

tion. The independently measured values of $\Delta\bar{H}_i$ for these components are plotted vs. mole fraction of cyclohexane in Figure 7. The area test shows them to be inconsistent and hence of uncertain accuracy. This test should always be applied to data of this sort.

NOTATION

f_i = fugacity of pure i at the T and p of the solution
 \bar{f}_i = fugacity of component i in solution
 G = an extensive property of a binary system on a mole basis

G_i = an extensive property of pure i on a mole basis
 I_0 = an intercept at $x_A = 0$
 I_1 = an intercept at $x_A = 1$
 x_i = mole fraction of component i in solution
 γ_i = activity coefficient of component i in solution = $\bar{f}_i/x_i f_i$
 Δ = designates a property change as a result of mixing at constant T and p
 E = an excess property (superscript)
 \sim placed over the symbol for an extensive property designates the molal property in solution, that is, the partial molal property

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The Molecular Structure of Liquids

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This survey presents a rather qualitative description of the present knowledge of liquid structure. The physical picture of this structure, which has been drawn from the interpretation of experimental data will be employed to explain and justify the theoretical methods necessary in the development of a more quantitatively reliable description of the liquid.

Understanding of liquids is much less complete than of the other states of matter. In the case of liquids there would appear to be no obvious element of simplicity comparable to the scarcity of molecular encounters in gases or of the small amplitudes of the thermal motions and high degree of spatial ordering in solids. Despite these difficulties an understanding of the liquid state is gradually emerging, and although knowledge is still far from complete, a qualitative and in some cases almost quantitative explanation of liquid behavior is within reach.

Simple nonassociated liquids of spherical, structureless molecules will be discussed. The interaction of two molecules will in this case depend only upon the distance between their centers. These interactions, together with the thermal motions of the molecules, are responsible for the changes in the physical state of matter that occur when the density and temperature are varied. Indeed it is the object of this survey clearly to describe the roles played by these two factors in the establishment of the detailed molecular structure of liquids.

In principle a precise description of the intermolecular forces can be determined by direct quantum mechanical calculations; however in all but the simplest cases the success of this approach

has been severely limited by mathematical difficulties. Therefore the interactions of most molecular species are actually obtained not from rigorous quantum mechanical arguments but from the semiempirical analysis of experimental data. An excellent account of these methods is included in the recent treatise of Hirschfelder, Curtiss, and Bird (1). Despite the many limitations, such methods give a fairly complete description of the intermolecular forces. Thus it is found that for small separations of the molecules these forces are of a strongly repulsive nature, suggesting the existence of a hard molecular core. When the intermolecular separation increases beyond the diameter of this rigid core, the forces between the two molecules become weakly attractive and tend rapidly to zero.

In liquids one is not usually concerned with the interaction of a single pair of molecules but rather with the potential energy of a molecule due to its simultaneous interactions with several of its neighbors. The total force upon such a molecule is assumed given by the vector sum of its individual and separate interactions with the others. Although the validity of this assumption is certainly suspect, very little information is presently available concerning the affects of nonadditive intermolecular forces upon the behavior of liquids. Moreover it is probably safe to say that the other approximations included in the existing theories of liquids are more serious in their consequences.

A DESCRIPTION OF LIQUID STRUCTURE

A precise microscopic description for the state of a liquid would include a

complete specification of the positions and motions for all the molecules. This description is not only complicated, but is wholly lacking in operational significance. One does not experimentally observe the behavior of separate molecules in the liquid but instead observes the heat capacity, thermal conductivity, viscosity, etc. Since these properties bear only a statistical relationship to the molecular-scale description of the liquid, real significance can be associated only with the average or most probable behavior of the molecules and not with a detailed specification of their individual motions. In principle this information can be determined directly from the methods of statistical mechanics; however in practice the success of the statistical approach will depend very largely upon the ability to ascribe a simple and at the same time realistic description to the average behavior of the molecules. Therefore attention is directed toward a qualitative description of liquid structure and the characterization of the molecular-scale processes responsible for the observed macroscopic properties of the liquid.

In the absence of a direct experimental procedure for obtaining this information one must construct a model of the liquid upon the basis of intuitive arguments, its success being judged by its ability to account for the physical properties of the liquid. The rules for constructing this model have changed very little since they were first announced in 1937 by Eyring and Hirschfelder (2).

In the search for a clue to the structure of liquids no single source of information has proved so valuable as the analysis of X-ray diffraction experiments. In these experiments one allows a monochromatic

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beam of X rays to fall upon the liquid and then measures the intensity of the scattered radiation as a function of the angle between the primary and secondary beams. The arrangement of the electrons in the liquid somewhat resembles a diffraction grating from which the X rays are scattered or deflected. More correctly this arrangement actually corresponds to two diffraction gratings, one with a spacing characterized by the distribution of the electrons within the individual molecules and another with the coarser spacing provided by the separations between neighboring molecules in the liquid. One may interpret the observed scattering of X rays by the liquid as the superposition of two separate interference patterns, one pertaining to the spatial arrangement of the molecules and the other to their internal electronic structures. Experimentally this decomposition of the diffraction pattern into its component parts can be accomplished by separate measurements upon the dilute vapor and the liquid itself. Thus as the density of the vapor is diminished, there will be a corresponding decrease in the interference of X rays scattered by different molecules. In the limit of infinite molecular dilution this sort of interference is completely absent, and the intensity of the scattered radiation depends upon the internal structure of the particular molecular species present and upon the variable, $s = (2/\lambda) \sin (\theta/2)$. Therefore by measurements upon the dilute vapor one can directly obtain that contribution to the diffraction pattern of a liquid which arises from the internal structures of the molecules.

The spatial arrangement or mutual disposition of the molecules may be formally described by the pair distribution function, defined as the probability that the distance between two molecules has the magnitude r . An alternative interpretation of this function is provided by the observation that $2\pi n^{(2)}(r)r^2 dr$ gives the number of molecular pairs per unit volume whose separations lie between r and $r + dr$. In terms of this function the intensity of radiation scattered by the liquid can be written as $J(s) = J_0(s) \cdot E(s)$, where

$$E(s) = 1 + n^{-1} \int_0^\infty [n^{(2)}(r) - n^2] \frac{\sin(sr)}{sr} 4\pi r^2 dr \quad (1)$$

In the limit of infinite dilution, correlations among the positions of the molecules vanish, and the pair distribution function approaches n^2 as a limit. The factor $E(s)$ then tends to a value of unity, and the experimental scattering is fully described by $J_0(s)$. In liquids $E(s)$ exhibits considerable departure from unity, an indication that the pair distribution function is no longer given by its

limiting value. This much can be immediately deduced from (1), but a direct evaluation of the pair distribution function from experimental determinations of $E(s)$ is desired. A way to accomplish this was first suggested by Debye, who found that by Fourier inversion of (1) the pair distribution function could be related to the experimental scattering data according to the relationship

$$n^{(2)}(r) = n^2 + \frac{n}{2\pi^2 r} \cdot \int_0^\infty [E(s) - 1] s \sin(sr) ds \quad (2)$$

Therefore by numerical integration of (2) one can construct the pair distribution function from the experimental values of $E(s)$. Curves of the radial distribution function $g(r) = n^{(2)}(r)/n^2$ ob-

shows that the location of the first peak in $g(r)$ practically coincides with that for the solid. Furthermore the very existence of these pronounced first peaks in $g(r)$ proves that a certain amount of local or short-range order persists even in the liquid. The broad and rather diffuse appearances of these peaks show that this local order is by no means so well defined as it is in the solid phase. A further distinction between the local structures of liquids and solids is to be found in the actual number of neighbors surrounding a particular molecule. By measuring the areas beneath the various peaks of $g(r)$, Eisenstein and Gingrich have calculated the occupancy of the first two shells of neighbors in liquid argon. Their results, obtained by measurements upon the curves of Figure 1, are presented in Table 1.

TABLE 1

°K.	First peak distance, Å	First peak occupancy	Second peak distance, Å	Second peak occupancy
(crystal)	3.82	12	5.4	(6)
84.4	3.79	10.5	5.3	
91.8	3.79	7	4.7	4
144.1	3.8	(4.2)	5.4	
149.3	4.5	6		
(vapor)	4.1	2		

tained in this manner are given in Figure 1. These curves describe the radial disposition of neighbors about a typical molecule in the liquid. The peaks in $g(r)$ indicate the most probable locations of these neighbors, and the integral $\int_{r_1}^{r_2} 2\pi n^2 g(r) r^2 dr$ gives the number lying within a spherical shell of radii r_1 and r_2 about the central molecule.

The indistinctness of all but the first of these peaks testifies to the absence in liquids of the long-range order or regularity characteristic of crystalline solids. Of course it is just the loss of this long-range order which is associated with the process of melting. The transition from the highly ordered arrangement in the solid to the less rigid, fluid structure of the liquid results from the disrupting effect of the molecular motions, since as the temperature of the solid rises past its melting point, the intermolecular forces responsible for the rigidity of the crystalline lattice must give way before the increasingly violent thermal motions of the molecules. Fusion occurs when the molecules occasionally acquire sufficient thermal energy to overcome the confining field of their neighbors and wander away from their former locations in the crystalline lattice.

Despite the translational freedom acquired upon melting, a molecule in the liquid will still find its motions severely restricted by the presence of neighboring molecules. The density of a solid and its melt usually differ so little that the mean distance between molecules must remain almost unchanged upon fusion. Figure 1

These data illustrate that even near the melting point (84°K.) the occupancy of the shells is somewhat less than in the solid. As the temperature is further elevated, the number of neighbors decreases progressively until, at the critical point (151°K.), the first shell is scarcely half full. Consequently the translational motions of the molecules will be less and less hindered as the temperature of the liquid rises. This accounts for the characteristic increase in the fluidity of liquids, which always accompanies a rise in temperature.

It seems quite unlikely that in liquids the geometrical disposition of the neighboring molecules should retain much evidence of the intricate lattice structure of the solid. In fact one may safely assume that the grosser molecular motions in the liquid will obliterate these finer geometrical features and give rise to a more or less spherically symmetrical distribution of neighbors about the central molecule.

This discussion suggests a cell-like description for the structure of the liquid. Thus for short intervals of time one may picture a molecule as trapped within a sort of shell-like arrangement of its neighbors. The thermal motions of the molecule will then be temporarily limited to oscillations about the center of the cell or cage to which it is confined. Of course the molecules are moving far too rapidly for this local structure to persist over the intervals of time required for the usual performance of experimental observations. The cellular

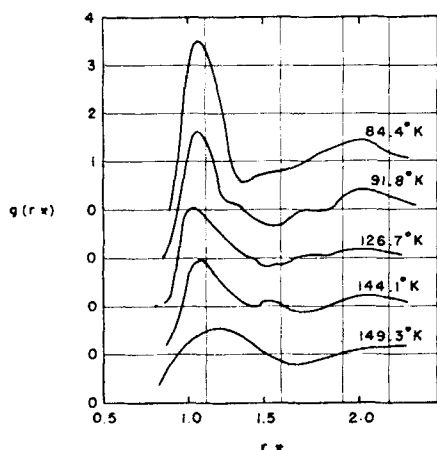


Fig. 1. Experimental curves of the radial distribution function in liquid argon. Curves are functions of the reduced distance $r^* = r/\sigma$, where $\sigma = 3.42$ Å. (33, 34). The vertical traces give the locations of the neighbors in solid argon.

description of liquids is therefore introduced only in the hope of providing a simple explanation for the average motions of the molecules and is not intended as a static description of the liquid structure. Thus the utility of this description will depend upon whether the cellular structure can maintain its identity over periods of time which are significantly longer than the interval between successive collisions of a molecule with its neighbors. (In liquids this interval is about 10^{-12} to 10^{-14} sec.) At first thought it might be imagined that each collision of the central molecule with one of its neighbors would result in the destruction of the local structure. This conclusion must be modified however because of the lagging response of the neighbors to the rapidly changing position of the central molecule. To find the cause for this viscous retardation of the molecular motions one need only observe that each neighbor to a particular molecule is itself surrounded by neighbors of its own. Therefore the dislodgment of a molecule from its position in a shell of neighbors is strongly resisted by the restraining actions of these other molecules. In this way the collective behavior of the molecular motions tends to stabilize briefly the cellular structure of the liquid. A major disruption of this local order will then occur only when a molecule finally accumulates, by repeated collisions with its neighbors, a sufficient excess of kinetic energy to overcome fully their confining influences. On the molecular scale of time mentioned above such a catastrophic event should occur rather infrequently, and even when it does the escaping molecule can proceed but a short distance through the liquid before its excess energy is lost and it once again lies trapped within a new shell of neighboring molecules.

From this discussion one sees that the

wanderings of the molecules, as they move from cell to cell throughout the liquid, closely resemble the random motions of Brownian particles. The validity of this conclusion has been established by the detailed theoretical analysis of Kirkwood (3), who, proceeding from a fundamental statistical approach, was able to show that the average motions of a molecule in the liquid are indeed governed by precisely the same dynamical equations that describe the Brownian motions of colloidal particles. He then demonstrated that this description of the molecular motions can be transformed into a theoretical method of obtaining the transport coefficients in liquids, that is the viscosity, thermal conductivity, and diffusion coefficients. It should be mentioned, that the essential success of this approach lends further support to this simple picture of the molecular-scale processes in liquids.

A simpler and less refined theory of irreversible processes in liquids has been suggested by Eyring (4). In his development the transport coefficients are calculated by a more direct appeal to the cellular structure of the liquid. As a brief illustration of Eyring's scheme the viscous flow resulting from the imposition of an external shear upon the fluid will be considered. In adjusting their motions to this shearing force the molecules must flow past one another. However a particular molecule can join in this flow only if it possesses an energy sufficient to escape from its cell of neighbors. From simple statistical arguments it is known that the probability that a molecule will have this much energy will be proportional to the Boltzmann factor, $\exp(-E/kT)$. This factor is in turn proportional to the actual number of molecules participating in the flow and hence to the fluidity of the liquid. Thus the resistance of the liquid to the impressed shear (the viscosity of the liquid) will vary as $\exp(E/kT)$. Experimentally it is found that the viscosity of most liquids is well represented by the empirical Andrade equation $\eta = A \cdot \exp(B/T)$, and so the qualitative realism of Eyring's simple arguments seems assured. The quantitative success of this theory does of course depend upon the accuracy with which one can predict the coefficients occurring in Andrade's equation. Although no truly satisfactory means of performing these calculations have yet been discovered, the qualitative predictions of this theory do offer strong evidence in favor of the cellular description for the liquid.

The remainder of this survey will be devoted to the determination of the thermodynamical behavior of liquids. For this purpose one is more interested in the average arrangements and environments of the molecules than in their grosser motions through the liquid. Thus the brief and rather infrequent transits of

the molecules from one cell to another should have very little influence upon the description of the average arrangement of the molecules in the liquid. To be sure the disorder arising from these random flights is responsible for the rather large entropy of the liquid, but in calculating the internal energy and equation of state one should be able to ignore these gross molecular displacements and limit his attention to the average potential energy of a molecule confined within its shell of neighbors.

THE THEORY OF LIQUIDS

In the previous section it was illustrated that the extent to which the individual molecules participate in the transfer of momentum, heat, and mass through the liquid will depend upon the average spatial arrangement of neighbors about these molecules. Thus any fundamental approach to transport phenomena should be based upon or include a complete description of the local structure in the liquid. The nonequilibrium conditions giving rise to transport phenomena result in distortions of this molecular structure, thereby introducing complications not present at thermodynamical and mechanical equilibrium. Accordingly it seems practical first to investigate the undistorted structure of a liquid at equilibrium, not only as a first step in the study of transport phenomena but also as a means of calculating the thermodynamical properties and equation of state for the liquid. Thus the remainder of the paper is a summary of the theoretical methods which have been developed to characterize the structure of liquids in equilibrium. These theoretical schemes fall into two categories: the first a direct attempt to calculate the pair distribution function and the other a more intuitive approach based upon previous cellular description of the liquid.

Both the thermal motions of the molecules and their interactions will certainly contribute to the thermodynamical description of the liquid. The effects stemming directly from the thermal motions are however so simple to calculate that one need really be concerned solely with the structural or configurational contributions arising from the molecular interactions. Thus from elementary considerations one knows that the average kinetic energy of a molecule will be $3kT/2$ and that the thermal motions alone provide a contribution of nkT to the static pressure of the liquid; the effects of thermal motions upon the other thermodynamical properties can be easily derived.

The method of the pair distribution function and the superposition principle

From the previous definition of $n^{(2)}(r)$ it follows that the average potential energy of a molecule is given by

$$n^{-1} \int_0^\infty \varphi(r) n^{(2)}(r) \cdot 2\pi r^2 dr$$

(These arguments are subject to the assumption of pair-additive molecular interactions mentioned in the introductory remarks.) Consequently the thermodynamical internal energy per molecule may be written as

$$u = 3kT/2 + 2\pi n \int_0^\infty \varphi(r) g(r) r^2 dr \quad (3)$$

In a similar manner the virial theorem of mechanics can be transformed into the equation of state

$$p = nkT - \frac{2\pi}{3} n^2 \int_0^\infty g(r) \frac{d\varphi(r)}{dr} r^3 dr \quad (4)$$

These two relationships, together with a similar expression for the chemical potential, provide a complete description of the thermodynamical behavior of the liquid in terms of the radial distribution function and the potential of the intermolecular forces. From this it might be concluded that the experimentally determined curves for $g(r)$ could be used to calculate the thermodynamical properties of the liquid. In practice this procedure is not too satisfactory, since the experimental measurements fail to possess the high degree of accuracy required for quantitative calculations.

An alternative scheme, involving the theoretical evaluation of $g(r)$, is one of the most ambitious and formidable objectives of the theory of liquids. [The requirements placed upon a quantitative theory of the radial distribution function are likely to be quite stringent since calculations based upon (3) and (4) are rather sensitive to minor variations in $g(r)$.] The development of such an exact theory has been prevented by enormous mathematical difficulties. Although exact integral equations for the pair distribution

function can be derived, these equations also involve $n^{(3)}(r_{12}, r_{13}, r_{23})$, the generalization of the pair distribution function to the case of three molecules; that is, $n^{(3)}$ is the probability that three molecules will be so located that their separations are given by r_{12} , r_{13} , and r_{23} . In turn the integral equation for $n^{(3)}$ includes the distribution function for a set of four molecules, etc., *ad infinitum*. An exact solution of this set of coupled integral equations is of course completely out of the question, and some approximate means of terminating the sequence must be invoked. The only approximation of this sort that has received serious attention is the so-called "superposition principle," which asserts that

$$\begin{aligned} n^{(3)}(r_{12}, r_{13}, r_{23}) \\ = n^{(2)}(r_{12}) \cdot n^{(2)}(r_{13}) \cdot n^{(2)}(r_{23}) / n^3 \end{aligned} \quad (5)$$

When this relationship is substituted into the equation coupling $n^{(3)}$ and $n^{(2)}$, an ordinary integral equation for the pair distribution function is obtained. However owing to the approximations involved in (5) the precise manner in which this substitution is to be effected cannot be uniquely specified. Thus use of the superposition principle has led to two different equations for the pair distribution function, one proposed by Kirkwood (5) and the other by Born, Green, and Yvon (6, 7). The two equations can be solved by numerical methods and their results used for the calculation of the thermodynamical properties of the liquid. The differences in the predictions of the two methods will then provide a crude measure of the error produced by the superposition principle. Extensive calculations based upon these equations have been carried out by Kirkwood and coworkers.

If the distance between molecules 1 and 2 is assigned the value r_{12} , one may then ask for the probability that a third molecule is so located that its separations from the first two are given by r_{13} and r_{23} , respectively. This conditional probability may be constructed from a knowledge of $n^{(3)}$ and $n^{(2)}$ and written in the form $n^{(3)}(r_{12}, r_{13}, r_{23}) / n \cdot n^{(2)}(r_{12})$. A geometrical illustration of the situation is provided by Figure 2, where the third molecule has been pictured as lying at the center of two concentric spheres of radii r_{13} and r_{23} .

According to the superposition principle one should assign equal probabilities to all arrangements of the three molecules, for which the first lies anywhere upon the sphere of radius r_{13} and the second anywhere upon the sphere of radius r_{23} . More precisely the conditional probability defined above is assumed to be independent of the value for r_{12} and given by the product of $n^{(2)}(r_{13})/n^2$ and $n^{(2)}(r_{23})$. This assumption is completely equivalent to replacing the conditional probability by its average over all ar-

rangements of the molecules for which the distances r_{13} and r_{23} are held fixed.

In the case of dilute gases this is a valid approximation, and its use leads to correct values for the second and third virial coefficients. Although this correct limiting behavior certainly lends an air of respectability to the approximation, it does not indicate the general validity of the superposition principle. Indeed direct calculations of the thermodynamical properties and equation of state for the liquid based upon this principle provide virtually the only means presently available for testing its validity. A rough estimate of its limit of applicability can be inferred however from the observation that the predicted expressions for the fourth and higher-order virial coefficients are only approximately correct.

Kirkwood, Maun, and Alder (8) have calculated the radial distribution function and the thermodynamical properties for a liquid composed of rigid spheres. Their results for the equation of state are shown in Figure 3, where $v_0 = \sigma^3/\sqrt{2}$ is the specific volume at closest packing of the spheres. The predictions of the Kirkwood and of the Born, Green, Yvon theories are scarcely distinguishable at the low densities for which the superposition principle is known to be valid; at higher densities the agreement is less satisfactory.

They found that at $v/v_0 = 1.24$ (or at $v/v_0 = 1.48$ for the Born, Green, Yvon theory) an abrupt change occurred in the analytical behavior of the radial distribution function. Kirkwood, Maun, and Alder interpreted this transition as evidence of a high-density limit of stability for the liquid phase. If this conclusion is correct, then for higher densities a crystalline phase should be more stable than the liquid. During the past few years there has been wide-spread disagreement concerning the physical significance of these results and the capability of a fluid of rigid spheres to crystallize. On the one side it has been argued that the phase transition predicted by the theory is of no real significance and occurs only because of the approximate nature of the superposition principle. However recent evidence indicates that such a transition really does occur. Thus by employing the Monte Carlo method (to be described later in the text) Wood and Jacobson (9) have experimentally confirmed the existence of a high-density phase transition in a fluid of rigid spheres. Their results, which are substantiated by the independent researches of Alder and Wainwright (10), indicate that there is a sharp discontinuity in the isotherms at a reduced volume of about $v/v_0 = 1.5$ (see Figure 4).

Calculations based upon a more realistic choice for the intermolecular forces have been performed by Kirkwood, Levinson, and Alder (11), who assumed that the interaction energy was given by

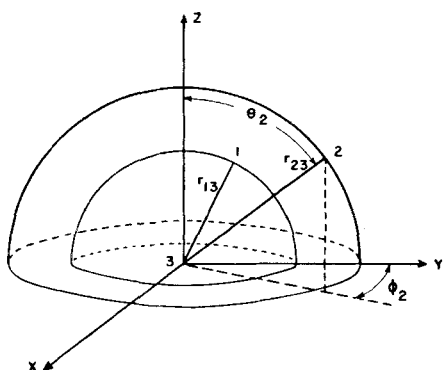


Fig. 2. A geometrical representation of the spatial configuration for three molecules. Molecule 3 has been chosen to lie at the origin of a Cartesian coordinate frame; the other two molecules are located on the surface of two spheres of radii r_{13} and r_{23} .

$$\varphi(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]; r \geq \sigma \quad (6)$$

$$+ \infty \quad ; r < \sigma$$

which for separations greater than the hard-core diameter reduces to the familiar Lennard-Jones 12-6 law. In Figure 5 the results of their calculations are compared with the experimentally determined radial distribution function in liquid argon.

In Figure 6 the experimentally determined equation of state for argon is compared with the theoretical predictions of Kirkwood, Levinson, and Alder. Although the agreement at low density is fairly good, it becomes very unsatisfactory at high densities. This behavior may well reflect the inadequacy of the superposition principle.

The qualitative successes of these calculations lead to the conclusion that, despite its many limitations, the principle of superposition gives a surprisingly realistic picture of the local molecular arrangement in liquids. This provides ample incentive for further investigations directed toward the discovery of an approximation which would retain the qualitative realism of the superposition principle and, at the same time, admit a higher degree of quantitative success. Although progress along these lines has been limited, the recent studies of Mazur and Oppenheim (12) may well result in such a discovery.

From this discussion one sees that the method of the radial distribution function is a formal mathematical approach to the theory of liquids, deriving little benefit from the qualitative considerations presented at the beginning of this survey. This suggests that in the absence of a thoroughly satisfactory theory of the radial distribution function efforts should be directed toward the development of a theory based upon a more direct appeal to an intuitive model for the liquid. This conclusion undoubtedly accounts for the numerous attempts in recent years to work improvements upon the so-called "cell" or "free-volume" theories of the liquid phase.

The cell theory of liquids

The cell theory of liquids stems from the pioneering studies of Eyring and

$$U_N = 3NkT/2 + \int_V \int_V \cdots \int_V \Phi_N$$

$$W_N d\tau_1 d\tau_2 \cdots d\tau_N \Big/ \int_V \int_V \cdots \int_V W_N d\tau_1 \cdots d\tau_N \quad (7)$$

$$= 3NkT/2 + kT^2(\partial \ln Q_N / \partial T)_V$$

Hirschfelder. Their investigations together with those of Lennard-Jones and Devonshire revealed that a fairly satisfactory theory could be developed from the simple and qualitative picture of liquid structure presented earlier in

this survey. However these early studies were based almost solely upon intuitive reasoning, and so it was not until 1950 that a rigorous mathematical justification of the cell theory was established. This important achievement by Kirkwood (13) has been instrumental in reviving interest in the cell theory of liquids. Thus during the past 6 or 7 years there have been several significant advances in the development of this method.

Since the modern adaptations of the cell method are all little more than elaborations upon Kirkwood's original approach, a brief review of his analysis will be given. To establish the relationship between this theoretical development and the previous qualitative arguments it becomes necessary to transform the intuitive description of liquid structure into a mathematical representation. As a first step in this direction a more quantitative description of the probability of a particular arrangement of the molecules in the liquid is established by associating with each molecular configuration the corresponding value for

$$\Phi_N = \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i=1}^N \varphi(r_{ij})$$

the total potential energy of the N molecules. The probability of a molecular configuration will then be proportional to the Boltzmann factor $W_N = \exp(-\Phi_N/kT)$ that is associated with that particular spatial arrangement. Hence the most probable dispositions of the molecules are those for which the total potential energy lies near its minimum value.

Now it is a further consequence of the statistical mechanics that each molecular configuration contributes to the thermodynamical description of the liquid only in proportion to its probability of occurrence. Thus the average potential energy will be given by

$$\frac{\int_V \int_V \cdots \int_V \Phi_N \cdot W_N d\tau_1 d\tau_2 \cdots d\tau_N}{\int_V \int_V \cdots \int_V W_N d\tau_1 d\tau_2 \cdots d\tau_N}$$

It then follows that the thermodynamical internal energy may be written as

$$Q_N = \frac{1}{N!} \int_V \int_V \cdots \int_V W_N$$

$$\cdot d\tau_1 d\tau_2 \cdots d\tau_N \quad (8)$$

is the so-called "configuration integral."

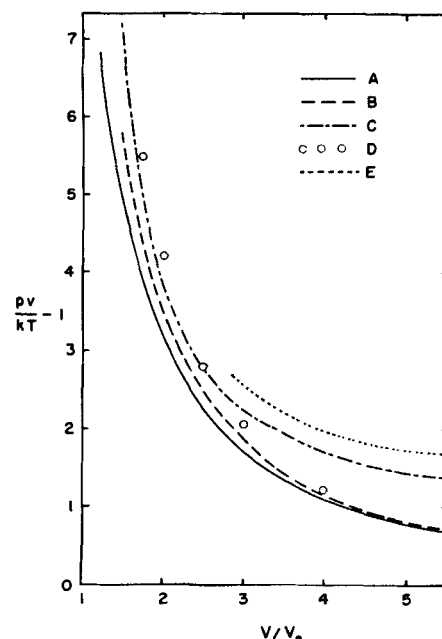


Fig. 3. Equation of state for rigid spheres: A, Kirkwood theory; B, Born, Green, Yvon theory; C, Lennard-Jones and Devonshire cell theory; D, Monte Carlo; E, cell-cluster theory (double-cell approximation).

By similar considerations it can be established that the other thermodynamical properties are functions of this same configuration integral; for instance the Helmholtz free energy or the work function is related to Q_N in the manner

$$A_N = 3NkT/2 \ln(h^2/2\pi mkT) - kT \ln Q_N \quad (9)$$

From this relationship one sees that the equation of state has the form

$$p = -(\partial A_N / \partial V)_T = kT(\partial \ln Q_N / \partial V)_T \quad (10)$$

These results illustrate the importance of Q_N in determining the thermodynamical properties of the liquid. If one should succeed in calculating this configuration integral, he would then possess a completely rigorous theory of the liquid. (Of course this would also be true if an exact value for the pair distribution function discussed previously could have been obtained.) Actually to perform the $3N$ -fold integration of Equation (8) is of course an impossible task, and one must therefore content himself with an approximate evaluation of this complicated integral. It is in the performance of this approximate calculation that the previous qualitative description of liquid structure can be of immense value. Thus one may hope to characterize intuitively those molecular arrangements that will make significant contributions to the configuration integral and to disregard those of minor importance.

Were the liquid frozen, then, since each molecule would be constrained to lie near

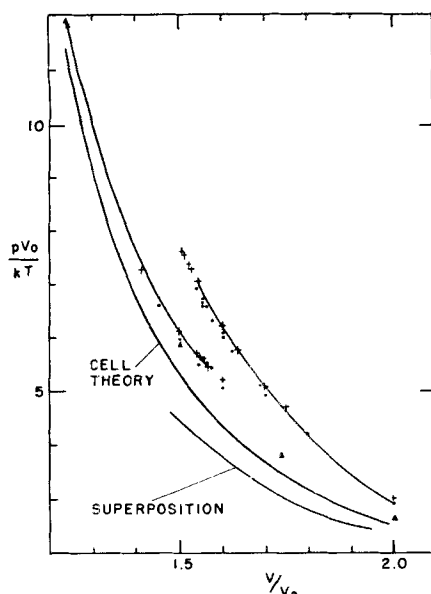


Fig. 4. Equation of state for rigid spheres. The unlabeled solid curve represents Alder and Wainwright's 108-molecule results; +, their 32 molecule results. ● and ▲ respectively represent the Wood and Jacobson and the Rosenbluth and Rosenbluth Monte Carlo results.

a particular site of the crystalline lattice, the volume of the system could be divided into N identical cells so arranged that the center of each is located at a site of the lattice. As the crystal is permitted to melt, one should expect that the local structure will retain a portion of its original identity, although to be sure the arrangement of neighboring molecules will lose much of its former rigidity. The more statistically favored arrangements of the molecules will certainly be those for which each cell is occupied by a single molecule. However one cannot completely exclude those configurations for which one or more cells are multiply occupied. It is the essence of Kirkwood's method to order these various arrangements according to their relative importance in determining the average structure of the liquid.

If the N cells are labeled $\Delta_1, \Delta_2, \dots, \Delta_N$, each integration involved in Equation (8) can be written as a sum of integrals extending over the individual cells; for example

$$\int_V d\tau_i = \sum_{h_i=1}^N \int_{\Delta_{h_i}} d\tau_i$$

The configuration integral may then be written as the sum of N^N terms corresponding to the N^N different ways of placing N molecules in N cells.

$$Q_N = (N!)^{-1} \sum_{h_1=1}^N \sum_{h_2=1}^N \cdots \sum_{h_N=1}^N \int_{\Delta_{h_1}} \int_{\Delta_{h_2}} \cdots \int_{\Delta_{h_N}} W_N \cdot d\tau_1 d\tau_2 \cdots d\tau_N \quad (11)$$

Each term in this multiple summation may be characterized by the number of molecules assigned to the individual cells. Thus a typical term is labeled $Q_N(m_1, m_2, \dots, m_N)$. Since the total number of molecules is N , each set of occupation numbers $\{m\} = (m_1, m_2, \dots, m_N)$ will be subject to the condition $N = \sum_i m_i$. Furthermore because the molecules are indistinguishable from one another, there will generally be several terms in (11), each of which corresponds to the same set of occupation numbers. In fact it is not difficult to show that for a given set m_1, m_2, \dots, m_N there will be precisely $N! / \prod_i m_i!$ equivalent terms in (11). Consequently one may rewrite this expression

$$Q_N = \frac{\sum_{\{m\}} Q_N(m_1, m_2, \dots, m_N)}{(\prod_i m_i!)} = \bar{\sigma}^N Q_N^{(1)} \quad (12)$$

where

$$Q_N^{(1)} = Q_N(1, 1, \dots, 1) \quad (13)$$

and

$$\bar{\sigma}^N = \sum_{\{m\}} (\prod_i m_i!)^{-1} \cdot Q_N(m_1, m_2, \dots, m_N) / Q_N^{(1)} \quad (14)$$

The function $Q_N^{(1)}$ describes the most important contribution to the configuration integral, namely the molecular arrangement for which each cell is singly occupied. The term $\bar{\sigma}^N$ represents the effects due to the other less probable configurations of the molecules. At very high densities the repulsive forces between the molecules eliminate the possibility of multiply occupied cells, and so only the configuration $\{m\} = (1, 1, \dots, 1)$ can contribute to the summation in (14). In this limit $\bar{\sigma}$ becomes equal to unity. On the other hand in the limit of infinite dilution the cells grow so large that all occupancies occur with equal probability. Furthermore in this limit each of the

entropy. It is therefore quite obvious that $\bar{\sigma}$ provides an index to the degree of order present in the system. Since it was this same molecular disorder which was previously associated with the Brownian motions of the molecules, it follows that $\bar{\sigma}$ will also describe the ease with which the molecules move from cell to cell within the liquid.

$\bar{\sigma}$ is a slowly varying function of density, rising monotonically from a value of unity in the crystal to a value $e \approx 2.7$ at infinite molecular dilution; moreover, $\bar{\sigma}$ probably will have an equally weak dependence upon the temperature. Therefore this function should be of little importance in determining the equation of state or the internal energy of the liquid. [From Equations (7) and (10) one sees that p and U_N depend only upon the derivatives of $\bar{\sigma}$ with respect to density and temperature.] One may thus conclude that it is $Q_N^{(1)}$ which will be principally responsible for these properties of the liquid. This conclusion provides a theoretical justification for the previous characterization of the most probable molecular arrangements in the liquid. Except in the calculation of the entropy one may confine his attention to those configurations for which each cell is singly occupied. It is only when the entropy is calculated that the possibility of multiply occupied cells must be considered. At liquid densities one is almost certain that there will be little contribution to the summation in (14) from cells that are more than doubly occupied. Owing to this simplification the calculation of $\bar{\sigma}$ for liquids is by no means an impossible task. Although no truly adequate calculations have yet been performed, the exploratory work of Pople (14) has been very useful in obtaining a qualitative estimate for the behavior of $\bar{\sigma}$. By employing several approximations he found that for a liquid composed of rigid sphere molecules this factor depends upon density in the manner shown by Table 2.

TABLE 2. THE DENSITY DEPENDENCE OF THE DISORDER PARAMETER IN A LIQUID OF RIGID SPHERES

v/v_0	1.000	4.887	7.761	10.0	15.0	20.0	$+\infty$
$\bar{\sigma}$	(1.000)	1.04	1.34	1.57	1.86	1.99	(2.414)

$Q_N(m_1, m_2, \dots, m_N)$ separately approaches a value of v^N . Therefore

$$\bar{\sigma}^N = \sum_{\{m\}} (\prod_i m_i!)^{-1} = e^N$$

and $\bar{\sigma}$ has the limiting value of e .

The contribution of $\bar{\sigma}$ to the entropy of the liquid is given by $Nk \ln \bar{\sigma}$. In the limit of high density the molecules are rigidly confined within their cells, and this entropy contribution vanishes. At infinite dilution, however, the molecules are completely free to lie anywhere within their container, and $\bar{\sigma}$ makes a contribution of $Nk = R$ e.u./mole to the

It should be mentioned that in place of the correct value $e \approx 2.7$ these calculations predict a low density limit of $\bar{\sigma} \approx 2.414$. This error is not very significant however and simply reflects the neglect of cells which are occupied by three or more molecules. It is much more interesting to see that $\bar{\sigma}$ remains very near unity until the specific volume becomes about five times that for the close-packed lattice. Thus Pople concluded that the entropy contribution $Nk \ln \bar{\sigma}$ will be practically zero for the liquid. It seems quite probable that a similar behavior would be observed for more realis-

tic choices of the intermolecular forces. In the absence of any contrary proof one may accept this conclusion and assume that $\bar{\sigma}$ maintains an almost constant value of unity throughout the entire range of liquid densities.

To calculate $Q_N^{(1)}$ one must carry out the integration of Equation (8) subject to the condition that each cell contains but one molecule. To perform this calculation exactly would be almost as difficult as the direct evaluation of the configuration integral itself. However one is guided by symmetry arguments and intuitive reasoning to envision a rather simple picture of the situation. Since each molecule is subject to precisely the same environmental conditions, a description of the situation within one particular cell should be equally applicable to any other. Although this is not meant to imply that the positions of molecules in adjacent cells are independent of one another, it does suggest the probability distribution may be chosen to be the same in each cell of the liquid. The simplest but by no means the only way in which this statement can be mathematically formulated is to assume that the probability distribution function inside the i th cell depends only upon the coordinates of the molecule confined within it. Thus Kirkwood suggested that the probability distribution function within a cell be represented by a function which depends only upon the vector displacement of a molecule from the center of its cell. Since each molecule lies within a single cell, this function must satisfy the normalization condition $\int_{\Delta} s(\mathbf{r}) d\tau = 1$. This assumption closely resembles the superposition principle. Thus the probability for the indicated configuration of molecules 1 and 2 should be proportional to $n^{(2)}(r_{12})$; however this probability is taken to be $s(\mathbf{r}_1) \cdot s(\mathbf{r}_2)$. As in the case of the superposition principle the adequacy of such an approximation can be judged only by its success in accounting for the observed physical properties of the liquid.

In accordance with this approximation the average potential energy of molecule 1 due to its interactions with all the others is

$$\Phi(\mathbf{r}_1) = \sum_{j \neq 1}^N \int_{\Delta_j} s(\mathbf{r}_j) \varphi(r_{1j}) d\tau_j \quad (15)$$

Furthermore all the thermodynamical properties can be expressed as integrals of $s(\mathbf{r})$, that is as functionals of $s(\mathbf{r})$. For instance the configurational contributions to the entropy and internal energy are

$$S_N^{(1)} = -Nk \int_{\Delta} s(\mathbf{r}) \ln s(\mathbf{r}) d\tau \quad (16)$$

$$\begin{aligned} U_N^{(1)} &= (N/2) \int_{\Delta} s(\mathbf{r}) \Phi(\mathbf{r}) d\tau \\ &= (N/2) \cdot U_0(v, T) \end{aligned} \quad (17)$$

where terms involving $\bar{\sigma}$ have not been included.

To calculate the values of these thermodynamical properties one must first prescribe the function $s(\mathbf{r})$. The better the choice of this function, the better will be the resulting description of the liquid. However since correlations among the

positions of the molecules have been neglected, no choice of this function can ever give an exact description of the molecular arrangement characterizing the equilibrium state of the liquid. Thus each function $s(\mathbf{r})$ must necessarily describe a nonequilibrium state of the system, and from the principles of thermodynamics one knows that the degree to which a particular state of the system departs from equilibrium is reflected by the corresponding value for the Helmholtz free energy. The nearer the system lies to thermodynamical equilibrium, the lower will be the associated value of this free energy. Therefore the optimum choice for the distribution function should be that for which the Helmholtz free energy is a minimum. When this minimization is actually carried out, one finds that the optimum function is given by the solution to the integral equation,

$$s(\mathbf{r}) = v_f^{-1} \cdot \exp(-\psi(\mathbf{r})/kT) \quad (18)$$

where $\psi(\mathbf{r}) = \Phi(\mathbf{r}) - U_0(v, T)$ and v_f is defined by

$$v_f = \int_{\Delta} \exp(-\psi(\mathbf{r})/kT) d\tau \quad (19)$$

Until very recently solutions for the integral Equation (18) had been demonstrated in only two instances: for rigid spheres and for molecules bound to one another by harmonic forces. In the case of rigid spheres, each of diameter σ , if the lattice chosen for the calculations is taken to be the face-centered cubic arrangement, the unit cells will be dodecahedrons of v , and the distance between neighboring sites will be d_0 , where $d_0^3 = \sqrt{2}v$. Wood (15) has shown that the solution to the integral equation may then be written as

$$\begin{aligned} s(\mathbf{r}) &= v_f^{-1}, \text{ if } \mathbf{r} \text{ lies within } \Delta' \\ &0, \text{ if } \mathbf{r} \text{ lies outside } \Delta' \end{aligned} \quad (20)$$

where Δ' is a dodecahedron of altitude $(d_0 - \sigma/2)$. V_f is then just the volume of this smaller dodecahedron, and the equation of state is given by

$$pv/kT = (1 - \sigma/d_0)^{-1} \quad (21)$$

This equation of state has been plotted in Figure 3, where it is compared with

that derived by the method of the pair distribution function. Although the shapes of the curves are similar in the two cases, the cell theory predicts larger values for the compressibility factor pv/kT .

If the molecular interactions are of the harmonic type $\varphi(r) = A + Br^2$, the solution to (18) is

$$s(\mathbf{r}_i) = \frac{\exp\left(-B \sum_{j \neq i}^N (\mathbf{r}_{1j} - \mathbf{r}_i)^2/kT\right)}{\int_{\Delta_i} \exp\left(-B \sum_{j \neq i}^N (\mathbf{r}_{1j} - \mathbf{r}_i)^2/kT\right) d\tau_i} \quad (22)$$

This distribution function is a Gaussian of the type which is associated with the situation in crystalline solids, and thus despite its relative simplicity it should be of little significance in the studies of the liquid. To obtain results of some consequence Equation (18) must be solved for a more realistic choice of the interaction potential.

In accordance with the Kirkwood version of the cell theory a molecule will be surrounded by its neighbors in the manner illustrated by Figure 7a; that is, this method implies that the local geometrical structure in the liquid is the same as that in a crystal. However it has been mentioned previously that there is no evidence for such a lattice structure in liquids, and in fact the previous qualitative arguments suggest that the average arrangement of the neighbors would form an almost spherical shell about a molecule. Thus the large amplitudes of the thermal motions in a liquid would smear the arrangement of neighbors into a structure resembling that of Figure 7b.

On the basis of this argument there would seem to be an excellent physical justification for suppressing the dependence of $s(\mathbf{r})$ and $\Phi(\mathbf{r})$ upon the lattice geometry. Accordingly it is reasonable to assume that the cell-distribution function depends only upon the value of the radial coordinate $r = |\mathbf{r}|$. Furthermore the physical description of the situation strongly suggests that the average potential field within a cell should be defined as the angle-averaged value of $\Phi(\mathbf{r})$, that is by the function

$$\begin{aligned} \Phi(r) &= (4\pi)^{-1} \\ &\cdot \int_0^{2\pi} \int_0^\pi \Phi(\mathbf{r}) \sin \theta d\theta d\phi \end{aligned} \quad (23)$$

Other definitions for the average cell potential have been considered by Dahler, Hirschfelder, and Thacher (16).

Employing the same arguments as before, one finds that the optimum spherically symmetrized cell-distribution function is given by the solution of the integral equation

$$s(r) = \bar{v}_f^{-1} \exp(-\psi(r)/kT) \quad (24)$$

where $\psi(r)$ is completely analogous to $\psi(\mathbf{r})$, and the spherical free volume is

$$\bar{v}_f = 4\pi \int_0^{r_0} \exp(-\psi(r)/kT) r^2 dr \quad (25)$$

The volume of this spherical cell is usually somewhat less than the specific volume, since otherwise adjacent cells will overlap one another. In accordance with these definitions (23) is given explicitly by

$$\Phi(r_1) = \pi \sum_{n=1} c_n \cdot \int_0^\pi \int_0^\pi \int_0^{r_0} s(r_n) \varphi(r_{1n}) r_n^2 \cdot \sin \theta_1 \sin \theta_n dr_n d\theta_1 d\theta_n \quad (26)$$

Figure 8 provides an illustration of the coordinates involved in these multiple integrations.

For rigid spheres the solution to this new integral equation retains the form given by (20), where Δ' is here a *sphere* of radius $(d_0 - \sigma)/2$. Although the value for the free volume is larger by a factor of 1.35 than in previous considerations, the equation of state is unchanged.

For the harmonic interaction $\varphi(r) = A' + B'(r - a)^2$ the cell-distribution function is given by the simple Gaussian $s(r) = \bar{v}_f^{-1} \exp(-Cr^2/kT)$, where

$$\bar{v}_f = 4\pi \int_0^{r_0} \exp(-Cr^2/kT) r^2 dr$$

and C depends only upon d_0 , a , and B . All the thermodynamical properties may therefore be expressed in terms of the tabulated incomplete gamma function.

For a more realistic choice of the intermolecular forces Equation (24) must be solved by numerical methods. At the time of this writing extensive calculations based upon the Lennard-Jones 12-6

These calculations have revealed that the theoretical isotherms for pv/kT vs. v consistently lie below the experimental curves, and although the differences between theory and experiment are considerably lessened by the introduction of holes or empty cells, the final results are by no means so satisfactory as one should like. It is believed that a thorough analysis and interpretation of these results will lead to a better understanding of the cell theories and suggest means for their improvement.

Early theories based upon the cell model involved no such elaborate calculations as those outlined above. Instead they employed various approximations to estimate the behavior of the cell distribution function and of the potential field within a cell. An outstanding feature of Kirkwood's approach is the relationship it reveals between these approximations and the solutions to the integral Equation (24). For instance the method of Lennard-Jones and Devonshire (18) corresponds to a very unsymmetrical approximation in which the neighbors are treated on a different par from the molecules within the cells. Thus in their calculation of the cell potential the neighbors were assumed to lie upon the surface of a spherical shell of radius $d_0 = |R_{12}|$, and so Equation (26) was replaced by the approximate expression

$$\Phi(r_1)_{LJD} = (c_1/2) \cdot \int_0^\pi \varphi(\sqrt{(r_1 - R_{12})^2}) \sin \theta_1 d\theta_1 \quad (27)$$

Inserting this approximation into Equations (24) and (25), one obtains the Lennard-Jones and Devonshire estimate for the cell distribution function,

$$s(r)_{LDJ} = \exp(-\Phi(r)_{LDJ}/kT) / 4\pi \int_0^{r_0} \exp(-\Phi(x)_{LDJ}/kT) x^2 dx \quad (28)$$

interaction [Equation (6)] are nearing completion (17). To simplify these calculations it has been assumed that one may neglect the second and further removed shells of neighbors in determining the cell distribution function. The effect of this approximation is to confine the motions of the molecules to the vicinity of their lattice sites somewhat more than would otherwise be the case. The validity of this last assertion is confirmed by the observation that the second and further removed neighbors always lie separated from the central molecule by distances in excess of the range for the repulsive interactions. Although this same assumption can not be employed in the calculation of the internal energy and of the equation of state, the contributions to these quantities that arise from the second and further removed shells do not depend so critically upon the exact form of $s(r)$. Therefore one is presumably justified in using less rigorous methods to evaluate these contributions (32, 17).

This may be considered as the first step in an iterative solution to Equation (24). The next step in this procedure would be to recalculate the cell potential by inserting $s(r)_{LDJ}$ into Equation (26) and thereby obtaining a second approximation to the cell distribution function. Higher-order approximations are simply obtained by successive repetitions of this process. In fact it is just this sort of scheme which has been employed in the numerical solution of the integral equation (17).

Despite the approximate nature of the Lennard-Jones and Devonshire method it has been remarkably successful in predicting the qualitative behavior of liquids. For rigid spheres the *LJD* cell distribution function is of the form given by Equation (20). However the free volume is now much larger than in either of the previous calculations, being eight times greater than the value predicted by the exact solution of Equation (24). The equation of state is unaffected by this difference and given by (21). In their

original presentation Lennard-Jones and Devonshire applied this method to the 12-6 interaction, and a considerable extension of their calculations has since been conducted by Wentorf, Buehler, Hirschfelder, and Curtiss (19). The equation of state is included in Figure 6, but another, more useful illustration is provided by Figure 10. Generally it is found that at very high densities the Lennard-Jones and Devonshire theory is more successful than that of the superposition principle; however at low densities the cell model becomes physically unrealistic and the predictions of this theory become very unsatisfactory. It is just at these low densities that the method of the superposition principle has proved most successful, and so the two schemes have a sort of complementary relationship to one another.

As yet no theory has been devised which is truly applicable over the entire range of liquid and vapor densities. Although numerous extensions of the cell method have been proposed in an effort to achieve such a theory, the results have not been outstanding. Nevertheless these schemes have been very instructive in providing a superior theoretical description of the liquid itself. Most significant among these advances is the development of the so-called "hole theory." From the evidence provided by the experimentally determined radial-distribution function one knows that the number of nearest neighbors to a molecule is progressively lessened as the density of the liquid decreases. However the average distance from the central molecule to these neighbors changes very little with variations in the density. When this information is compared with the picture provided by the cell theory of Kirkwood, attention may be confined in the range of liquid densities to those configurations for which each cell is singly occupied. As the density of the liquid is decreased, the size of these cells and hence the distance from the central molecule to its neighbors steadily increases. However the actual number of neighbors remains unaltered and is taken to the coordination number of the crystalline lattice. Thus in contrast to the experimental evidence of Figure 1 (and Table 1) the cell theory predicts that with decreasing density the curves of $g(r)$ should exhibit a progressive radial displacement and that the area under the first peak (and all the others) should remain unaltered.*

To correct this unrealistic behavior Eyring and Cernuschi (20) introduced "holes," or unoccupied cells, into their description of the liquid. According to their model, an expansion of the liquid produces an increase in the number of these holes but leaves the volume of an

*The precise mathematical relationship between $g(r)$ and the cell-distribution function has recently been established (21). Calculations based upon this relationship are in agreement with the qualitative description of the situation presented in this paper.

individual cell almost unaltered. Thus the volume of a cell is taken to be $w = V/L = xv$, where $x = N/L$. If one employs the spherical approximation previously discussed, the radius of a cell will be $r_0' = (x)^{1/3}r_0$.

Thus while the cell theory depends upon the production of multiply occupied cells to account for the increased disorder at low densities, the hole theory explains this disorder in terms of an increased number of cells. There is of course an intrinsic disorder associated with the $L!/N!(L-N)!$ different ways in which the N molecules may be distributed among the $L \geq N$ cells. In the absence of holes only one such arrangement is possible, but with increasing dilution more holes appear and the number of possible arrangements approaches a limiting value of e^N .^{*} Thus the factor $L!/N!(L-N)!$ rises monotonically from a value of unity in the crystal (no holes) to a value of e^N in the limit of infinite dilution (infinite number of holes). Although this is precisely the behavior of the function $\bar{\sigma}^N$, occurring in the theory of Kirkwood, there is certainly no reason for these two quantities to be equal over the entire density range.

Mayer and Careri (22) have shown how this hole model of the liquid can be combined with Kirkwood's method of determining the cell-distribution function. Using their approach one can derive an integral equation for the cell distribution function that has precisely the same form as Equation (24). Of course this function, the cell potential, and the free volume will now exhibit a parametric dependence upon the number of holes present in the liquid. The analytical nature of this dependence is very simple however, and the results of this hole theory are obtained from Equations (24), (25), and (26) by replacing the absolute temperature by T/γ and the specific volume by the cell volume $w = xv$. Thus at first it would appear that the introduction of holes necessitates no calculations beyond those already involved in the ordinary cell theory. Actually several complications arise. The dependence of γ upon the number of holes must be determined. If the holes and molecules were distributed randomly among the cells, then γ would be equal to $x = N/L$. However this is not the case, since just as in a binary solution there will be different *a priori* probabilities for the cells neighboring a molecule to be occupied by other molecules or by holes. This same problem is encountered in the study of all physical systems which exhibit so-called "order-disorder phenomena," and although no exact solution of this problem has yet been found, several satisfactory approxi-

mation schemes are available (23, 24, 25).

There remains only the problem of choosing the correct number of holes.

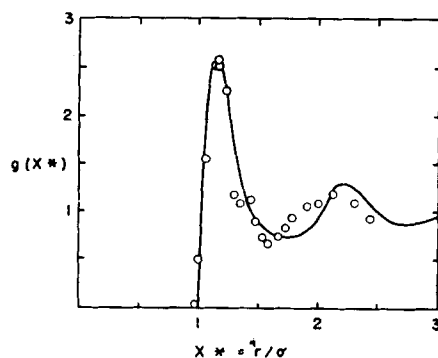


Fig. 5. A comparison of experimental and theoretical radial distribution functions for liquid argon at 91.8°K. and 1.8 atm. The experimental values are those of Eisenstein and Gingrich.

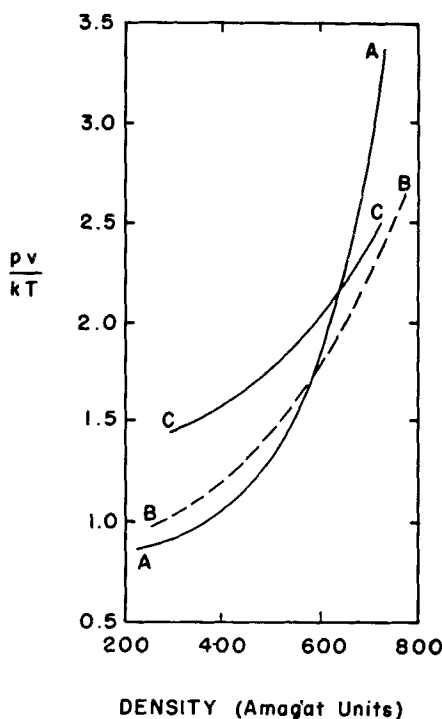


Fig. 6. A comparison of experimental and theoretical equations of state for argon at 273°K.: A, experimental values of (35); B, radial distribution function method; C, cell theory (11).

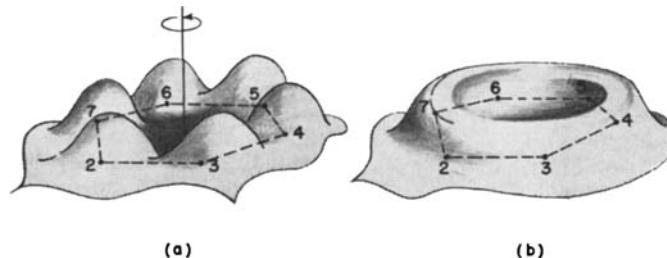


Fig. 7. A schematic representation for the distribution of neighbors about a cell in a two-dimensional hexagonal lattice. The location of the central site is labeled by 1; those of the neighbors by 2, 3, . . . , 7. These contours illustrate the arrangement of the neighboring molecules in (a) the crystalline form and (b) the smeared or angle-averaged approximation.

^{*}From Stirling's approximation $m! \approx (m/e)^m$ it follows that $L!/N!(L-N)! \approx (1 + 1/y)^N y^N$, where $y = (1 - x)/x$ and $x = N/L$. Then since $\lim_{y \rightarrow \infty} (1 + 1/y)^y = e$, the validity of this assertion is established.

will not be too serious, since the theory is constructed in such a manner that the larger clusters are significant only when the molecular disorder becomes quite pronounced. In fact clusters of two cells should introduce corrections comparable to those arising from the doubly occupied cells in Kirkwood's theory. There are however great differences between the usual cell theory and deBoer's formulation of the cell-cluster method. For example when clusters of two or more cells are neglected, his theory reduces directly to that of Lennard-Jones and Devonshire. Thus the double-cell contributions provide the only means by which this method can improve upon a rather crude first approximation, that is the Lennard-Jones and Devonshire theory. Although these double cells do provide an adequate estimate of the entropy of the liquid (27, 28), they are by no means so successful in explaining the equation of state. Thus from Figure 3 one sees that the inclusion of double cells actually leads to an equation of state for rigid spheres which is less satisfactory than that of the simple *LJD* method. (It will subsequently be shown that the *Monte Carlo* isotherm of Figure 3 is the most realistic.) This suggests that the principal drawback of the cell-cluster theory is its reliance upon a rather unrealistic first approximation. Thus one really should employ the best possible cell theory as a starting point for the cluster method. One step along this path has been taken by Dahler and Cohen (29), who generalized the cell-cluster theory to include the possibility of holes. However a more general theory would include Mayer and Careri's method of the cell distribution function (for a liquid with holes) as its first approximation and then describe the molecular disorder in terms of deBoer's clusters. Although such a development has been demonstrated, no numerical tests have yet been conducted. This lack of numerical verification really characterizes the present status of all developments based upon the cluster method. During the next few years calculations based upon these schemes should gradually become available, and then a truly comprehensive appraisal of the cluster theory will be possible.

This survey has touched upon a variety of theories for the liquid state, but, except for the calculations based upon the superposition principle and those using the Lennard-Jones and Devonshire approximation, none have been subjected to an adequate numerical test. Although the hole and cell-cluster methods hold considerable promise, their true worth will depend upon their ability to predict the thermodynamical behavior of the liquid. Within the next few years great activity is expected in the performance of numerical calculations designed to provide tests for these theories. [The investigations of (17) constitute such an

endeavor.] However all the schemes discussed contain two sources of error: the mathematical approximations involved in the calculation of the configuration integral and the physical assumption

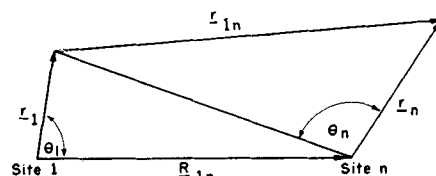


Fig. 8. Coordinates involved in the calculation of the cell potential-energy field. (For a face-centered cubic lattice $|R_{1n}| = n d_0$.)

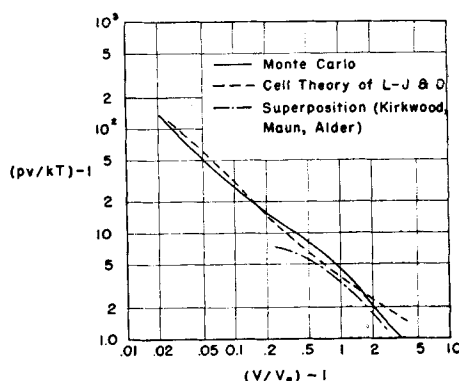


Fig. 9. A log-log plot of $(pv/kT) - 1$ vs. $(v/v_0) - 1$ for hard spheres. $v_0 = \sigma^3/\sqrt{2}$ is the volume per molecule at the closest possible packing. The solid line is the result of the Monte Carlo method as compared with the Lennard-Jones and Devonshire theory (dashed line) and the superposition theory of Kirkwood (dot-dashed line).

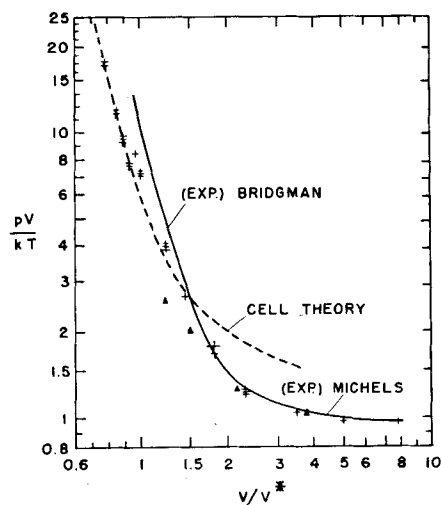


Fig. 10. Compressibility factor vs. reduced volume. The horizontal bars represent the positions of the Monte Carlo average values. The vertical extent of these symbols indicates the uncertainty due to the approximate treatment of second and/or further removed neighbors. The solid curves represent the measurements of (35, 36) on argon. The triangles indicate results obtained by the superposition method.

that the interactions among the molecules may be represented by various empirical laws such as that of the Lennard-Jones 12-6 potential. Therefore in comparing these theories with experimental measurements one is always confronted with uncertainty about the origin of the observed discrepancies. Of course this uncertainty could be resolved if one could perform experiments upon a liquid composed of rigid spheres or of molecules which actually interact according to the 12-6 law. Such experiments can indeed be performed by a numerical procedure known as the *Monte Carlo method*. For an accurate and detailed description of this method one should refer to the original papers on the subject. However it is possible to illustrate the more essential elements of the procedure by considering the situation in a fluid of rigid spheres. For this purpose one can consider a box containing a collection of N billiard balls numbered 1, 2, \dots , N . A computing machine is then instructed to move the first from its original position to a new location within the box. The magnitude and direction of this displacement are chosen by the machine in a random manner, hence the name Monte Carlo. If the molecule is prevented from lying in its new position by the presence of another, the machine is then told to replace it in its original location; otherwise the move is allowed. In either event the machine then plays this same game with a second molecule and so on, until each has been considered. If this process is repeated a sufficient number of times, the spatial distribution of the molecules within the box approaches that of thermodynamical equilibrium (30). Thus using a sample of 256 spheres Rosenbluth and Rosenbluth (31) ascertained that equilibrium was established after each molecule had been moved a total of one hundred times. By examining the surrounding of each molecule they were then able to construct the radial-distribution function as the average description of the molecular environments. Once $g(r)$ had been determined at a particular density and temperature, the corresponding values for the compressibility factor, internal energy, and other thermodynamical properties could be calculated from the equations given earlier. Thus by repeating the Monte Carlo calculations at a number of densities Rosenbluth and Rosenbluth were able to construct the equation of state shown in Figures 3 and 9. At high densities the predictions of the *LJD* method agree rather well with these results. In this same region there is a great disparity between the Monte Carlo calculations and those based upon the superposition principle. At low densities however the situation is reversed and the superposition theory becomes more satisfactory than that of Lennard-Jones and Devonshire.

Although these initial investigations gave no evidence of a discontinuous phase transition from solid to liquid, the radial-distribution function did exhibit a "clear evolution with increasing volume from a crystalline structure to a liquid type structure with the transition being completely at about $v/v_0 = 1.5$." It was also found that the lattice breakdown at $v/v_0 = 1.5$ marked the density at which molecules were first observed to slip past one another and escape from their immediate neighbors in the liquid, that is the onset of fluid behavior. Recently this problem has been reexamined by Alder and Wainwright (10) and by Wood and Jacobson (9), who find that for densities near $v/v_0 = 1.5$ the configuration states of the fluid described by $g(r)$ may be separated into two different classes, one characterized by a relatively free diffusion of the molecules and another for which diffusion is very restricted. Transitions between these two classes rarely occur; for example during calculation periods (IBM 704) as long as 10 to 30 hr. only zero to three such transitions may be observed. This behavior leads to the conclusion that over a narrow range of densities near $v/v_0 = 1.5$ the radial-distribution function is double valued, a conclusion which implies the coexistence of two distinct physical phases. By adopting this interpretation of their results Wood and Jacobson were able to construct the discontinuous isotherm shown in Figure 4. Therefore the existence of the phase transformation theoretically predicted by Kirkwood, Maun, and Alder has been confirmed by the Monte Carlo experiments. Since most theories of crystallization rely heavily upon the presence of attractive intermolecular forces, an explanation of the results for rigid spheres would seem to require the discovery of an alternative mechanism for this process; no such mechanism has yet received wide acceptance.

The Monte Carlo method is of course applicable to cases other than those of rigid spheres. Thus Wood and Parker (32) have recently used this technique to study the thermodynamical behavior of a fluid whose molecules interact according to the Lennard-Jones 12-6 law.* They find that at low densities (Figure 10) there is excellent agreement between the Monte Carlo calculations and the predictions of the superposition method. For higher densities this agreement is less satisfactory however, and instead it is the theory of Lennard-Jones and Devonshire which more closely resembles the Monte Carlo results.

It is significant that at high densities neither theory nor the Monte Carlo

method agrees very well with the few experimental p - v - T data that are presently available. (The existing data are for Argon.) Although this fact may simply evidence the inadequacy of the 12-6 potential, it could also reflect the existence of nonadditive molecular interactions in the real fluid. However this is all merely speculation, and before any definite conclusions can be drawn one must probably await the accumulation of more accurate experimental information at high densities.

NOTATION

A, B	= coefficients
$d\tau_i$	= differential element of volume for i th molecule
E	= energy
$g(r)$	= radial distribution function
h	= Planck's constant
$J_0(s)$	= intensity of X radiation
L	= total number of cells
m	= mass of molecule
m_i	= number of molecules lying in i th cell
n	= number density of molecules
$n^{(2)}(r)$	= pair distribution factor
\mathbf{r}	= vector displacement
r_0	= radius of spherical cell to which molecule is confined
\mathbf{R}_{ij}	= vector directed from i th to j th lattice sites
s	= cell distribution function
$s(r)$	= probability distribution function within a cell
v	= specific volume
v_f	= free volume
V	= total volume of liquid

Subscript

n	= any one of c_n molecules lying in the n th shell of neighbors to the central molecule
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Greek Letters

γ	= fraction of occupied cells neighboring an occupied cell
Δ'	= dodecahedron of altitude $(d_0 - \sigma)/2$
θ, ϕ	= polar angles of vector \mathbf{r}
λ	= wavelength of impinging X rays
σ	= hard-core diameter
$\bar{\sigma}$	= disorder parameter
θ	= angle between primary and secondary beams
$\phi(r)$	= interaction energy of two molecules separated by a distance r

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The calculations of Wood and Parker were carried out for a reduced temperature of $T^ = kT/\epsilon = 2.74$, which in the case of Argon corresponds to about 55°C. Accordingly the reduced temperature at the critical point should have a value of approximately 1.26.

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