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Van der Waals Picture of Liquids, Solids, and Phase Transformations

David Chandler, John D. Weeks, Hans C. Andersen

Summary. The van der Waals picture focuses on the differing roles of the strong short-ranged repulsive intermolecular forces and the longer ranged attractions in determining the structure and dynamics of dense fluids and solids. According to this physical picture, the attractive interactions help fix the volume of the system, but the arrangements and motions of molecules within that volume are determined primarily by the local packing and steric effects produced by the repulsive forces. This very useful approach, its limitations, and its successful application to a wide variety of static and dynamic phenomena in condensed matter systems are reviewed.

A remarkable revival of the van der Waals picture of liquids occurred during the past two decades. This renaissance was spurred by the discovery (*1*) from computer simulations that a system of hard spheres (impenetrable "billiard balls") has a first-order fluid-solid transition that is intimately related to the freezing and melting transitions of real materials (*2*). The van der Waals picture stresses the dominant role of the short-ranged harshly repulsive intermolecular forces (which are nearly hard core interactions) in determining the structural arrangements of molecules in a liquid, while neglecting the influence of the longer ranged attractive interactions on the structure. Though originally developed to describe the liquid-gas critical point (*3*), this approach is now known to be most useful and accurate at the high densities that characterize a liquid away from the critical point, since at those densities the nearly incompressible nature of the fluid tends to inhibit the fluctuations that would invalidate a van der Waals theory.

The successful exploitation of this picture is found in textbook (*4*) descriptions of perturbation theories of simple atomic liquids. But the range of utility of the van der Waals picture is far broader than this limited application might suggest. Its validity and usefulness have been documented in numerous studies extending from computer simulations of condensed materials, to analytical equilibrium theories of polyatomic organic liquids and mixtures, to models of transport, and even to vibrational relaxation in liquids. In this article we review this powerful perspective and some recent developments.

The Basic Idea

According to the van der Waals picture, the average relative arrangements and motions of molecules in a liquid (that is, the intermolecular structure and correlations) are determined primarily by the local packing and steric effects produced by the short-ranged repulsive intermolecular forces. Attractive forces, dipole-dipole interactions, and other slowly varying interactions all play a minor role in the structure, and in the simplest approximation their effect can be treated in terms of a mean field—a spatially uniform background potential—which exerts no intermolecular force and hence has no effect on the structure or dynamics but merely provides the cohesive energy that makes the system stable at a particular density and pressure.

Thus an atom in a monatomic fluid is like a billiard ball and molecules are much like the familiar space-filling models. If one imagines a collection of such objects moving about within a certain volume, colliding elastically with each other and oblivious to any attractive or long-ranged forces between them, then one has a physical picture that captures many essential features of liquid structure and dynamics on a molecular level.

In the modern literature, perhaps the first explicit statements of this picture for monatomic liquids were given by Reiss (*5*) and by Longuet-Higgins and Widom (*2*). The idea is much older, however, since it is the primary (though not sole) physical content of the van der Waals equation of state (*3*). For that reason we attribute the concept to van der Waals, but this historical expedient is not meant to detract from the significance of contributions made by many recent workers to our current understanding of the idea.

The attractive intermolecular interactions rigorously have no effect on the structure only in the hypothetical and unrealistic limit in which the attractive interactions are both infinitely weak and infinitely long-ranged (*3, 6, 7*). In that case, each particle in the system feels attractive interactions from all the other particles. These interactions exert no net vector force, while the resulting potential energy is accurately described in terms of a spatially uniform mean field. What is significant, however, is that the attractions often continue to have little influence on the structure of real condensed materials, where every atom has several nearest neighbors and packing suppresses large density fluctuations. The spatial variation of real attractions in the intermolecular structures allowed by

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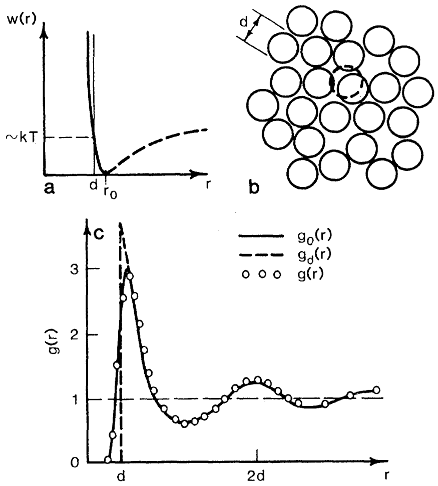

Fig. 1. Structure and pair interactions of a simple liquid. A schematic view of a region of a liquid composed of spherical particles interacting via a pair potential $w(r)$ is shown in (b). The repulsive branch of the potential at $r < r_0$ is indicated by a solid curve. For the Lennard-Jones system, the repulsive force reference system potential, $u_0(r)$, is $w(r) + \epsilon$ for $r < r_0$ and zero otherwise, as given in Eq. 3. A hard sphere potential, $u_d(r)$, which is infinite for $r < d$ and zero otherwise, is associated by Eq. 10 with $u_0(r)$ as shown schematically in (a). The radial distribution function, $g(r)$, for the Lennard-Jones liquid at a state near the triple point with $\rho\sigma^3 = 0.85$ and $k_BT/\epsilon = 0.88$ is plotted in (c). It is compared with $g_0(r)$ and $g_d(r)$, the radial distribution functions of the repulsive force systems with pair potentials $u_0(r)$ and $u_d(r)$, at the same temperature and density. [After Chandler (74)]

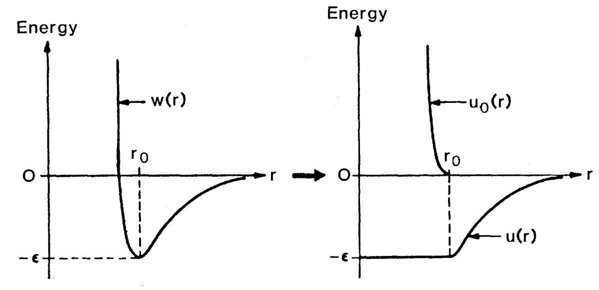

Fig. 2. The unique separation of the Lennard-Jones potential $w(r)$ into a part $u_0(r)$ which gives repulsive forces identical to those found in $w(r)$ (and no attractive forces) and a part $u(r)$ which contains all the attractive forces (and no repulsive forces). Since the repulsive forces are equal, the potentials $w(r)$ and $u_0(r)$ can differ by only a constant for $r < r_0$. The value ϵ (see Eq. 3) of that constant is determined by requiring that $u_0(r)$ vanish at r_0 where the repulsive force vanishes. Note that the remainder, $u(r)$, is smooth and relatively slowly varying with this separation.

the repulsive forces is weak enough that the van der Waals uniform mean field treatment remains accurate and provides useful predictive power.

Part of the explanation for this fact rests on the differing physical bases for repulsive and attractive intermolecular forces. In cases where the van der Waals picture is useful, the attractions usually arise from electrostatic effects such as fluctuating dipole-induced dipole interactions (the so-called dispersion interactions). These forces are not associated with significant distortions of intramolecular charge distributions, and hence their magnitudes usually are not large. Typically, the spatial variations of attractive interactions are ~ k_BT_t per one molecular diameter, where k_B is Boltzmann's constant and T_t is the triple point temperature of the material.

In contrast, the short-ranged repulsions arise from the Pauli exclusion principle, which does not allow electrons on different molecules to be in the same part of space at the same time. Any attempt to push two molecules together too closely will cause the electron clouds on each molecule to distort in such a way as to resist such overlap. The forces generated in this way are very strong and rapidly varying functions of the molecular positions and orientations. Indeed, the typical spatial variation for these short-range repulsions is ~ k_bT_t per one-tenth of an atomic or molecular diameter. These forces are responsible for the nearly incompressible nature of many dense fluids, since neighboring particles are close enough together that an attempt to decrease the volume will be strongly resisted by the repulsive forces.

In many cases the repulsive forces are sufficiently harsh that one can approximate their effect by hard core interactions, though notable exceptions exist, as discussed below. We define a van der Waals material as a system composed of hard core molecules, the sizes and shapes of which are chosen to mimic the repulsive branches of the intermolecular potentials, and held at a particular density by a uniform mean field potential. The thesis of this article is that the properties of many real condensed matter systems can be accurately described by using the appropriately chosen van der Waals material.

Simple Atomic Liquids

To establish the quantitative validity of these statements, it is useful to consider, as an example, the interparticle correlations in a monatomic fluid such as liquid argon. The radial distribution function, $g(r)$, provides a simple mathematical description of the structure of an atomic liquid (4). It is defined by

$$\rho g(r) = \text{average density of atoms at } r \text{ given that another atom is located at the origin} \quad (1)$$

where ρ is the average number of atoms per unit volume, N/V. The radial distribution function gives information about the average relative arrangements of pairs of atoms. More complex descriptions of the structure will involve triples, quadruples, and so on, but $g(r)$ suffices for many purposes. It is the pair function, $g(r)$, that is measured by diffraction experiments, since the scattering of neutrons or x-ray radiation from a liquid is dominated by the interference from the distributed pairs of scattering centers (4).

The total potential energy of an atomic fluid is often represented by a sum of radially symmetric pair potentials (8), $w(r)$, like that pictured in Fig. 1. The extensively studied Lennard-Jones fluid has the potential

$$w(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] \quad (2)$$

The properties of this fluid are known from the results of computer simulations (9–11), and, with appropriately chosen values of the energy and length scale parameters ϵ and σ, it serves as an accurate model for real atomic liquids such as argon (12).

The intermolecular force is given by the gradient of the potential $-dw(r)/dr$; hence particles repel each other at separations less than the potential minimum at $r_0 = 2^{1/6}\sigma$. The repulsive branch at $r < r_0$ should be carefully distinguished from the merely positive portion of the potential at $r < \sigma$, or from the first term in the arbitrary algebraic combination in Eq. 2, since only the sum has physical significance.

As first pointed out by the authors (13, 14), one can directly test the differing roles of attractions and repulsions as assumed in the van der Waals picture for such a model of an atomic liquid by comparing its $g(r)$ to $g_0(r)$, the radial distribution function at the same temperature and density produced solely by the repulsive forces. (Throughout this article, the subscript zero refers to the repulsive forces.) The latter is determined by studying the properties of a system with the repulsive pair potential

$$\begin{aligned} u_0(r) &= w(r) + \epsilon \qquad & r \le r_0 \\ &= 0 & r > r_0 \qquad (3) \end{aligned}$$

The properties of the hypothetical fluid for which the total potential energy is the sum of repulsive pair potentials, $u_0(r)$, have been studied by computer simulation and by analytical theory (see below).

In Fig. 1, we compare the repulsive force fluid $g_0(r)$ with that for the full Lennard-Jones liquid at a typical high-density and low-temperature thermodynamic state near the triple point. We see from Fig. 1 that

$$g(r) \approx g_0(r) \tag{4}$$

is an excellent approximation. This striking correspondence (*13, 14*) provides direct verification of the van der Waals picture, and occurs because the density is sufficiently high that neighboring particles are extremely close to one another, as is evident from the position of the first peak in $g(r)$. The change in energy associated with any local (that is, short wavelength) displacement, such as the one depicted in Fig. 1 with the dashed circle, will clearly be dominated by the interparticle repulsive forces. The attractive forces, on the other hand, are much weaker and tend to cancel one another, leaving only an averaged uniform background energy.

Hard Sphere Model

Perhaps more remarkable is the fact, also illustrated in Fig. 1, that there exists a hard sphere system for which the radial distribution function $g_d(r)$ is closely related, indeed (except for r less than r_0) nearly identical to $g_0(r)$. The hard sphere fluid is characterized by the magnitude of the sphere diameter, d, appearing in the hard sphere potential

$$\begin{aligned} u_d(r) &= \infty \qquad r \le d \\ &= 0 \qquad r > d \end{aligned} \tag{5}$$

(Throughout, we use the subscript d to refer to hard spheres of diameter d.) The similarity between the structure of the continuous repulsive force system and the appropriately chosen hard sphere fluid is apparent despite obvious differences at short times (more precisely, at high frequencies) in the impulsive hard sphere dynamics and the dynamics arising from a continuous interaction. The agreement is evidently a consequence of the fact that the length scale over which the pair potentials for the two differ significantly, roughly $r_0 - d$, is relatively small compared to d, the single length scale of the hard sphere fluid. The softness (non–hard core nature) of a realistic repulsive potential should therefore play a minor role in the structure except at short wavelengths.

It is for this reason that the similarity between a monatomic liquid and the hard sphere fluid appears especially striking when pair correlations are described with the structure factor

$$S(k) = 1 + \rho \int e^{i\mathbf{k}\cdot\mathbf{r}}[g(r) - 1]\, d^3\mathbf{r} \tag{6}$$

While short wavelength differences are noticeable in the main peaks of $g_0(r)$ and $g_d(r)$, the differences between $S_0(k)$ and $S_d(k)$ are not substantial until one considers relatively large values of the wave vector k, where $S(k)$ is already close to its asymptotic value of unity.

The Fourier-transformed representation of the radial distribution function is directly determined by scattering experiments. The close correspondence between the structure factors of real liquids and that of the hard sphere fluid was established empirically in the 1960's by Ashcroft and Lekner (*15*) with their hard sphere model of liquid metals and by Verlet (*10*) in his computer simulation study of the Lennard-Jones fluid. Verlet showed that at a given density ρ and temperature T, a hard sphere diameter $d(T,\rho)$ could be chosen such that the liquid structure factor $S(k)$ was accurately fit by the hard sphere fluid structure factor, $S_d(k)$. In effect, this procedure determined the "size" of the particles, and its success clearly pointed toward the qualitative validity of the van der Waals picture of liquids.

WCA Theory

Motivated by this discovery and by Longuet-Higgins and Widom's compelling physical arguments (*2*) in favor of the van der Waals concept, we developed a quantitative theoretical explanation of these observations in what has become known as the WCA theory of liquids (*13, 14, 16*), the principal results of which we have already discussed in connection with Fig. 1. The WCA theory exploits the van der Waals picture. As a result, the first and crucial step in the development is the division of the intermolecular potential into the short-ranged repulsive portion and the longer ranged more slowly varying part. For monatomic liquids, the division we introduced is unambiguous as described above. The repulsive branch is given uniquely by $u_0(r)$ in Eq. 3, and the remainder

$$u(r) = w(r) - u_0(r) \tag{7}$$

contains all the attractions and no other forces (see Fig. 2). According to the van der Waals picture, we may neglect the role of $u(r)$ in determining $g(r)$, and the problem of explaining the validity of the hard sphere model reduces to the calculation of $g_0(r)$ and showing how this function is related to the properties of the hard sphere fluid.

The radial distribution function due to the repulsive forces depends upon the potential $u_0(r)$ through the Boltzmann factor, $\exp[-u_0(r)/k_BT]$, and complicated integrals involving this factor. This function rises from zero to one over a small range of r values, while the Boltzmann factor for the hard sphere potential, $\exp[-u_d(r)/k_BT]$, is a step function that changes from zero to one at precisely $r = d$. This difference, illustrated in Fig. 3, gives rise to the differences between $g_0(r)$ and $g_d(r)$ shown in Fig. 1. These can be understood by introducing the indirect (or cavity) distribution function, $y_0(r)$, defined by

$$g_0(r) = \exp[-u_0(r)/k_BT]y_0(r) \tag{8}$$

The Boltzmann factor describes the effect of the direct interaction between a pair of particles separated by a distance r (such as particles 1 and 2 in Fig. 3). That factor would be the full $g_0(r)$ in the dilute gas phase. In a liquid, however, the correlations between that pair of particles are affected by all the surrounding particles, and this effect is described by $y_0(r)$. [In the limit $\rho \rightarrow 0$, there is no surrounding environment and $y_0(r)$ tends to unity.] Since we envision a situation in which $r_0 - d$ is much smaller than d, it is reasonable to approximate the indirect effects by those of a hard sphere fluid at the same density with an appropriately chosen diameter d and therefore write

$$y_0(r) \approx y_d(r) \tag{9}$$

This approximation is the first term in a systematic functional expansion of $y_0(r)$ about $y_d(r)$ (*16, 17*). Its physical meaning is illustrated schematically in Fig. 3b.

The systematic expansion also provides a simple way of choosing the appropriate value of the hard sphere diameter for any density and temperature. This criterion, first proposed in a somewhat different context by Percus and Yevick (*18*), is

$$\int d^3\mathbf{r}\, y_d(r)\, \Delta f(r) = 0 \tag{10}$$

Here $\Delta f(r)$ is the difference between the Boltzmann factors for $u_d(r)$ and $u_0(r)$, as shown in Fig. 3c. Thus the diameter is chosen so that the difference $\Delta f(r)$ vanishes when integrated over the volume while taking account of the environment through the factor $y_d(r)$. The resulting $d(T,\rho)$ is a weakly decreasing function of temperature and/or density, in just the way Verlet's empirically determined diameter (*10*) was. Indeed, the theory reproduces Verlet's diameters to better than 1/2 percent (*14, 16*). By combining the computed diameter with Eqs. 4 and 9, one obtains the formula

$$g(r) \approx g_0(r) \approx \exp[-u_0(r)/k_BT]y_d(r) \tag{11}$$

which is indistinguishable on the scale of the graph from the solid line in Fig. 1. Equation 11 thus provides a complete theory for the pair structure of a fluid in terms of the pair correlations of a hard sphere fluid. The latter are known in analytical form from the results of approximate theory (*19*) and "exact" computer simulations (*20*). Further, it is not difficult to show that, except for large wave vectors, Eqs. 6, 10, and 11 imply $S(k) \approx S_d(k)$, thus justifying the hard sphere model for the structure factor.

Thermodynamic Perturbation Theory

An immediate consequence of the structural ideas underlying the WCA theory is a simple theory for the thermodynamic properties. In particular, when $g(r) \approx g_0(r)$, thermodynamic properties can be obtained from first-order perturbation theory, which estimates the role of attractions by performing a reference system (that is, repulsive force system) average of the energy. This is analogous to the familiar perturbation result of Schrödinger quantum mechanics in which one computes the expectation value of the energy by employing the wave function of the unperturbed Hamiltonian. The standard first-order result (*4*) for the Helmholtz free energy per unit volume is

$$A/V \approx A_0/V + (\rho^2/2) \int g_0(r)u(r)d^3\mathbf{r} \tag{12}$$

where A_0 is the free energy of the reference fluid, which can be related to the free energy of the hard sphere fluid by the same procedure used to derive Eq. 9. Corrections to this formula are obtained from corrections to $g(r) \approx g_0(r)$, and if the attractions truly had no effect on the structure, Eq. 12 would be exact. When ordered in powers of $u(r)/k_BT$, the correction terms to Eq. 12 generate the thermodynamic perturbation series first discussed in this context by Zwanzig (*21*) and by Buff and Schindler (*22*). Fortunately, when the van der Waals picture is accurate, these complicated correction terms are negligibly small (*14, 20, 23*) and calculations are simple enough to be performed on a desk calculator (*20, 24*).

Other thermodynamic perturbation theories, using different potential separations, have relied on the corrections to Eq. 12 rather than the accuracy of the van der Waals picture. The best known of these alternatives is the Barker-Henderson (BH) theory (*25*), which was widely influential and stimulated much interest in the theory of liquids. In the BH theory the potential, $w(r)$, is divided into its positive ($r < \sigma$) and negative ($r > \sigma$) parts. Such a separation seems reasonable for a discussion of a dilute gas, where particles are often far apart and the natural zero of energy is the large separation value of the potential. The close proximity of neighbors in a dense liquid, however, makes it profitable to focus on the change in energy for small displacements, that is, the force between particles, and allow the uniform background to rescale the zero of energy to the potential minimum at r_0, where the force changes from repulsive to attractive.

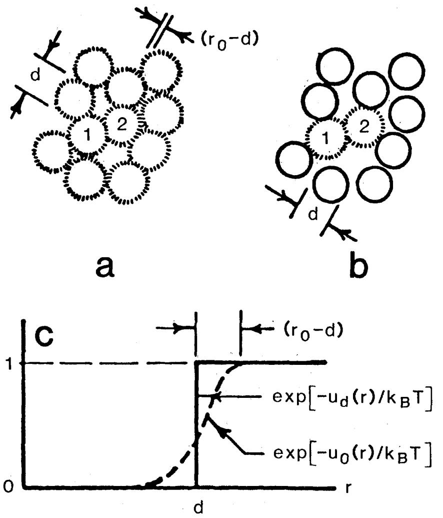

Fig. 3. Relation between a fluid with soft repulsive force (schematically indicated by fuzzy lines) and the hard sphere fluid (shown by solid lines). (a) All particles interact with continuous repulsive forces and $r_0 - d$ gives a measure of the softness of the repulsive forces. (b) Illustration of Eq. 9, where the effects of the environment on the correlations between particles 1 and 2 are approximated by those of a hard sphere fluid. (c) Boltzmann factors for the soft and hard sphere fluids.

Since the BH reference potential leaves out the repulsive forces between σ and r_0, it underestimates the "size" of the particles, the most important structural parameter in the van der Waals picture. The degree to which this issue is important is illustrated in Fig. 4. With the BH reference system, $g(r) \approx g_0(r)$ is not a good approximation and the complicated second-order correction term to Eq. 12 is required to achieve accuracy comparable to that of the first-order WCA theory. While such calculations are possible for atomic fluids, they are generally impractical for polyatomic systems. We believe that the van der Waals picture, with its emphasis on optimizing the simple first-order term, offers a more useful starting point, both conceptually and for practical calculations.

Lesson

The preceding discussion of simple monatomic liquids has emphasized that the accuracy of the van der Waals picture depends on a clear separation of the intermolecular potential into a short-ranged harshly repulsive portion and a longer ranged (usually attractive) part which is a relatively slowly varying function of atomic coordinates. When such a separation exists, the intermolecular structure of the dense fluid can be accurately described by the van der Waals picture. Following standard chemical practice, we call such systems nonassociated liquids.

Often the repulsive forces are harsh enough that these systems can be modeled as hard core van der Waals materials. This provides a significant reduction of the complexities that would follow from realistic representations of intermolecular interactions, and it permits a simple phenomenological description of systems whose potentials are not accurately known by taking the size and shape parameters associated with the hard core model as adjustable parameters.

The problems associated with understanding the van der Waals material are those of determining the entropic effects of packing. The van der Waals picture itself gives no information on how these packing effects should be calculated. Thus it does not provide a self-contained theory, but rather a physical picture that focuses attention on the dominant role of correlations produced by hard cores. Fortunately, the statistical mechanics of hard core systems, while nontrivial, can often be successfully analyzed in terms of accurate approximations, and the solutions of these problems can usually be easily visualized.

For example, when considering the hard sphere model of liquid argon, the properties of this van der Waals material can be well estimated from the analytical solutions of the Percus-Yevick equation (*19*) or even more accurate approximations (*26*) for the hard sphere fluid. The pictures drawn from these calculations resemble both the qualitative observations of a child playing with a box of marbles and those of more detailed statistical analyses of randomly packed spheres as performed by Bernal (*27*) and co-workers. Similarly, the arrangements of molecules in liquid benzene (*28, 29*) are similar to the average arrangements of neighboring Cheerios in a bowl of the breakfast cereal, and a solution of argon in benzene should be similar to the structure achieved when blueberries are mixed in the Cheerios.

Exceptions and Qualifications

Just as nature is abundant with examples of condensed phases that can be successfully modeled as van der Waals materials, it is also not difficult to identify those which cannot be. The hydrogen bonds, which give rise to the local tetrahedral ordering of molecules in aqueous systems (*30*), and the ionic interactions, which produce charge layering in fused salts (*31*), are examples of attractive forces that are so strong that they are competitive with typical repulsions. For these cases the van der Waals picture breaks down.

In the absence of detailed knowledge of intermolecular forces, one may never be sure if this simplified characterization of a particular liquid is valid. However, if there are no intermolecular hydrogen bonds, directional intermolecular covalent bonds, or ionic forces, then one may be fairly confident that the fluid is nonassociated and that at high densities it can be modeled as a van der Waals material. Liquids composed of CCl_4, C_6H_6, and even CH_3CN (a molecule with dipole moment of 4 debyes) are all examples of nonassociated liquids and, as discussed below, all have been successfully analyzed with the van der Waals picture.

Of course, even for these cases where there are no strong associative forces, the picture will break down at low densities where the compressibility is sufficiently high to allow for relatively long wavelength fluctuations [that is, at lower densities, the repulsive cores are not nearly as effective in screening (*16*) the interparticle correlations caused by the attractions]. For example, Eq. 12 predicts incorrect (classical) behavior at the critical point.

Still another source of inaccuracies in the van der Waals picture exists in liquid mixtures. While the high density of the fluid will hinder fluctuations in the total density, concentration fluctuations are not necessarily suppressed. The latter can lead to important structural effects which must be associated with the longer ranged interactions. This point is illustrated by a model system invented and studied by Alder and co-workers (*32*) which is composed of hard spheres of diameter σ mixed with a square-well species with the same hard core diameter and an attractive well of range 1.5σ. The attractions between the square wells tend to make these particles cluster, and this clustering can occur without changing and competing with the excluded volume correlations produced by the hard cores.

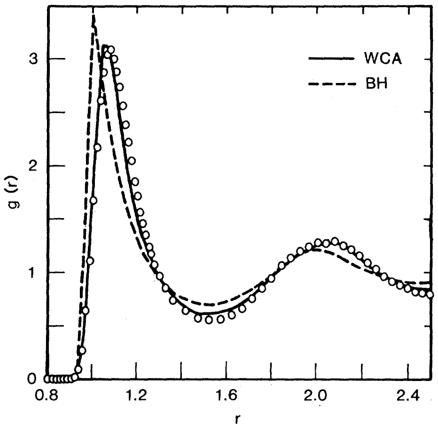

Fig. 4. Radial distribution functions for the repulsive force fluid $g_0(r)$ (solid line), the Barker-Henderson reference fluid $g_{BH}(r)$ (dashed line), and the Lennard-Jones liquid (circles) at a state near the triple point with $\rho\sigma^3 = 0.87$ and $k_BT/\epsilon = 0.75$ as determined by molecular dynamics simulations (*75*). Here r is measured in units of σ.

The use of hard cores to mimic the effects of realistic repulsions provides an enormous practical simplification when applying the van der Waals picture. Unfortunately, it can also be a noticeable source of error. At extremely high densities or for soft enough potentials, the differences from the hard core model must become more significant than the short wavelength differences seen in liquid argon and easily understood with WCA theory. Examples are found in the comparison of the hard sphere structure factor with $S(k)$ for liquid metals (*33*) (where the effective repulsive cores between atoms are relatively soft), and when the structure of the hard sphere solid is compared with that of the Lennard-Jones solid (*34*) (where the density is very high). These are practical quantitative issues, however, and they do not contradict the qualitative validity of the hard sphere model or the general van der Waals picture. Indeed, in both examples mentioned the attractive interactions have little effect on the structure.

Finally, in all these remarks it is assumed that it is possible to make a physically meaningful separation of the interparticle potential into a short-ranged harshly repulsive portion and a relatively slowly varying part. This is an essential step in developing an accurate theory based on the van der Waals picture. If an incorrect separation is made, fluids as simple as liquid argon or methane would appear to be exceptions to the van der Waals picture. Identifying this separation for molecular fluids where the intermolecular potential depends on many variables can be difficult, and a useful separation may not always be possible.

Several Examples

We now list several successful examples of condensed phase theories based on the van der Waals perspective.

Molecular liquids, structure. The intermolecular pair correlations of many polyatomic fluids have been interpreted with the reference interaction site model (RISM) theory (*35*). In this theory, molecules are assumed to be composed of overlapping rigid spheres which are space-filling representations of the atoms. A picture of an acetonitrile molecule modeled in this way is shown in Fig. 5. The resulting total molecular shape is therefore nonspherical, giving rise to significant orientational correlations, though these correlations have little to do with those induced by molecular dipoles. The theory then employs an integral equation (called the RISM equation) which yields an approximate though accurate treatment of the pair correlations associated with the packing of molecules in such a system (*36*). The theory has succeeded in interpreting the results of scattering experiments performed on various liquids including CCl_4 (*28*), C_6H_6 (*28, 29*), CS_2 (*28, 37*), $CHCl_3$ (*38*), and CH_3CN (*39*). Figure 5 shows a representative comparison between theory and experiment for CH_3CN.

Molecular liquids, diffusion. The hard sphere model for self-diffusion in liquids dates back to the time of Enskog (*40*). Quantitative calculations, however, began with the computer simulation studies of Alder and co-workers (*41*). With the simulation results in hand, Levesque and Verlet (*11*) showed that the self-diffusion constant of an atomic liquid can be well approximated by that of the hard sphere fluid. For molecular fluids, however, the nonspherical shape of particles introduces the additional feature of rotation-translation coupling. This coupling tends to lower the diffusion constant from what one would find in its absence since the coupling introduces additional channels for dissipating velocity correlations.

Although a quantitative theory directly treating diffusion in a fluid of hard nonspherical objects has not yet been developed, it can be argued (*42*) that a reasonable account of this phenomenon is given by

$$D \approx AD_d, \qquad 0 < A \leqslant 1, \qquad (13)$$

where D is the self-diffusion constant of the molecular liquid, D_d is the diffusion constant of the hard sphere fluid at the same packing fraction (that is, ρ times the space filling volume of a molecule or particle in the fluid), and the parameter A differs from unity according to the extent of the translation-rotation coupling. For liquid CCl_4 (*42*), $A \approx 1/2$. Equation 13 and its extension to the mutual diffusion constants of mixtures (*43*) have been successfully applied to numerous liquids and have provided a law of corresponding states for diffusion in nonassociated liquids (*44*). The model also provides a basis for understanding Hildebrand's concept of fluidity, which says that the inverse of viscosity is proportional to the free volume available to molecules in a liquid (*45*). Further, the extension of this model to rotational diffusion (*46*) has provided a means for interpreting the density and temperature dependence of rotational relaxation times measured by nuclear magnetic resonance in terms of the average collision frequencies in a hard sphere fluid (*47*).

Liquid metals. While properties associated with the conduction electrons are beyond the scope of a simple van der Waals theory, the hard sphere model has proved successful in several studies of the structure (*15, 48, 49*), diffusion (*50–52*), and viscosity (*53*) of liquid metals. The various workers differ in the procedures used to estimate the temperature-dependent hard sphere diameters, but they all find reasonable values for those parameters. The model succeeds at predicting both the magnitude and the temperature dependence of the transport coefficients. For the structure factor, $S(k)$, precise agreement with the hard sphere model is not to be expected because of the effects of the softness of the interatomic potentials. Indeed, it has been shown how information concerning the softness of the potential can be extracted from the deviations of the experimental data from the hard sphere structure factor, $S_d(k)$ (*33, 49*).

Waseda (*48*) reviewed data for 42 liquid metals and concluded that the hard sphere fluid provides a suitable model for understanding all of them. Furthermore, he classified them into three categories according to the extent of the similarity between the measured structure and the hard sphere structure. Thirty-three of the 42, including all the transition metals studied, are in the category that agrees most closely with the hard sphere fluid. Waseda also studied metal-metal alloys and concluded that, while many of them had structures consistent with the structure of a fluid of a mixture of hard spheres, some metal-metal alloys showed evidence of compound formation, indicating that they are not well described as van der Waals materials.

Solutions. No discussion of the van der Waals picture would be complete without mentioning Hildebrand's regular solution theory (*54*). It is a remarkable observation (*55*) that when hard spheres of various different sizes appropriate for solutions of real molecules are mixed together in such a way that the total volume is unchanged, the entropy of mixing is well approximated by the ideal solution formula. While the fundamental reasons for this behavior are not entirely understood, the implication of this observation is clear. According to the van der Waals picture, entropic properties are determined by packing effects, and therefore the entropy of mixing of solutions of approximately spherical molecules at constant total volume should be the same as that for an ideal solution. Indeed, this behavior is the premise of regular solution theory, which has been developed into a very successful way of estimating the thermodynamic properties of solutions, and the many liquid mixtures which act in this way are called regular solutions (*54*). In more quantitative work, Snider and Herrington (*56*) applied the theory of Longuet-Higgins and Widom (*2*) to a number of binary mixtures and found generally good agreement with experiment.

Vibrational dephasing. The relaxation of intramolecular vibrational modes of molecules in condensed phases has been the focus of much recent research (*57, 58*). The dephasing processes are strongly affected by the fluctuating force fields associated with molecules that move about in the neighborhood of the tagged molecule. Van der Waals theories for these fluctuating forces were developed by Fischer and Laubereau (*59*) and by Oxtoby (*60*). In these theories, fluctuations are assumed to scale with the collision frequency (or viscosity) and the dephasing rate is therefore predicted to be proportional to the collision frequen-

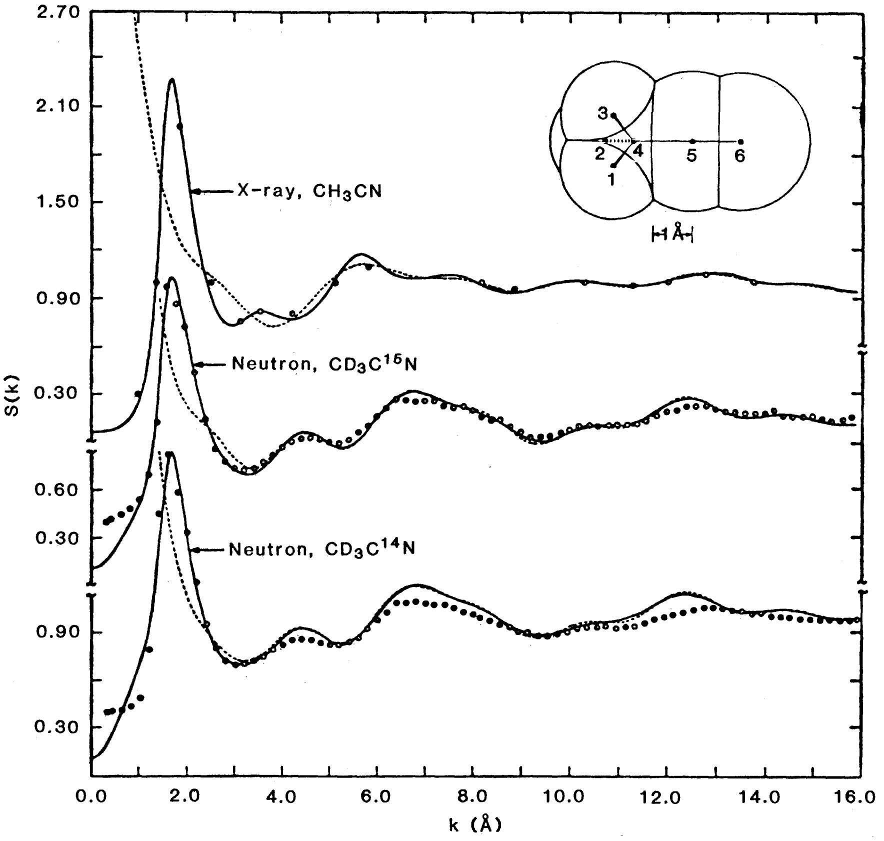

Fig. 5. Structure factors, $S(k)$, for scattering neutrons and x-rays from liquid acetonitrile. The circles represent experimental points. The solid lines are the predictions of the RISM theory, using the hard core model drawn at the upper right (atoms 1, 2, and 3 are hydrogens; atoms 4 and 5 are carbons; and atom 6 is nitrogen). The dashed line shows the scattering cross section associated with only single independent molecules as opposed to the full liquid intermolecular correlations. [After Hsu and Chandler (*39*)]

cy (or viscosity) in a hard sphere fluid. However, experiments by Jonas and coworkers (*61*) show that dephasing rates increase with pressure or density to a much smaller extent than predicted by the collision theories. In fact, in certain cases, the dephasing rate decreases with increasing liquid density. An explanation of this curious behavior was recently developed (*62*) by considering the different roles of repulsions and attractions. While the fluctuations in the former are short wavelength and do increase with pressure as predicted by hard sphere collision frequencies, the fluctuations in the latter are relatively long wavelength and as such tend to decrease with increasing density or pressure. Since vibrational modes of molecules will couple to the environment with both types of interactions, two competing effects are present. A van der Waals treatment with this perspective succeeded in explaining the dephasing data in a variety of systems (*62*).

Liquid crystals. Nematic liquid crystals are made up of long molecules whose axes are oriented in roughly the same direction. Onsager (*63*) first used the van der Waals picture to study such systems, but his treatment of the packing effects is valid only in an unphysical limit. Modern approaches, such as the scaled particle theory (*64*), have improved the situation somewhat, but to date no fully satisfactory theory for the statistical mechanics of long hard objects has been applied. As a recent simulation on an idealized system of hard platelets has indicated (*65*), such a theory should capture many qualitative features of the nematic phase and the transition from the isotropic liquid, although the realistic shape and/or flexibility of the long molecules will undoubtedly have to be taken into account in comparisons with real experiments.

Freezing and melting. Since packing considerations induced by the repulsive forces dominate the structure of dense nonassociated liquids, it is natural to suppose they will play an equally important role at the still higher densities of the crystalline or amorphous solid states and in the fluid-solid transition. The good agreement between the distribution functions in Fig. 6 shows the validity of this idea for the Lennard-Jones solid near the triple point. Both the repulsive force and Lennard-Jones systems have a face-centered cubic (fcc) lattice structure, consistent with efficient packing of the repulsive cores. The peaks in the (angularly averaged) $g(r)$ are broadened by thermal vibrations but clearly show the successive neighbor shells in the fcc lattice. As first recognized by Longuet-Higgins and Widom (*2*), the attractive interactions in the van der Waals picture play an essentially passive role in the fluid-solid transition, widening the region of two-phase coexistence over that found in the repulsive force system alone (*66*), but introducing no new structural correlations (*67*).

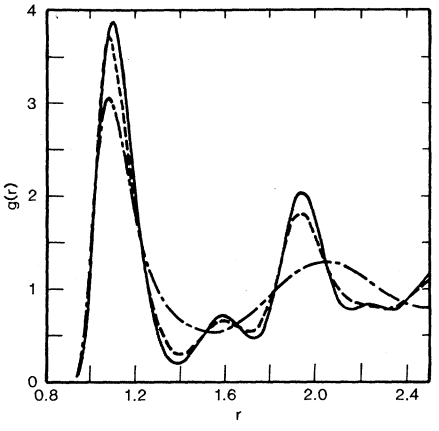

Fig. 6. Radial distribution functions for the Lennard-Jones solid (solid line) and the repulsive force solid (dashed line) at a state near the triple point with $\rho\sigma^3 = 0.98$ and $k_BT/\epsilon = 0.75$. For comparison, $g(r)$ for the coexisting Lennard-Jones liquid (chain-dotted line) at $\rho\sigma^3 = 0.87$ (shown in Fig. 4) is also included. Here r is measured in units of σ.

An exception to this picture, related to that discussed earlier for liquid mixtures, arises when there are different solid structures for the repulsive force system with very nearly the same free energy (*68*). For example, the fcc structure is only very slightly favored by entropy over the hexagonal close-packed structure for hard spheres and both structures have the same limiting close-packed density (*69*). In such a case, the detailed form of the attractive interactions can favor one nearly degenerate structure over the other.

It is interesting to compare the solid $g(r)$ to that of the coexisting liquid, also shown in Fig. 6. The higher density of the solid has been accommodated by a transition to a topologically different structure—an ordered fcc lattice where molecules in one layer fit into the interstitial "holes" in the layers above and below. Although the high density and interlocking structure of the solid prevent significant diffusion or particle exchange, there is still freedom of motion for a molecule within the "cage" formed by its nearest neighbors as well as long-wavelength distortions of the cage structure itself. This configurational freedom provides a source of entropy which stabilizes the ordered solid, relative to a disordered structure, at high densities. A study of the repulsive force system, and particularly the limiting case of the hard sphere system, is instructive in bringing out the importance of density, packing efficiency, and entropy in the fluid-solid transition. Such features are often slighted in conventional treatments of the solid based on the harmonic approximation.

Amorphous and glassy materials. The hard sphere model also gives us insight into nonequilibrium amorphous and glassy solid structures. Computer simulations have shown that for densities $\rho > \rho_m$, where ρ_m is 73 percent of the close-packed density ρ_{cp}, the ordered fcc solid structure is the thermodynamically stable phase (*69*). However, it is possible to arrange hard spheres in a disordered structure at densities greater than ρ_m. Following Bernal (*70*), Scott (*71*), and Finney (*72*), one can experimentally produce such packings by jamming an array of ball bearings into an irregularly shaped container so that nearest neighbor spheres are touching one another. If the walls of the container are corrugated so that the "nucleation" of a close-packed solid layer is inhibited, usually one ends up with a disordered arrangement which is called a random close-packed structure. The maximum packing density that can be so achieved is only about 85 percent of ρ_{cp}.

Bernal (*70*) suggested that the random close-packed structure be taken as a model for the equilibrium structure of a dense fluid. This suggestion was historically very important, since it emphasized the role of repulsive forces and packing in determining the structure of a fluid and pointed out the topologically disordered nature of the fluid state at a time when lattice models and hole theories of liquids were very popular. However, in detail the model is unsatisfactory. Particles are jammed in one configuration so that very little diffusion or particle exchange is possible. Yet the ability to change configurations—that is, to flow—is one of the characteristic differences between a fluid and a solid and a major source of the increase in entropy on melting.

Rather, it has been recognized that the random close-packed models are more appropriate to describe the properties of supercooled liquids and, in particular, liquid metal mixtures below the "glass transition." By very rapidly quenching a liquid, it is sometimes possible to avoid crystallization and achieve a metastable glassy state in which one particular configuration of the disordered liquid is "frozen in." Diffusion and structural relaxation occur at rates many orders of magnitude lower than that observed in the stable fluid state. The fact that the effective hard sphere diameter increases as the temperature is decreased allows a qualitative understanding of one important source of the reduced freedom of motion in the supercooled glassy state. For many purposes it is useful to picture particles in the glass as locked into place by the repulsive cores of their neighbors, as suggested by the random close-packed model.

Of course, any static model cannot describe the detailed properties of a nonequilibrium system, which depend on the past history, the rate of cooling, the amount of structural relaxation, and other features which only a dynamical theory could hope to explain. Nonetheless, such is the dominance of packing considerations that a model which correctly takes them into account will correctly describe many gross structural features. Thus the random close-packed models serve as the starting point for more sophisticated (and complicated) treatments (*73*).

As we apply the van der Waals ideas to more and more complex systems we will undoubtedly find that a more detailed analysis is needed for quantitative agreement with experiment. The case of simple liquids is somewhat anomalous, in that the van der Waals picture provides so complete a description. However, in more complex systems, these ideas may prove even more important, not as a quantitative theory, but as a conceptual guide in emphasizing the important packing constraints which more detailed theories must satisfy. Even today, a century after the time of van der Waals, these ideas continue to play a central role in understanding the properties of condensed matter.

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