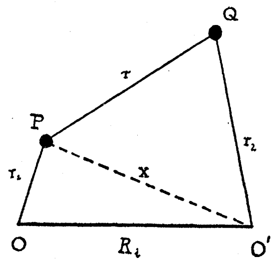

FIG. 3. Mean positions O and O' of the atoms P and Q.

moves independently of its neighbors, vibrating to and fro about a fixed center in some kind of average field which is determined by the rest of the substance. (See papers by Lennard-Jones and Devonshire.[7]) Thus, in Fig. 3, O and O' are the mean positions of two atoms P and Q. R_i, i.e., the length OO', is then the mean radius of the shell in which Q is found relative to P. We denote the average potential field in which each atom is assumed to move independently of its neighbors, by $\phi(s)$, and suppose that it is spherically symmetrical. Then the probability that P lies in a small volume element dV_1, distant $s=r_1$ from O, is proportional to $\exp[-\phi(r_1)/kT]dV_1$; similarly the probability that Q lies in dV_2, distant $s=r_2$ from O', is proportional to $\exp[-\phi(r_2)/kT]dV_2$. And in fact, the joint probability that P lies in dV_1 and Q in dV_2 is

$$\frac{1}{v^2}e^{-[\phi(r_1)+\phi(r_2)]/kT}dV_1dV_2, \tag{1}$$

where

$$v=\int e^{-\phi(r_1)/kT}dV_1=\int e^{-\phi(r_2)/kT}dV_2.$$

The probability that the length PQ lies between r and $r+dr$ is the integral of (1) taken over all those coordinates of P and Q for which $r\leqslant|PQ|\leqslant r+dr$: thus, if $\rho_i'(r)$ denotes the density contribution per atom in the ith coordination shell, it follows that

$$4\pi r^2\rho_i'(r)dr=\frac{1}{v^2}\int e^{-[\phi(r_1)+\phi(r_2)]/kT}dV_1dV_2,$$

subject to

$$r\leqslant|PQ|\leqslant r+dr.$$

Now if there are N_i atoms in the ith shell, $\rho_i(r)=N_i\rho_i'(r)$: further, if we denote the length $O'P$ by x, and angles about the lines R_i and x by χ_1 and χ_2, then we may write

$$dV_1=xr_1dxdr_1d\chi_1/R_i,\quad dV_2=rr_2drdr_2d\chi_2/x.$$

Introducing these results into (1), and taking the integration over dV_2 to precede that over dV_1, we find that

$$r\rho_i(r)=\frac{\pi N_i}{R_iv^2}\int_{r_1=0}^{\infty}\int_{x=|Ri-r_1|}^{Ri+r_1}\int_{r_2=|r-x|}^{r+x}r_1e^{-\phi(r_1)/kT}\cdot r_2e^{-\phi(r_2)/kT}\cdot dr_2dxdr_1.$$

Now owing to the shape of $\phi(s)$—see Fig. 1 of Lennard-Jones and Devonshire[7]—we can assume that there is a length σ such that $\phi(s)$ is effectively infinite for $s\geqslant\sigma$. The integration over r_2 gives a factor

$$\psi(r+x)-\psi(|r-x|),$$

where $\psi(t)=\int_0^t s\exp[-\phi(s)/kT]ds$. Now $r+x$ is necessarily greater than σ, and clearly $\psi(t)=\psi(\sigma)$ if $t\geqslant\sigma$, so this factor is equal to

$$\psi(\sigma)-\psi(|r-x|).$$

For the integration over r_1 also, only the range from $r_1=0$ to $r_1=\sigma$ is significant, and so we find

$$r\rho_i(r)=\frac{\pi N_i}{R_iv^2}\int_0^{\sigma}r_1e^{-\phi(r_1)/kT}\times\left[2r_1\psi(\sigma)-\int_{Ri-r_1}^{Ri+r_1}\psi(|r-x|)dx\right]dr_1. \tag{2}$$

This is a function of $|r-R_i|$ and vanishes if $|r-R_i|\geqslant 2\sigma$. It therefore represents a contribution to the total function $r\rho(r)$, in the form of a symmetrical peak with a spread at the base given by 4σ, i.e., independent of R_i, and therefore the same for each coordination shell. Wall's Eq. (10) is a particular example of our equation for the case in which $\phi(s)$ is constant for $s\leqslant\sigma$.

According then to Wall's theory, or to any theory based on an Einstein model for a liquid, $4\pi r\rho(r)$ is resoluble into peaks of equal width (4σ) and similar shape. We give below, Fig. 4(a), the result of an empirical attempt which we have made to separate into symmetrical peaks the curve for $4\pi r\rho(r)$ which pertains to the experimental data of Trimble and Gingrich[1a] for liquid

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[7] J. E. Lennard-Jones and A. F. Devonshire, Proc. Roy. Soc. **A163**, 53 (1937); **A165**, 1 (1938).

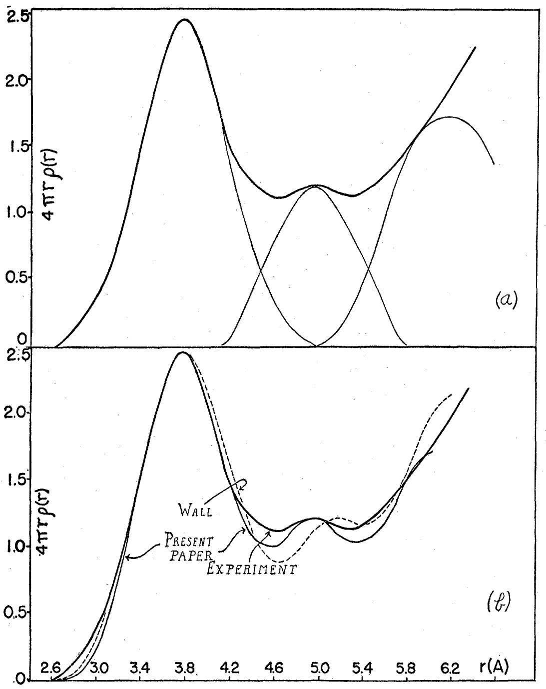

FIG. 4. Distribution curves for liquid sodium at 100°C. (a) Empirical separation into symmetrical peaks. (b) Comparison of predicted distribution curves with the experimental curve.

sodium at 100°C, and we see that the peaks are approximately of equal width and similar in shape. This is as satisfactory as we can reasonably expect, bearing in mind that the peaks are successively more sensitive to the precise shape of the first peak, i.e., to the position of its maximum and its form for small values of r, for which we cannot be certain of the experimental values.

The first two or three peaks do not overlap much and therefore may be supposed to correspond to coordination shells which have some physical meaning. But subsequently there is very considerable overlapping, and so there is little geometrical basis for assigning atoms, at these greater distances from the central atom, to definite coordination shells about that atom. This is even more the case at higher temperatures, and eventually the peaks can have little significance as far as the geometrical structure of the liquid is concerned; for whether this is interpreted in terms of coordination shells or small cybotactic groups, which will subdivide as the temperature is raised, it loses its significance as the structure of the liquid approaches that of a very imperfect gas.

In liquid sodium there will be no structural units other than atoms (or ions) and possibly a small percentage of diatomic molecules if the temperature is great enough. At 100°C, i.e., 2.4° above the melting point, we can ignore the possibility of the latter. We shall make the assumption, which in this case seems to us most reasonable, of molecular homogeneity, and interpret the peaks in the $4\pi r\rho(r)$ curve as corresponding to coordination shells. Unfortunately the small, 2.5 percent, volume change of sodium on melting does not rule out the possibility of cybotactic groups in the way that the comparatively large changes of -9 percent and 11 percent for water and argon, respectively, seem to do in those cases: for large volume changes must imply a radical change of structure, but small volume changes leave the question open.

§3. REAPPLICATION OF WALL'S THEORY TO LIQUID SODIUM AT 100°C

Wall's theory is based on the assumption that for each atom (or ion) of the liquid there is a sharply defined, spherical volume of radius σ, in which its center can move without increasing the potential energy of the liquid as a whole. This implies among other things, that the atoms (or ions) behave as hard rigid spheres. On this assumption Wall finds a theoretical form for the shape of an isolated peak, *viz*:

$$y \equiv 4\pi r\rho_i(r) = \frac{3N_i}{5\sigma R_i}\left\{1-\frac{5(R_i-r)^2}{4\sigma^2}\times\left[1-\frac{|R_i-r|}{2\sigma}+\frac{|R_i-r|^3}{40\sigma^3}\right]\right\}. \quad (3)$$

This depends on three unknown parameters σ, N_i and R_i. σ has been defined already; N_i is the number of atoms in the coordination shell corresponding to the peak for which R_i is the mean radius. To get the complete distribution curve, $4\pi r\rho(r)$ against r, it is necessary to add together the effects of successive peaks; σ will be the same for each of them but their N's and R's are further unknown parameters. Wall determines N_0, R_0 and σ, where N_0 and R_0 appertain to the first shell, by making the left-hand side of the first peak, $r \leqslant R_0$, coincide as closely as possible with the experimental curve. He then uses some semi-empirical calculations of Bernal[4] to find, from N_0 and R_0, the N's and R's which correspond to more distant shells. Knowing these, the complete distribution curve can be constructed, and Wall gets a curve which agrees fairly well, but by no means exactly, with the experimental one. Unfortunately, in drawing a curve through the experimental points a small, but quite definite, peak (strictly speaking the second), was smoothed out; this makes the agreement Wall has obtained (reference 2, Fig. 2) seem rather better than it really is.

Now the values of σ and N_0 found in this way are very sensitive to the precise shape of the first peak in the experimental curve. Moreover, we must not expect Wall's theoretical peaks to fit the experimental curve exactly, since that would imply that the atoms (or ions) behaved as rigid spheres. Finally it seemed to us better to try to test Bernal's formulae for N_i and R_i in terms of N_0 and R_0, rather than to assume them in the course of this theory. So to find σ and N_0, $N_1 \cdots$ we proceed rather differently.

An essential feature of Wall's theory, and indeed of any theory based on an Einstein model, is that, for any shell, N_i is proportional to $R_i Y_i$, where Y_i is the value of y in Eq. (3) which corresponds to $r = R_i$. We find the correct values of R_i and Y_i, for each peak, from our empirical resolution of the experimental distribution curve into separate peaks. We then determine N_0 and N_1 from the two conditions

$$N_0/N_1 = R_0 Y_0 / R_1 Y_1, \tag{4}$$

$$1 + N_0 + N_1/2 = 4/3 \cdot \pi \cdot R_1^3 \rho_0, \tag{5}$$

where ρ_0 is the density of the liquid in atoms per unit volume. We use the experimental value for sodium at 100°C,[8] which is $\rho_0 = 0.0247\text{A}^{-3}$. The first formula (4) is essential to Wall's theory and the second (5) is the result of assuming that if we take a small imaginary sphere of radius R_1 then it will enclose the same number of atoms wherever it be situated in the liquid. This is approximately true for a crystalline solid body, and we may suppose that it will be even more so for a liquid.

We find

$$R_0 = 3.78\text{A}, \quad R_1 = 4.96\text{A},$$
$$Y_0 = 2.45, \quad Y_1 = 1.21,$$

and with these values, (4) and (5) then give

$$N_0 = 8.78, \quad N_1 = 5.69.$$

The empirical resolution of the distribution curve into peaks, as shown in Fig. 4(a), suggests that the third peak is specified by $R_2 = 6.18\text{A}$, $Y_2 = 1.74$. But when we come to use Wall's formula to construct the curve theoretically, we find that we get a much better fit if we move the third peak a little to the left, and have $R_2 = 6.06\text{A}$, $Y_2 = 1.74$. This shift of R_2 lies within the uncertainties unavoidable in any graphical separation of the peaks. The formula $N_2/N_1 = R_2 Y_2 / R_1 Y_1$ then gives $N_2 = 10$. The results, are summarized in Table I. We give Wall's values for comparison. In Fig. 4(b) we show the distribution curve obtained on using our values for the parameters in Wall's theoretical formula. σ is given by $3N_0/5R_0 Y_0$ and is found to be 0.57, whereas Wall's value was 0.60. Wall's curve is shown by the broken line in Fig. 4(b).

We shall not give the details of a similar analysis of Trimble and Gingrich's experimental curve for liquid sodium at 400°C, because we do not suppose that, at that temperature, a resolution into peaks will have much meaning. The calculations give, at 400°C:

$$N_0 = 8.50, \quad N_1 = 6.81;$$
$$R_0 = 3.80, \quad R_1 = 5.14.$$

TABLE I. *Comparison of constants.*

	N_0	N_1	N_2	R_0	R_1	R_2	R_1/R_0	R_2/R_0	σ
Values; this note	8.78	5.69	10	3.78	4.96	6.06	1.31	1.60	0.57
Wall's values	9.28	6	13	3.79	5.1	6.2	1.34	1.63	0.60

Finally the entropy change on melting (ΔS) and the associated latent heat of fusion (L) are estimated as in Wall's paper; the results are shown in Table II.

§4. DISCUSSION OF THE RESULTS

We do not wish to attach any importance to the precise numerical values which we have found and given above; indeed it would be unreasonable to expect better agreement than that

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[8] E. Rinck, Ann. de Chemie **18**, 395 (1932).

TABLE II. *Melting of sodium.*

	$[\Delta S]$	L (KILOJOULES/MOL.)
Present paper	$0.747\,R$	2.31
Wall's paper	$0.906\,R$	2.8
Experimental	$0.861\,R$	2.65

shown in Table II from so simple a theory, but we believe that certain conclusions can, legitimately, be drawn from them.

In the first place, at 100°C, i.e., only 2.4° above the melting point, N_0 differs quite appreciably from its value, which is 8, for sodium in the solid state. The first two shells together contain nearly the same number of atoms (14.4) as in the solid state (14). We have tried to obtain a fit with the experimental curve on the assumption that $N_0=8$, but could not obtain even reasonably good agreement. We conclude therefore that there is quite a definite change of structure on melting. Moreover N_0 (400°C) is less than N_0 (100°C) while N_1 (400°C) is greater than N_1 (100°C), so that it appears that at higher temperatures the number of atoms in the second shell increases at the expense of those in the first. The liquid, then, does not tend to become close-packed at high temperatures.

Secondly, on comparing the predictions of Bernal's paper, i.e., that for $N_0=8.78$ we shall have $N_1=8$, $N_2=12$, $R_1/R_0=1.33$ and $R_2/R_0=1.63$, with the results of Table I, we find that Bernal's values for R_1/R_0 and R_2/R_0 are in good agreement with those we have found empirically; but his values for N_1, N_2 $\cdots$ are not those which we have found. The only agreement here is that if N_0, when in the neighborhood of 8, decreases, then N_1 increases. Bernal himself states that his estimates of successive N's are less reliable than those of successive values of R/R_0.

Next we observe that using the same N's and R's as in Table I, we could have got a better, and almost perfect, fit with the experimental curve if Wall's theoretical shape for a single peak had been rather fatter at the base. This would have been so if the atoms (or ions) had not been treated as hard spheres, with sharply defined free volumes, but their repulsive interactions had been taken into account, as in Lennard-Jones' picture of a liquid.[7] This is an essential defect of Wall's theory.

Finally, since our value for the latent heat of fusion is too low, we are led to enquire whether this also is due to the essential limitations of a model in which the atoms are treated as hard spheres, or whether it is due to our having neglected a communal-entropy term (see, in particular Lennard-Jones and Devonshire, 1938). We are driven to the former conclusion and end with a discussion of this point.

§5. THE MEANING OF COMMUNAL ENTROPY

The introduction of the notion of a free-volume for each atom of a liquid, in which, effectively, it can move without influencing the other atoms, at once elicits the idea of communal entropy.[9]

Free volume may be defined in two ways. We shall say that it is defined thermodynamically if it is defined purely formally from the partition function. The partition function $F(T, V, N)$ is supposed known (though in practice only approximations to it are known) as a function of T, V and N, where T is the temperature, V the volume and N the total number of atoms of the liquid; the thermodynamic free-volume v_{th}, is then defined by the equation:

$$F(T, V, N)=(2\pi mkT/h^2)^{3N/2}\cdot v_{\text{th}}{}^N, \qquad (6)$$

where m is the atomic mass, and the other symbols have their usual meanings.

On the other hand, we shall speak of the geometrical free-volume v_{geom} when we approximate to the liquid by an Einstein model. v_{geom} is then v of Eq. (1) and replaces v_{th} in Eq. (6). It has a well-defined meaning geometrically in the simple approximation in which it is supposed that each atom may be treated as a rigid sphere imprisoned in a cell whose size is fixed by the density of the liquid; this is the approximation on which Wall's theory is based.

If we restrict ourselves to Einstein models for liquids, v_{th} is an ideal quantity to which we try to approximate by assuming suitable forms for v_{geom} as a function of T, V and N. v_{th} is an

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[9] (a) O. K. Rice, J. Chem. Phys. **6**, 476 (1938); (b) R. W. Gurney and N. F. Mott, J. Chem. Phys. **6**, 222 (1938); (c) L. Tonks, Phys. Rev. **50**, 955 (1936).

average determined by all the positions of all the atoms of the liquid, though only those that are at all likely will count significantly. v_{geom}, in which each atom is confined to the neighborhood of a certain site, may then be too small, since by confining the atoms to particular regions of space, large fluctuations in the interatomic distances are ruled out; but it need not be too small because exact agreement with v_{th} may be obtained, at any one temperature, by suitable choice of the potential field ϕ. Of course it may not be possible to get a good approximation to v_{th} at all temperatures by choice of a potential field ϕ, which must depend explicitly only on the density and be otherwise independent of the temperature. For this reason an approximation to the partition function is sometimes made (e.g. Lennard-Jones and Devonshire, 1938) in which a reasonable form for ϕ is chosen, and then the resulting "Einstein" partition function is multiplied by another factor, frequently e^N, to take account of large fluctuations in the atomic distances. It is this extra factor which is called the communal entropy term and e^N is chosen because that is the difference which would be made to the partition function of a perfect gas of N molecules if its volume were to be subdivided into N equal cells and each molecule be confined to one cell. But of course the factor ought strictly to be temperature dependent and its nature must depend on the initial choice of ϕ.

Now at any temperature, the measurable properties of a liquid depend on all the possible positions of all the atoms of the liquid, and to predict them theoretically we must use a good approximation to v_{th}. If we include parameters in the potential field ϕ of v_{geom}—for example in Wall's case the radius of his spherical free volume—and so choose these that some physical properties of the liquid have their correct experimental values, then we are not at liberty still to include a communal entropy term in the partition function. If the resulting formulae do not give the correct experimental values of other measurable properties, this is because we do not have sufficient parameters in ϕ, i.e., to an essential limitation of the model used.

This is the case in the present instance. We have chosen σ in Wall's theoretical formula for an atomic distribution curve, Eq. (3), so as to get as good a fit as possible with a distribution curve found experimentally, and the fact that Wall's theory does not then give a good value for the entropy of melting is due, we suggest, not to omission of a communal entropy term—inclusion of which would mean that there were positional distributions of the atoms which affected the entropy but not the atomic distribution curve—but to the essential limitations of a model which treats the atoms (or ions) of the liquid as hard spheres.

The writers would like to acknowledge helpful discussion of the ideas in this paper with Mr. J. Corner.