Statistical mechanics of simple fluids: beyond van der Waals

Equilibrium properties of dense fluids, notoriously difficult to treat theoretically, can now be understood by reference to model systems, such as a fluid of "hard spheres," and to calculations on high-speed computers.

Joel L. Lebowitz and Eduardo M. Waisman

Dense fluids, defined to include both dense gases and liquids, have the reputation of being especially difficult to deal with theoretically. This reputation is not undeserved. Unlike dilute gases and crystalline solids, which can be thought of as deviants from well understood ideal states, the ideal gas and the ideal harmonic crystal, the dense fluid lies far from any recognizable landmark. This rules out the use of straightforward, convergent or asymptotic, expansions—the all-purpose tool of the theoretical physicist—and makes even the hardy wince.

In recent years, there have, nevertheless, been some significant advances in the theory,[1] particularly for very dense fluids, for which we now have approximations to the free energy and structure function that are accurate to a few percent. This progress has come about from the recognition that while there is no analytically simple reference system there does exist a practical reference system for dense fluids. It is a model fluid of hard spheres, that is, a system of little billiard balls having the same density ρ as the real fluid and a diameter d that is a prescribed but rather complicated function of the density ρ and temperature T of the real fluid. The tractability of the hard-sphere fluid and the realization that it can serve as a quantitatively useful reference system owe a great deal to the availability of high-speed computers. Figure 1, for example, shows the results of two such calculations: a plot of the position of the atoms in a crystal of "computer argon" that is just starting to melt and a picture of a drop of liquid computer argon. It is our purpose to describe the ideas used in this work, which, as we shall see, go back over a century to van der Waals.

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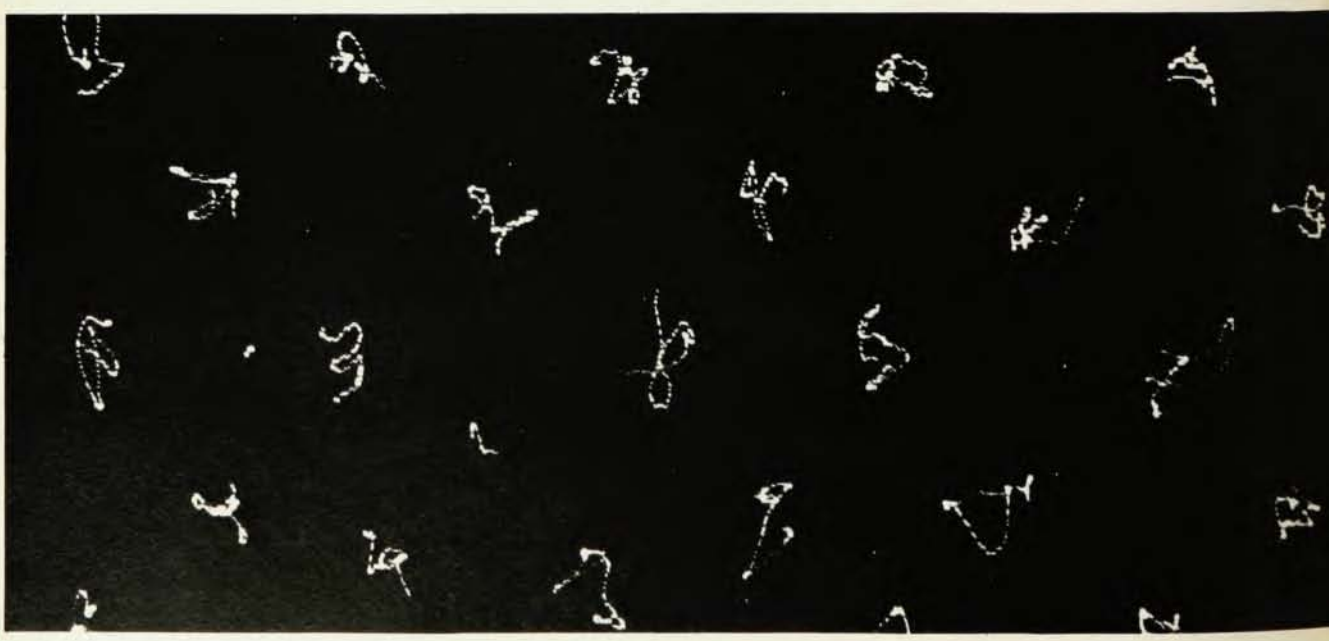
Formulation of the problem

We shall assume here that, for the range of temperatures and densities we are interested in:

- It is permissible to consider our system as consisting of electrically neutral particles interacting through pair potentials that depend only on the distance r between their centers, and
- A macroscopic system of such particles can be described by classical statistical mechanics.

We will not discuss the justification of this description, that is, its deduction from an analysis of a system consisting of electrons and nuclei obeying quantum mechanics. Indeed, we expect that a full description would involve very compli-



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cated many-body interactions between the atoms, so that the pair potential we will consider is best thought of as an "effective" interaction. Remarkably enough, this potential can be adequately represented over a wide range of temperatures and densities by a simple analytic formula, such as that due to Sir John Lennard-Jones.

In this comparison computers play a central part. By computer simulation we can, at selected temperatures and densities, solve "exactly" the classical many-body problem. The result of these "computer experiments" can then be compared with

- experiments on real fluids to test the adequacy of the classical description and of the assumed interparticle potential,
- theoretical predictions to test the (unavoidable) approximations.

For example, the data on the zero-pressure densities of real fluids shown in figure 2 are in excellent agreement with theoretical results based on the Lennard-Jones potential.

The intermediary role of the computer is important since direct comparison of results obtained from a theoretical approximation scheme with experiment tests simultaneously both the basic description and the approximation scheme and frequently leaves in doubt the sources of discrepancy. Even more important, the computer permits experiments on idealized test systems, such as hard spheres, that are not available on Nature's shelf. Such models play a very important role in the development of useful theories of real fluids.

A typical form of the pair potential, commonly used for simple fluids, is the Lennard-Jones "6–12" potential

$$v(r) = 4\epsilon\left[(\sigma/r)^{12} - (\sigma/r)^{6}\right] \qquad (1)$$

The potential $v(r)$ is sketched in figure 3. The "appropriate" values of ϵ and σ for different simple fluids, determined either from low density properties or from other fits such as that shown figure 2, are remarkably consistent. They can be found in reference 1.

The important features of the pair potential are the strong short-range repulsion at small r and the relatively weak longer-range attraction at larger r. As a consequence, each particle in a dense fluid feels simultaneously the attractive (but not repulsive) part of the interaction of many other particles. This suggests that it may be useful to separate the effects of the different parts of $v(r)$: the short-range part keeps the particles apart and is responsible for the local correlations while the long-range part sees only the gross (macroscopic) density profile of the fluid and provides an attractive potential well (mean field) for the fluid particles. The latter is also responsible for the condensation from the gas into the liquid below the critical temperature T_c. We shall discuss later how this separation can be implemented formally by writing $v(r)$ as a sum of two parts, a short-range repulsive part, $q(r)$, and a long-range attractive part, $w(r)$:

$$v(r) = q(r) + w(r) \qquad (2)$$

The different roles that $q(r)$ and $w(r)$ play in determining the structure of a dense fluid are essential to useful approximation schemes.

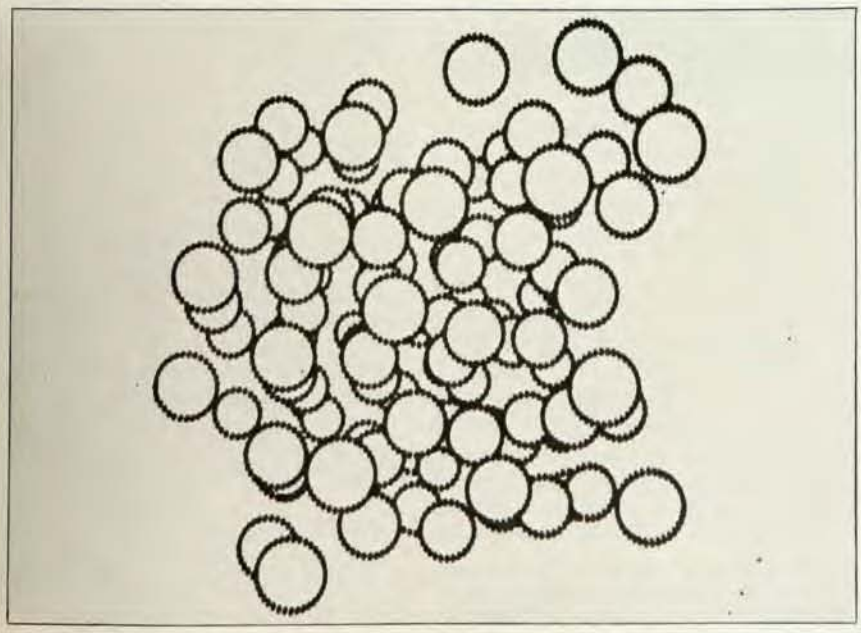
Van der Waals's equation of state

The recognition of the different roles played by q and w dates back at least to Johannes van der Waals (figure 4) who used it in 1873 to develop the equation of state that bears his name,

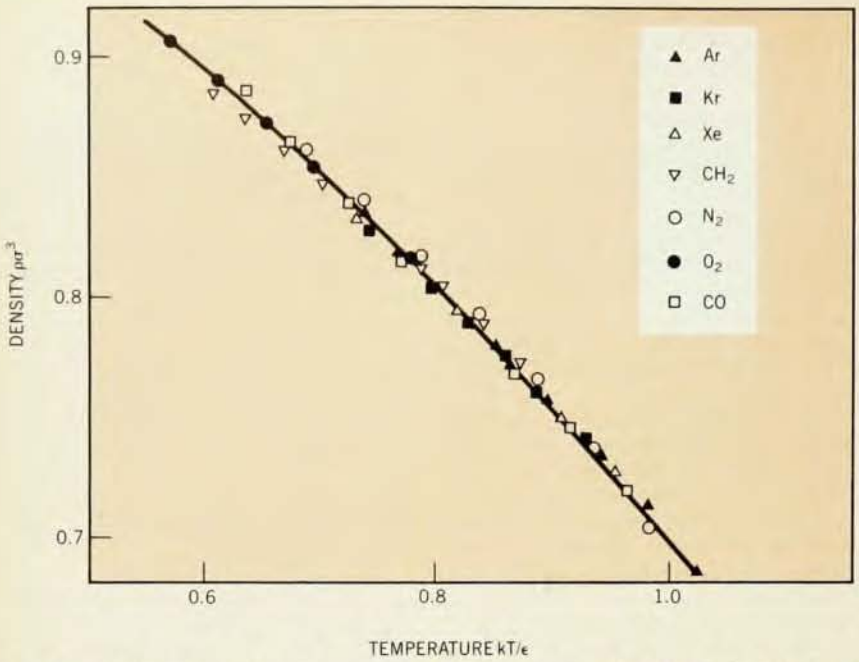
$$p(\rho,T) = kT\rho/(1 - \rho b) - a\rho^2 \qquad (3)$$

Figure 5 shows van der Waals's graphs of this relationship. (A centennial conference[2] celebrating this discovery by van der Waals was held in Amsterdam in 1973.) In equation 3 the positive parameters a and b are related to the attractive and repulsive parts of the potential. As described in any number of textbooks, b is the "volume" taken up by a molecule in "excluding" other molecules from it, thereby decreasing the space available for the motions of the other molecules. This increases the effective density and thus increases the pressure to $kT/(\rho^{-1}-b)$ from the ideal-gas value $kT\rho$. The term $-a\rho^2$, which also appears in van der Waals's approximation for the free energy, represents the energy per unit volume of the attractive part of the potential. This energy acts to hold the system together and thus decreases the external pressure needed to maintain the fluid in a given volume.

The van der Waals equation gives a good qualitative representation of the isotherms of a real fluid at "high" temperatures. For T less than the critical temperature $T_c = 8a/27bk$, however, each isotherm contains a part that has a negative slope; that is, the equation predicts that a decrease in pressure results in a decrease in the volume of the system. Such a situation is thermodynamically unstable and can be proven[3] *never* to arise from a *correct* statistical mechanical computation of the equilibrium pressure of a macroscopic system whose particles interact via reasonable potentials. James Clerk Maxwell read and appreciated van der Waals's paper, his thesis, immediately after its publication. (Maxwell's interest can be gauged from his statement[4] that the thesis "has certainly directed the attention of more than one inquirer to the study of the Low Dutch language in which it is written.") He interpreted parts of the van der Waals isotherms at low temperatures as representing metastable and unstable states of matter (rather than equilibrium states) and amended the van der Waals equation of state for $T < T_c$ by Maxwell's equal-area construction that we describe in figure 5. This construction is designed to make the chemical potentials equal in the two phases. With this amendment the van der Waals equation, with suitably chosen constants a and b, gives a qualitatively reasonable equation of state for many fluids: better than some purely empirical equations of state with many more adjustable param-



Computer simulations of dense liquids. The plot on the left shows the motion of the atomic centers in a crystal of "computer argon" that is just beginning to melt; here the atoms are starting their disorderly motion that will eventually turn the crystal into a liquid. The "exposure time" for this plot by Aneesur Rahman at Argonne National Laboratory was 3.4 picosec. On the right we show a drawing of a super-cooled droplet of computer argon, from a molecular-dynamics study by Myron Mandell of Systems, Science and Software. Figure 1



Zero-pressure densities of some simple liquids. The curve shows the results of Monte Carlo calculations for the Lennard-Jones potential; the points are experimental data reduced by values of ϵ and σ chosen to give the best fit to the curve. After McDonald and Singer.[1] Figure 2

eters. Indeed, George Uhlenbeck has complained that the successes of the van der Waals equation "were so remarkable that they practically killed the subject for more than fifty years."[5]

Rigorous derivation

The Maxwell amendment of the original van der Waals equation is an *ad hoc* addition to an approximation that is qualitatively correct above T_c but leads to non-physical, certainly non-equilibrium, isotherms below T_c. The reason for this failure lies in the assumption that all particles of the fluid see the same average attraction $-a\rho$ (see equation 3). The system must then necessarily be in a single phase of density ρ; the assumption does not allow for coexisting liquid and vapor phases at different densities in different regions of the container. Clearly when these regions have linear dimensions larger than the range of $v(r)$ the energy density will be different in different regions. If the fraction of volume occupied by the liquid (density ρ_l) is α (and, of course, the fraction of vapor—density ρ_v—is $1 - \alpha$) then the attractive energy per unit volume is *not*

$$-a\,(\alpha\rho_l + (1-\alpha)\,\rho_v)^2 = -a\rho^2$$

but has the lower value

$$-a[\alpha\rho_l^2 + (1-\alpha)\rho_v^2]$$

It is precisely this latter value that corresponds to Maxwell's construction or the equivalent Gibbs double tangent construction for the free energy.

A very interesting derivation of the van der Waals equation of state with Maxwell's rule was given by Nicolaas van Kampen[6] in 1964. In this derivation the volume occupied by the system is divided into a large number of cells, each small compared with the range of the long-range attractive force, but large enough to contain many particles. Avoiding the pitfall of assuming a uniform distribution of particles over cells, van Kampen obtained the distribution over cells by minimizing the free energy. His method leads to the van der Waals equation of state, as modified by Maxwell, which implied a first-order phase transition.

An entirely different mathematically rigorous approach to the van der Waals equation of state was taken by Marc Kac, Uhlenbeck and Per Christian Hemmer.[7] Their work concerned a one-dimensional system of hard "spheres" (rods in one dimension), for which the repulsive potential of equation 2, $q(r)$, is infinite for $r < d$ and vanishes for $r > d$; we shall call this function $q_d(r)$. The attractive potential, $w(r)$, has a range $1/\gamma$:

$$w(r, \gamma) = -a\gamma e^{-\gamma r} \qquad (4)$$

Kac, Uhlenbeck and Hemmer were able to prove the validity of the van der Waals equation of state, *together* with the Maxwell rule, in the "van der Waals limit," where the potential has an infinite range, $\gamma \to 0$. (Such a limit was first considered by George Baker for the case of lattice systems.[8])

The limit $\gamma \to 0$ provides a clear distinction between the short range of $q(r)$ and the long range of $w(r, \gamma)$. Since this limit is taken *after* the "thermodynamic limit" (in which the size of the system becomes infinite) the range of $w(r, \gamma)$ is independent of and small compared to the size of the system or the size of coexisting liquid and vapor regions. By contrast, the usual mean-field theory (in which each particle moves in the average field due to the whole rest of the system) does not produce the Maxwell construction.

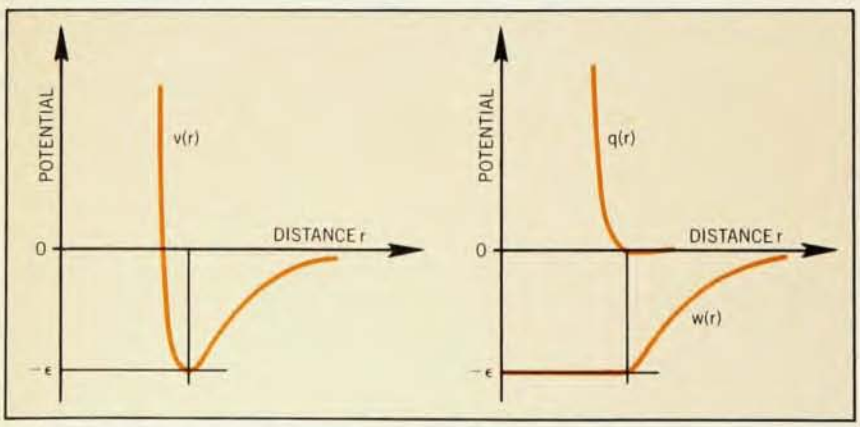
Joel Lebowitz and Oliver Penrose[9] combined the ideas of van Kampen with the use of the van der Waals limit. They considered systems with interparticle potential of the form given in equation 2 with $w(r)$ a "Kac potential"

$$w(r, \gamma) = \gamma^\nu \phi(\gamma r) \qquad (5)$$

where γ is a positive parameter and ν is the dimensionality of the space considered. This potential reduces to that given in equation 4 when $\nu = 1$ and $\phi(x) = -ae^{-x}$. By imposing certain conditions on $q(r)$ and $\phi(r)$, Lebowitz and Penrose showed that in the limit $\gamma \to 0$, taken in such a way that the range γ^{-1} remains small compared to the size of the system, one obtains the Maxwell construction:

$$\lim_{\gamma \to 0} p(\rho, T, \gamma) = \mathrm{MC}\,\{p^0(\rho, T) - a\rho^2\} \qquad (6)$$

where MC stands for the operation in-



The separation of the Lennard-Jones potential, $v(r)$, into a part $q(r)$ containing all the repulsive interactions of the potential (and no attractions), and a part $w(r)$ containing all the attractive interactions (and no repulsions). After Andersen, Chandler and Weeks.[1] Figure 3

volved in Maxwell's construction and $p^0(\rho, T)$ is the pressure of a reference system defined by $w(r, \gamma) = 0$, which may itself have a transition of its own. The van der Waals parameter a is given by

$$a = -\tfrac{1}{2} \int w(r, \gamma)\, d^3r = -\tfrac{1}{2} \int \phi(x) dx \qquad (7)$$

Metastable and critical regions

Penrose and Lebowitz also showed[10] that the correct equation of state for a system that is constrained to have uniform density on a scale large compared to the interparticle spacing but small compared to γ^{-1} is given in the limit $\gamma \to 0$ by that part of the curve $p^0(\rho, T) - a\rho^2$ that falls between the densities ρ_v and ρ_l. They further showed that for densities in the metastable region—but not in the unstable (spinodal) region—of the phase diagram, the lifetime of such a uniform state goes to infinity as $\gamma \to 0$. This property of theories of the van der Waals type appears to depend crucially on the length scale, γ^{-1}, of the attractive potential (which is responsible for the phase transition) going to infinity. It is generally accepted that the lifetime of the metastable state is finite for systems with realistic potentials. There is no general agreement, however, on whether the possibility of analytic continuation of the pressure into the coexistence region that is exhibited by the van der Waals equation also holds for real systems. Most workers feel it does not.

A similar situation exists also for the behavior of the system in the vicinity of the critical point. Near the critical point, many of the system's parameters vary with temperature according to some power of $T - T_c$. The behavior given by equation 6 and its analog for magnetic systems yields classical values for the critical exponents. This is in disagreement with experiments on real systems and with calculations on systems with fixed finite range (or rapidly decaying) potentials. The reason is the intrinsic long-range correlations in the neighborhood of the critical point. An equation of the van der Waals type, such as equation 6, is a reliable approximation only when the range of the attractive potential is large compared to the scale of the relevant correlations. Improved approximations that are like van der Waals's (such as those we describe below) therefore cannot be expected *a priori* to be useful for the immediate vicinity of the critical point.

Beyond van der Waals

We now outline the steps used in obtaining a good approximation to the properties of a classical fluid whose atoms interact via the Lennard-Jones potential given in equation 1.

▸ The most useful decomposition of the potential appears[11] to be the one shown in figure 3. The minimum energy of the Lennard-Jones potential is $-\epsilon$; it attains this value at a radius of $2^{1/6}\,\sigma$. One defines $q(r) = v(r) + \epsilon$ for $r < 2^{1/6}$ and zero otherwise; and $w(r) = v(r) - q(r)$. Both q and w and their derivatives are continuous for all r; q corresponds to a purely repulsive force while w corresponds to a purely attractive one. This is presumably the reason for the success of this decomposition.

▸ The thermodynamics and radial distribution function of the "reference system," one for which $v(r) = q(r)$, are obtained most conveniently by a perturbation about a "zero order reference system" of hard spheres of diameter d. The "correct" choice of d depends on the temperature and density of the fluid and is extensively discussed in the literature.[12] Suffice it to say that a good choice for d can be obtained from knowing only the form of the hard-sphere radial distribution function for r near d, at density ρ.

▸ Once the properties of the reference fluid are obtained the attractive part $w(r)$ becomes a weak perturbation, which is treated either in a straightforward expansion or in some self-consistent scheme.

For many purposes a useful—and often sufficient—description of the microscopic structure is given by the correlation function of molecular distances, that is by the variation of the fluid density with distance from a given molecule.

Let $\Delta N(r)$ be the average number of molecular centers within a spherical shell of thickness Δr at distance r from the center of the given molecule. We define the "radial distribution function":

$$g(r) = \Delta N(r)/(4\pi r^2 \Delta r) \text{ as } \Delta r \to 0 \qquad (8)$$

Because ρ is the average density, $g(r) = 1$ corresponds to no correlation between the particles. It is always assumed that $g(r)$ approaches unity as r becomes infinite in a single phase fluid; this is almost a definition of a pure phase.[3,9]

The radial distribution function determines the average value of all pair functions in a uniform fluid, including, in particular, the energy and pressure of a fluid with central pair potentials. Moreover, the Fourier transform of the function $h(r) = g(r) - 1$ is an experimental observable: the elastic scattering intensity of x rays and neutrons depends on it. The scattering is, in fact, proportional to the "structure factor" of the fluid $\hat{S}(k)$, which is defined as

$$\hat{S}(k) = 1 + \frac{4\pi}{k}\rho \int_0^\infty r h(r) \sin kr\, dr = 1 + \rho \hat{h}(k) \qquad (9)$$

The direct correlation function, $C(r)$, introduced by Leonard Ornstein and Frits Zernike[13] plays an important role in the modern theory of dense fluids. It is defined in terms of $h(r)$ as

$$h(r) = C(r) + \rho \int h(|\mathbf{r} - \mathbf{r}'|)\, C(|\mathbf{r}'|)\, d^3r' \qquad (10)$$

Johannes Diderik van der Waals. The question of improving the van der Waals equation "continually obsesses me, . . . it is with me even in my dreams." Figure 4

or in terms of Fourier transforms:

$$\hat{C}(k) = \hat{h}(k)/(1 + \rho \hat{h}(k)) \qquad (11)$$

The functions $C(r)$ and $h(r)$ contain, in principle, the same amount of information: given one of them for all r the other can be obtained from equations 10 or 11. It turns out, however that $C(r)$ is simpler and therefore easier to approximate (guess) than $g(r)$.

There are two ways of obtaining the equation of state from $g(r)$:

▸ from the virial theorem

$$p/kT = \rho - \frac{2}{3}\pi\rho^2 \int_0^\infty \frac{dv(r)}{dr} g(r)\, r^3 dr \qquad (12)$$

▸ from the compressibility

$$\frac{1}{kT}\frac{\partial p}{\partial \rho} = [1 + \rho \int h(r)\, d^3r]^{-1} = 1 - \rho \hat{C}(0) \qquad (13)$$

The two relations give the same results for the pressure with the exact $g(r)$ but will generally disagree for approximate distribution functions g.[1]

The hard-sphere fluid

The hard-sphere potential, $q_d(r)$, is infinite whenever r is less than the hard-core diameter d, and zero otherwise. In principle, one can obtain both the radial distribution function $g_d(r)$ and the excess Helmholtz free energy per particle $a_d(\rho, T)$ of the system from the prescriptions of equilibrium classical statistical mechanics. Yet, even for this simple zero-order reference system there are no exact results available at present. In the last twenty years however, following the first computer studies of hard spheres, some very good and simple approximations have been found for this system.[14] The computer results provide the radial distribution function and the equation of

state as a function of η, the volume fraction occupied by the hard spheres: $\eta = \pi\rho d^3/6$. The hard-sphere system has a maximum density at close packing with $\eta = \pi/(3\sqrt{2})$.

One of the most surprising findings of these computer studies is the presence of a fluid–solid phase transition at density corresponding to a value of η near 0.5, a value we shall call $\bar{\eta}$, although this system shows no temperature-dependent liquid–vapor transition. There is evidence[15] that this hard-sphere phase transition "underlies" the fluid–solid transition for simple fluids. This shows again the dominant influence of the repulsive short-range forces in determining the structure of simple dense fluids. For the liquid state we are describing in this article it is sufficient to consider densities smaller than $\bar{\eta}$. (A theoretical description of the fluid–solid phase transition remains an open challenge.)

We now describe briefly one of the most successful attempts to approximate the hard-sphere system in this regime. In 1958 Jerome Percus and George Yevick introduced[16] an approximate nonlinear integral equation for the radial distribution function of fluids. It is most successful for the hard-sphere system (see figure 6), for which the approximation consists of assuming that the direct correlation function $C(r)$ vanishes outside the core. This happens to be exact in the one-dimensional fluid of hard rods.[17] Michael Wertheim[18] and Everett Thiele[19] obtained the solution of the Percus–Yevick equation. It gives $C(r)$ as a cubic polynomial in r for $r < d$ with coefficients that are simple rational functions of η.

One can obtain equations of state from these polynomials *via* either equation 12 or 13, that is, from the virial theorem:

$$p^{(v)}/\rho kT = (1 + \eta + \eta^2 - 3\eta^3)/(1 - \eta)^3$$

or from the compressibility

$$p^{(c)}/\rho kT = (1 + \eta + \eta^2)/(1 - \eta)^3$$

For $\eta < \bar{\eta}$ the pressure obtained from the computer studies falls between $p^{(v)}$ and $p^{(c)}$. N. F. Carnahan and K. E. Starling obtained[20] an equation of state for hard spheres, which interpolates between $p^{(v)}$ and $p^{(c)}$ and is essentially indistinguishable from p for $\eta < \bar{\eta}$:

$$p/\rho kT = (1 + \eta + \eta^2 - \eta^3)/(1 - \eta)^3 \qquad (14)$$

From equation 14 it is easy to obtain the excess free energy a_d, that is, the free energy above that of an ideal gas at the same temperature and density:

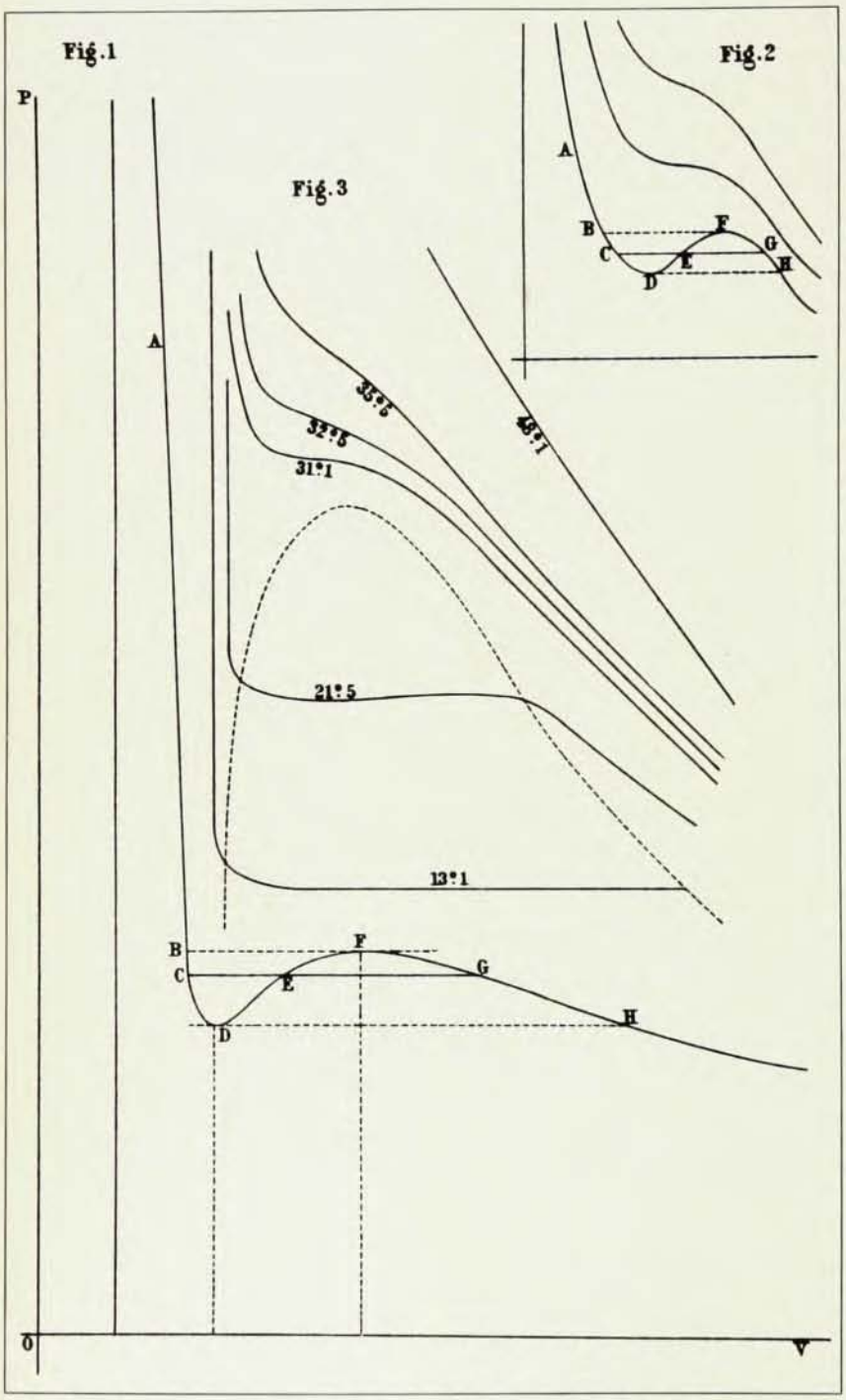
$$a_d(\eta)/kT = \eta(4 - 3\eta)/(1 - \eta)^2 \qquad (15)$$

Interestingly enough, the pressure obtained from the Percus–Yevick equation via the compressibility coincides exactly with an equation of state obtained earlier by means of an entirely different method—the scaled particle theory.[21]

Real fluids

There are several, more or less equivalent, prescriptions available in the literature[1] for calculating the properties of single-phase fluids, once the properties of the reference hard-sphere system are known. The most straightforward of these are the high-temperature expansion method of Robert Zwanzig and its self-consistent formulation by John Barker and Douglas Henderson. We present here, in outline form, a more refined method due to Hans Christian Andersen, David Chandler and John Weeks.[11]

We start from the decomposition of the Lennard-Jones potential shown in figure 3. The next step is to select a hard-sphere system with a temperature- and density-dependent diameter $d(\rho, T)$ to approximate the Lennard-Jones system with



Plots of isotherms from van der Waals's thesis, showing van der Waals's curves (labeled Fig. 1), unstable isotherms according to James Thomson (Fig. 2) and experimental curves from Thomas Andrews (Fig. 3). While van der Waals's recognized that the isotherm DEF represents unstable states, it remained for Maxwell to show exactly where to draw the line CEG that represents the stable states, namely, so as to equalize the areas CDE and EFG. Figure 5

potential $q(r)$. (We shall call the Lennard-Jones system the reference system and denote its properties with subscripts 0.) A good (but not unique) choice used by Andersen, Chandler and Weeks is the condition, introduced by Percus and Yevick,[22] that

$$\int [e^{-q(r)/kT} - e^{-q_d(r)/kT}] \times y_d(r)\, d^3r = 0 \quad (16)$$

The function $y_d(r)$ in equation 16 is defined as the hard-sphere limit of the function $e^{v(r)/kT} g_v(r)$, where $g_v(r)$ is the radial distribution function of a fluid whose pair potential $v(r)$ approaches the potential $q_d(r)$ as a limit. It is also possible to define $y_d(r)$ directly for a hard-sphere system by means of Mayer graphs. In any case, $y_d(r)$ is equal to $g_d(r)$, the distribution function for hard spheres, for $r \leq d$ and is smooth at $r = d$. In practice one can obtain $y_d(r)$ by extrapolating the function $g_d(r)$ from $r \gtrsim d$ into the small region $r \lesssim d$ where it is needed.

Having determined the effective hard-core diameter $d(\rho, T)$, which is generally quite close to σ (near the triple point of the Lennard-Jones fluid, for example, d is 1.02 σ), one approximates the properties of the reference fluid by those of the hard-sphere system:

$$g_0(r) \simeq e^{-q(r)/kT} y_d(r) \quad (17)$$

$$a_0(\rho, T) \simeq a_d(\eta) \quad (18)$$

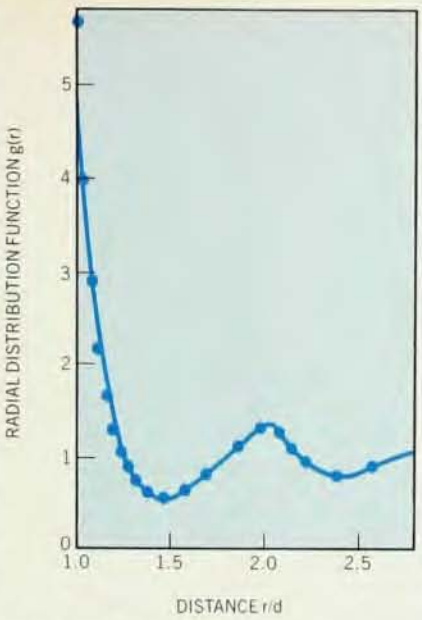
The next and final step is to obtain an approximation for the full system. For that, we note first that there are exact upper and lower bounds on the free energy $a(\rho, T)$ given by the Gibbs–Bogoliubov[3] inequalities:

$$a_0 + \tfrac{1}{2}\rho \int g(r)\, w(r) d^3r \leq a \leq a_0 + \tfrac{1}{2}\rho \int g_0(r)\, w(r) d^3r \quad (19)$$

where $g(r)$ is the radial distribution function of the full system. When the fluid is very dense $g(r)$ is very close to $g_0(r)$ (see figure 7). Therefore one can accurately approximate the free energy per particle at these high liquid densities, using equations 17 and 18, by

$$a(\rho, T) = a_d(\eta) + \tfrac{1}{2}\rho^2 \int g_0(r)\, w(r)\, d^3r \quad (20)$$

Equation 20 represents the first two terms in a high-temperature series (in powers of $1/kT$) for a system in which $q(r) = q_d(r)$, with d fixed. It is clear that this approximation is very close in spirit to van der Waals's analysis of the different roles played by $q(r)$ and $w(r)$ in determining the structure and thermodynamics of the very dense fluid. Indeed, equation 20 would agree with the van der Waals approximation for the free energy[9] when $q(r) = q_d(r)$ and $w(r)$ has a sufficiently long range for $g_0(r)$ to be approximately unity over most of the range of the integration. We remark that the actual computation of the right side of equation 20 is nowadays a relatively simple, desk-calculator task, due to the availability of very compact fits for the relevant quantities.[12]



Radial distribution function. The graph shows the results of a computer calculation (dots) and of a calculation with the Percus–Yevick approximation for a hard-sphere fluid with a normalized density η of 0.49—the largest density the fluid can have. Figure 6

When we consider lower fluid densities, $\rho\sigma^3 \lesssim 0.65$, the effect of $w(r)$ on the radial distribution function must be included to obtain quantitative agreement with laboratory and computer experiments. For example Andersen, Chandler and Weeks have obtained a non-linear integral equation for a "renormalized potential" $\xi(r)$ that is very similar in structure to the integral equation in the Percus–Yevick approximation for hard spheres. In the simplest version of their scheme, called the exponential approximation, $g(r)$ is obtained from $\xi(r)$ through

$$g(r) = g_0(r)\, e^{-\xi(r)/kT} \quad (21)$$

At low densities $\xi(r)$ goes to $w(r)$ but at large fluid densities it is smaller and has a shorter range than $w(r)$. In particular, if $g(r) \simeq g_0(r)$ (which is true for large fluid densities) then $\xi(r)$ vanishes.

The exponential approximation, and the corresponding thermodynamic functions, are found to give an accurate description of the dense single-phase Lennard-Jones fluid. In fact, for $\rho\sigma^3 \gtrsim 0.65$ the radial distribution function is within the "experimental" accuracy of the computer experiments,[21] so that in a scale such as that of figure 7 the two curves completely coincide; the accuracy is a few percent for $\rho\sigma^3$ between 0.65 and 0.1, as long as $T \lesssim 3\, T_c$. For very high temperatures the approximation of $q(r)$ by $q_d(r)$ is not so accurate, because the high kinetic energy of the particles permits them to penetrate deeper into the repulsive part of the potential.

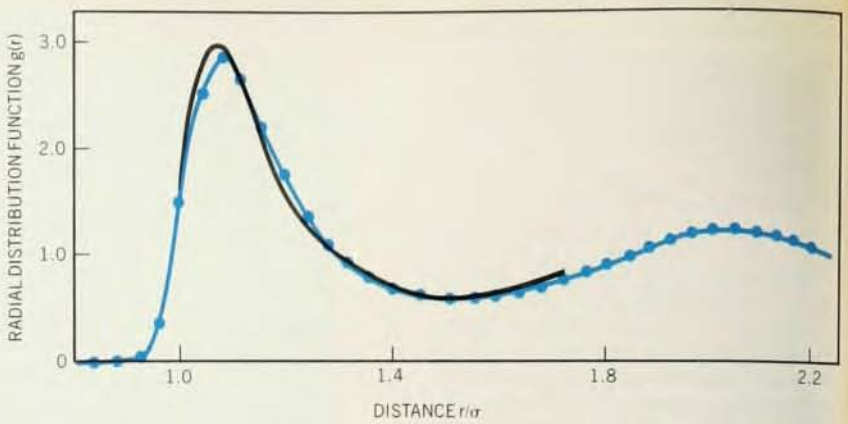
Other problems

We have presented here in outline form a relatively simple approximation scheme for obtaining a quantitatively accurate description of a dense, single-component, simple classical fluid. As mentioned earlier there are various other similar schemes,[1] which do about as well in the same situations.[23] All these approximations start from the recognition of the different roles played by the repulsive and attractive parts of the interactions. The former determines the microscopic structure of the fluid and may be idealized by a hard-sphere interaction while the latter can be treated by refined approximations of the mean-field type.

This approach generalizes in a natural way to mixtures of simple fluids.[1] Here again the solution of the Percus–Yevick equation for mixtures of hard spheres with different diameters[17] plays an important role. These types of approximations have also been applied with reasonable success to not-so-simple fluids in which the interparticle interactions are only roughly spherical,[1] such as methane. Analogous schemes have been developed and applied to ionic and polar fluids where the interactions decrease only very slowly with distance. Here too some successes have been achieved although much remains to be done. This is especially so for fluids such as water, where the interactions depend strongly on orientation. All these extensions are clearly of great practical importance and are currently under active investigation.

Another topic of current interest is the structure of non-uniform fluids particularly, the interface between gas and liquid. So far, however, the type of approach described in this article has only been qualitatively successful for these problems. Quantitatively, there is only little advance beyond the old van der Waals theory.[2] The reason for this appears to lie in the lack of any simple reference system for such an interface. Unlike the situation in the bulk fluid, the width and structure of the interface at temperatures away from the critical temperature are strongly affected by both the repulsive and the attractive parts of the interaction potential and there is no simple way to disentangle them.

This brings us to the final point we wish to make here: even in the case of simple dense fluids there is still much to do to understand why the schemes described here work as well as they do.[23] After all, the effective range of the attractive part of the Lennard-Jones potential is not really all that large compared to σ, as one can see in figure 3. Why then should van der Waals's, and similar theories, valid for very weak, very long-range potentials work so well for Lennard-Jones fluids? George Stell[1] calls this "the principle of



Comparison of radial distribution functions for a Lennard-Jones fluid near the triple point. The black line shows $g_0(r)$, the distribution function for the "reference system" whose potential is only the repulsive part of the Lennard-Jones potential; the colored line shows the result of the exponential approximation; the spots are from a molecular-dynamics calculation Figure 7

unreasonable utility of asymptotic estimates" and it bears further investigation. An understanding of this point will, we hope, also lead to new, useful and simple approximation schemes for systems that are not covered by the present methods.

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