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SCIENCE

Hard-Sphere Fluid

A simple molecular model for dense fluids illustrates a transition to the solid phase.

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The purpose of this article is to provide direct insight into the physical behavior of dense supercritical fluids composed of roughly spherical, and preferably monoatomic, molecules such as those of the inert gases. Specifically, I discuss the central equilibrium property, the equation of state relating pressure, density, and temperature of the fluid, and the simplest transport coefficient, the self-diffusion coefficient. I dispense with the usual mathematical apparatus of statistical mechanics of fluids but ask readers to recall the elements of the kinetic theory of gases and certain facts of thermodynamics (*1*).

If a fluid is sufficiently dilute, it can be described according to a simple physical model, the *ideal gas*. Referring to Fig. 1, a diagram of the intermolecular potential energy between two spherical molecules as a function of the distance r between their centers, we note that real molecules possess an essentially impenetrable volume called the "hard-core" volume, characterized by the hard-core diameter, a. The ideal gas is approximated by a real fluid when the fluid becomes so attenuated that the "hard core volume" of a molecule, which is proportional to a^3, can be considered negligibly small in comparison to the volume available to the center of a molecule (that is, the volume per molecule), whose reciprocal is the number density ρ. The ideal-gas molecules are statistically uncorrelated in their location in space. Actually there are two different ideal gases, depending on whether or not the degree of attenuation of the gas permits one to neglect the molecular cross sections to mutual collisions, πa^2 per pair of molecules, in comparison with the square of any linear dimension of the macroscopic sample of the gas. These are the Knudsen gas and the Boltzmann gas, respectively. In either case the equation of state (*2*) for the "ideal gas,"

$$p = kT\rho, \qquad (1)$$

applies, with p the pressure, T the absolute temperature, and k Boltzmann's constant.

Hard-Sphere Model

Since the volume occupied by the molecules in a dense fluid is often not negligible ($\rho a^3 \sim 1$), we seek a simplified fluid model which applies when even the Boltzmann ideal gas limit fails. Such a model system must, like a real fluid, be capable of existing in two states of aggregation: (i) a solid phase possessing long-range order, in which the molecules are statistically localized in the vicinity of a periodic space lattice, and (ii) a fluid phase in which the range of statistical spatial correlation of the molecules is much shorter than any linear dimension of the fluid sample. Referring again to the intermolecular potential energy diagram, in Fig. 1, we note that at temperatures high enough (say corresponding to the energy drawn as a dashed line in Fig. 1), so that the average kinetic energy of a fluid molecule is much greater than the minimum value of the intermolecular potential energy, the contribution to this potential made by the hard core is all-important in determining the properties of the fluid. At very high densities, furthermore, the soft, primarily attractive (nonhard-core) part of the potential can be thought of as a smoothed average potential not greatly affecting the properties of the fluid.

Thus we arrive at the *hard-sphere* model (*3*) in which only the hard-core repulsion is retained in the intermolecular potential energy. Hard-sphere molecules interact only when they collide elastically, that is, when both energy and momentum are conserved in the collision. Machine computations, either directly of the molecular dynamics (*4*) or by Monte Carlo simulation (*5*) in which a finite but large number (10^2 to 10^3) of such hard spheres is used, provide us with "experimental" data with which to compare theory. I will not describe these interesting computations but refer readers to reference (*4*).

Figure 2 shows the result of such a computation of the equation of state made by Alder and Wainwright (*6*) for a two-dimensional version of a fluid composed of hard spherical discs of diameter a. The ordinate in Fig. 2 is the product of the pressure p of the N hard discs and A_0, their area at closest packing, divided by NkT; the abscissa is the ratio of the actual area A (the two-dimensional analog of the volume) occupied by the discs to A_0. The graph is composed of two branches, a high-pressure (left) and a low-pressure (right) branch, connected by an S-shaped (van der Waals) loop. The low-pressure branch, as one can verify directly from the computation, is composed of states of aggregation in which the molecular spatial correlation extends over distances of the order of the macroscopic size of the sample. The system is essentially a thermally per-

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turbed space lattice that is characteristic of solids. The high-pressure, or fluid, branch is one in which such long-range spatial correlations have vanished. The loop is the transition region which presumably would deform as N,V increases without limit, with $\rho = N/V$ fixed to the horizontal line in Fig. 2, along which solid and fluid can coexist. Thus this system is capable of existing in two different states of aggregation (solid and fluid) and can exhibit a well-defined phase transition. Similar results are found with the three-dimensional hard-sphere system.

The solid branch of the machine-computed equation of state is adequately described by an imperfect solid equation of state (*4*). The basic concept underlying the derivation of this equation is that any hard sphere can be thought of as being essentially localized to a cell volume determined by its neighbors. We need thus concern ourselves primarily with the fluid branch.

The Pressure

Consider a container of our hard-sphere fluid maintained at a temperature T. The pressure of the fluid is the normal stress exerted against the macroscopic plane (rigid) wall of the container, that is, the volume derivative of the mechanical reversible work with the dimensions of force per unit area. Recollecting the simple kinetic-theory argument (*7*), we can write the pressure as the product of the average change in flux of molecular momentum at the wall, kT, and the density of molecules adjacent to the wall, $\rho_w = \rho_w(\rho)$:

$$p = kT\rho_w(\rho). \qquad (2)$$

In particular for an ideal gas, in which there is no spatial correlation, this density ρ_w is the uniform bulk density ρ (see Eq. 1).

For the gas of hard spheres this is no longer true, as can be seen from the so-called virial equation of state (*8*):

$$\frac{p}{\rho kT} = 1 + \tfrac{2}{3}\pi a^3 \rho g^{(h)}(a;\rho), \qquad (3)$$

where $g^{(h)}\ (a;\rho)$ is the radial distribution function, $g^{(h)}\ (r;\rho)$, evaluated at $r = a$ corresponding to contact between two spheres. The entity $\rho g^{(h)}\ (r;\rho)\ 4\pi r^2 dr$ is the conditional probability that another molecular center can be found within a spherical shell of radius r and thickness dr, of volume $dv = 4\pi r^2 dr$, from the center of a given fixed molecule. Thus the expected density of hard spheres in contact, that is, whose centers are separated by the distance a, is

$$n(a;\rho) = \rho g^{(h)}\ (a;\rho) = \left(\frac{p}{\rho kT} - 1\right) / \tfrac{2}{3}\pi a^3. (4)$$

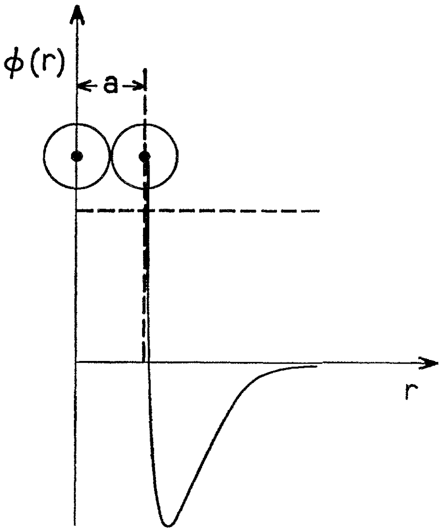

Fig. 1. Intermolecular potential energy plotted against distance between the centers of the molecules. The dashed line corresponds to the hard-sphere potential $\varphi = \infty$ for $r < a$ and $\varphi = 0$ for $r > a$.

The plausibility of the virial equation of state is made evident by the following device: Divide our container by a flat reflecting wall which is impermeable only to the *centers* of our hard spheres, as drawn in Fig. 3. This does not affect the density, pressure, or the bulk spatial correlations away from this wall. Now consider the average change of momentum flux across this wall, that is, the pressure p. This pressure consists of (i) the ideal gas contribution of the centers, ρkT, augmented by (ii) the average momentum flux transferred by molecules on the left of the wall but protruding through it to molecules with centers to the right-hand side of the wall. Except for a numerical factor of $4\pi/3$ this is proportional to the molecular cross section, πa^2, times the effective length a in which the center of a molecule on the left can lie, times the mean momentum change in collision of a pair kT, times the effective density of pairs in contact $\tfrac{1}{2}\rho n(a;\rho)$, $\tfrac{2}{3}\pi a^3 kT\ \ \rho n(a;\rho)$. Adding these two contributions to p we recover Eq. 3.

Spatial Correlation

The equation of state given by Eq. 3 is affected by spatial correlation through $g^{(h)}\ (a;\rho)$, the contact radial distribution function. Following the "scaled particle theory" (*9*) we can obtain reliable estimates of $g^{(h)}\ (a;\rho)$ by focusing attention on fluctuations in our fluid which produce a spherical cavity. By a spherical cavity of radius r I mean a spherical region of radius r devoid of hard-sphere centers as illustrated in Fig. 4*A*.

Let $p_0(r)$ be the probability of finding a spherical cavity of radius at least r centered at an arbitrary point of our fluid. When $r \leqq a/2$ we can calculate $p_0(r)$ exactly; $p_0(r)$ is equal to 1 minus the probability of occupation. For $r < a/2$, occupation can occur by at most a single hard-sphere center; thus $p_0 = 1 - 4/3\ \pi r^3 \rho$, since ρ is the density of single molecular centers and the volume of the cavity is $4/3\pi r^3$. Furthermore one can readily show that the first two derivatives of $p_0(r)$ with respect to r are continuous at $r = a/2$. More generally, we know from thermodynamic fluctuation theory that the probability of the spontaneous occurrence of some specified situation equals the negative exponential of the reversible work (Helmholtz free-energy change) necessary to create the situation divided by kT (*10*). Thus in our case

$$p_0(r) = \exp\left[-W(r;\rho)/kT\right] \qquad (5)$$

where $W(r;\rho)$ is the reversible work performed in forming the spherical cavity.

The probability that there will be a spherical cavity whose radius lies between r and $r + dr$ is $-(dp_0/dr)dr$ and can be written as a product of two factors: the probability that there will be a cavity of radius at least r, and the conditional probability that there will be a center of some hard sphere between r and $r + dr$ when there is none inside the sphere of radius r. Thus

$$-\frac{dp_0}{dr}\,dr = p_0(r)\,\rho G(r) 4\pi r^2 dr \qquad (6)$$

where the above-mentioned conditional probability is factored into the conditional probability density $\rho G(r)$ times the spherical volume element $dv = 4\pi r^2 dr$. The density $\rho G(r;\rho)$ is the average density of hard-sphere centers in contact with the boundary of our spherical cavity. Taking the logarithm

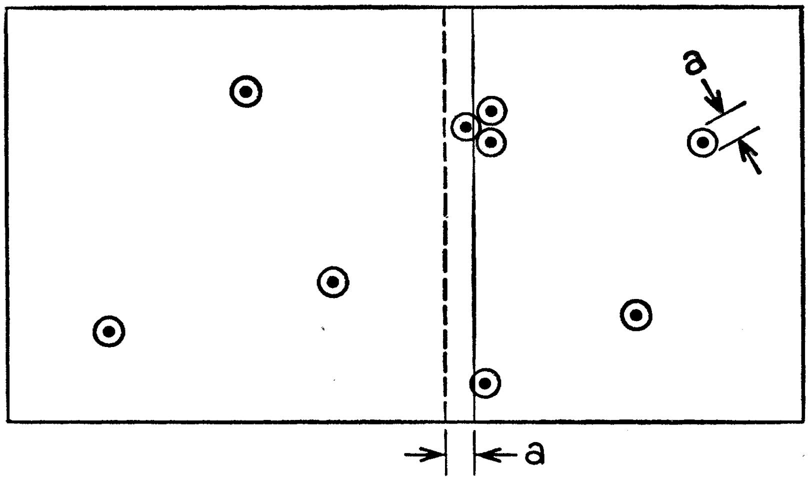

Fig. 3. Container of hard spheres separated by a reflecting wall (solid line) impermeable to hard-sphere centers.

of both sides of Eq. 5, differentiating with respect to r, and comparing the result with Eq. 6, one finds that

$$dW(r) = kT\rho G(r)4\pi r^2 dr = -kT d \ln p_o(r), \quad (7)$$

which relates the differential of $W(r)$ and $p_0(r)$ to $G(r)$. Since $p_0(r) = 1 - 4\pi r^3\rho/3$ for $r < a/2$, and $p_0(r)$ is continuous and possesses two continuous derivatives at $r = a/2$, we find from the second equality in Eq. 7 that

$$G(r) = \frac{1}{1 - \frac{4\pi r^3\rho}{3}} = d \ln p_o(r)/4\pi r^2\rho\, dr \quad (8a)$$

when $r < a/2$, and when $r = a/2$

$$G\left(\frac{a}{2}\right) = \frac{1}{1 - \frac{\pi a^3\rho}{6}} = -[d \ln p_o(r)/4\pi r^2\rho\, dr]_{r=a/2}, \quad (8b)$$

and

$$\left(\frac{dG}{dr}\right)_{r=a/2} = -\frac{\pi a^2\rho}{\left(1 - \frac{\pi a^3\rho}{6}\right)^2}. \quad (8c)$$

The physical significance of $G(r)$ is evident from Fig. 4B, which shows a cavity of radius $r = a$. Note that the effect on the remainder of the fluid is precisely that of a fixed hard sphere, as we readily see in Fig. 4B, where we can imagine we have filled the cavity with such a sphere (indicated by the shading). This implies that

$$G(a) = g^{(h)}(a;\rho). \quad (9)$$

This equivalence of the G and $g^{(h)}$ is true only for this one value of r, $r = a$.

To obtain further insight into the $G(r)$ we reexamine $dW(r)$. This differential of the reversible work of cavity formation consists of a contribution proportional to the spherical cavity volume element $dv = 4\pi r^2 dr$, with coefficient the pressure p, and another contribution proportional to the surface area element of our spherical cavity, $dS = 8\pi r\, dr$:

$$dW(r) = p\, dv + \sigma(r) dS. \quad (10)$$

In Eq. 10, $\sigma(r)$ is the surface tension of hard spheres against a rigid curved wall of mean curvature $2/r$, since a cavity acts like a curved rigid wall (see Fig. 4A). Thus dividing both sides of Eq. 10 by $kT\rho\, dv$ and using the first equality in Eq. 7, we obtain

$$G(r) = \frac{p}{\rho kT} + \frac{2\sigma(r)}{\rho kTr}. \quad (11)$$

Thus $G(r)$ is expressed in terms of entities familiar from thermodynamics.

One knows from conventional thermodynamics that the surface tension at a curved interface is not precisely the constant surface tension σ_0 of the flat interface but is a function of the curvature, $2/r$, which can be expanded in a power series in the curvature (*11*):

$$\sigma(r) \sim \sigma_0(\rho)\left[1 - \frac{2}{r}\,\delta(\rho)a\right], \quad (12)$$

since it generally suffices to retain only the first few terms. The scaled particle theory reveals that the development in the curvature shown in Eq. 12 applies to molecular dimensions with only a small remainder. Using Eq. 12 in Eq. 11 we have an explicit, albeit approximate, $G(r)$ if we can evaluate as functions of ρ the three coefficients p, $\sigma_0(\rho)$ and $\delta(\rho)$. The pressure can be

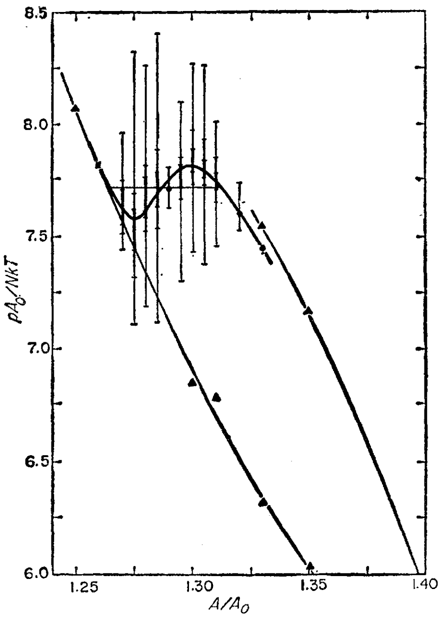

Fig. 2. The equation of state for a fluid composed of 870 hard discs in the phase-transition region. A_0 is the area of the system at close packing; triangles represent points for 72 particles; vertical bars indicate the range of fluctuation in the machine computed results.

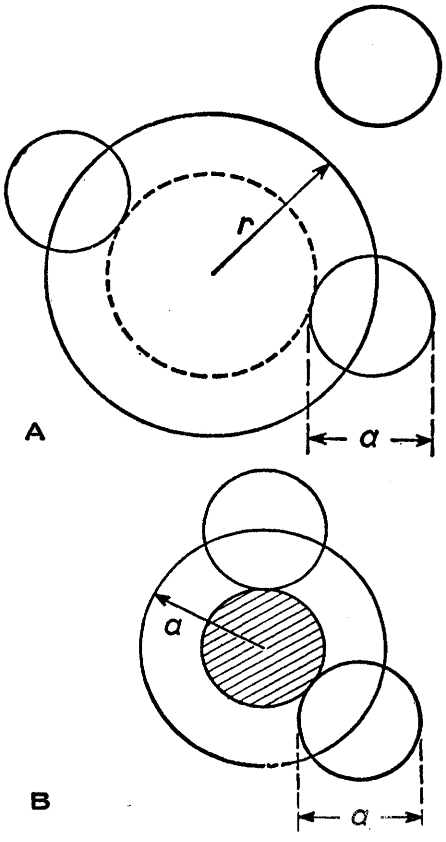

Fig. 4. (A) A spherical cavity of radius r in a hard-sphere fluid. (B) A spherical cavity of radius a (the diameter of the spherical shaded region is a).

eliminated by taking the limit as $r \rightarrow \infty$ of Eq. 11 [with $\sigma(r)$ given by Eq. 12] and the virial equation of state, Eq. 3, together with Eq. 9:

$$G(\infty) = \frac{p}{\rho kT} = 1 + \tfrac{2}{3}\pi\rho a^3 g^{(\mathrm{h})}(a;\rho) = 1 + \tfrac{2}{3}\pi\rho a^3 G(a). \qquad (13)$$

Since $\rho G(\infty)$ is just the density of hard spheres adjacent to a flat wall, $\rho_{\mathrm{w}}(\rho)$, we see that the first equality in Eq. 13 is just our old equation (Eq. 2). We can solve for the remaining coefficients by using our exact equations (Eq. 8), thus obtaining the approximate hard-sphere equation of state

$$\frac{p}{\rho kT} = (1+y+y^2)/(1-y)^3, \qquad (14)$$

where $y = \pi\rho a^3/6$, and the equation for the surface tension

$$\sigma_0(\rho) = -\left(\frac{kT\pi a^4\rho}{8}\right)\left[\frac{1+y}{(1-y)^3}\right]. \qquad (15)$$

We compare Eq. 14 with the results of molecular dynamics calculations, "experiment" so to speak, of Alder and Wainwright (*4*) in Fig. 5. The agreement (to a few percent) over the whole range of fluid densities is gratifying. Also shown in Fig. 5, for comparison, are the predicted equations of state obtained from the older Kirkwood (*12*), Born-Green (*13*), and "free volume" (*3, 14*) theories of liquids. When Eqs. 14 and 15 are expanded in powers of ρ, the first few terms are identical with the known exact result, and the next few are in error only by small percentages. The approximate equation of state (Eq. 14) also results from a systematically improvable theory, formulated by Percus and Yevick (*15*), which is also capable of describing the beginning of the low-pressure (solid) isotherm. The principal shortcoming of Eq. 14 is that it does not give an indication of the phase transition "revealed" by machine computations at densities ρ less than that of the densest regular close packing (as in a face-centered cubic or hexagonal close-packed lattice), which in turn is smaller than the density where Eq. 14 diverges ($y = 1$). The mathematical description of the phase transition is the central unsolved problem in this field of statistical mechanics. Through Eq. 14 we have an approximate expression for $n(a;\rho)$ which reduces to ρ in the Boltzmann limit ($\rho a^3 \rightarrow 0$).

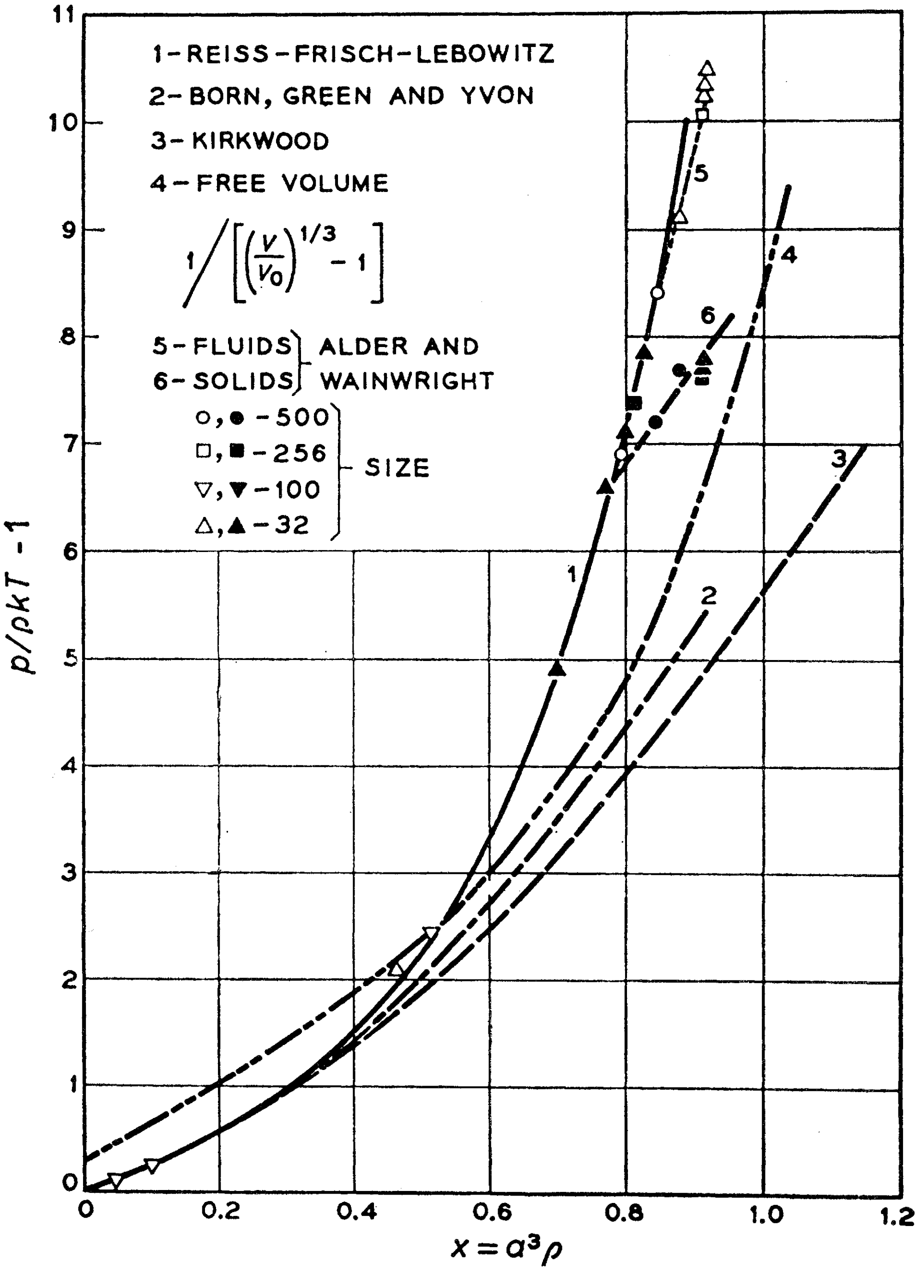

Fig. 5. Comparison of theoretical equations of state with the machine computations of Alder and Wainwright. Line 6 is freely drawn through the machine-computed points for the beginning of the "solid" branch and has no theoretical justification. The data for curves 2 and 3 are taken from (*14*).

Mean Free Path and the Self-Diffusion Coefficient

Transport coefficients, such as the self-diffusion coefficient D, are the most elementary topic in irreversible statistical mechanics because, by their definition, we must determine them under conditions of vanishingly small gradients in mass or by a molecular property such as the momentum. Thus self-diffusion, characterizing mass transport, in our hard-sphere fluid can be studied by painting a few hard spheres to distinguish them from the others. Let $\bar{N}$ be the mean density of painted hard spheres. In a volume element, Δv, small compared to the macroscopic volume of the fluid sample but large enough to contain many molecules, the local density $N(\Delta v)$ may differ from the mean by the excess $\Delta N = N(\Delta v) - N$. If J is the flux of painted molecules and $d\Delta N/dx$ the gradient of the number density excess of painted spheres, then D is by definition

$$D = -J/(d\Delta N/dx) \qquad (16)$$

in the limit as $d\Delta N/dx$ vanishes. Such a small gradient as $d\Delta N/dx$ can arise as a result of a local fluctuation in the number density of painted hard spheres even in a thermostatted (that is, equilibrated) system. One employs such systems experimentally in studying D in real fluids by means of the spin-echo technique where the nuclear spin on a molecule is used to "paint" a few molecules so that they can be distinguished.

We focus attention on D rather than on the property-transport coefficients such as those of viscosity (characterizing momentum transport) or heat conductivity, because at high densities properties, unlike mass, can be transported by two different mechanisms:

1) Free motion of the molecules between collisions; this motion is determined by the mean free path, $\lambda(\rho)$, the mean distance traversed by a molecule between two successive collisions. This is the kinetic contribution.

2) Instantaneous collisional transfer of a property such as the momentum over the diameter of a hard sphere. More generally, this is the potential contribution whose transfer is mediated through the intermolecular potential.

Obviously only the first mechanism can operate in mass transfer, no matter how dense the system. This is a considerable simplification.

Consider a fluctuation producing painted hard-sphere density excesses $\Delta N(x+u\lambda)$ at a volume element at $x + u\lambda$ and $\Delta N(x)$ at x separated by a mean free path $\lambda(\rho)$ as shown in Fig. 6. The flux of painted hard spheres, moving on the average with the mean thermal speed $\bar{c}$ in the thermostatted system, is

$$J = \bar{c}[\Delta N(x) - \Delta N(x+u\lambda)] \sim - u\lambda(\rho)\bar{c}\ d\Delta N/dx \qquad (17)$$

where u is a pure number obtained from averaging only all possible velocities in a binary collision and is known in the attentuated, Boltzmann limit of the hard-sphere gas to be $3\pi/8\ \sqrt{2}$ (*8*, p. 525). Thus, comparing Eq. 17 with Eq. 16, we have

$$D \sim \frac{3\pi}{8\sqrt{2}}\lambda(\rho)\bar{c}. \qquad (18)$$

The mean thermal speed is a function of the temperature and the hard-sphere molecular mass m and is given by elementary kinetic theory (*2*, p. 134) as

$$\bar{c} = 2(kT/m\pi)^{\frac{1}{2}}. \qquad (19)$$

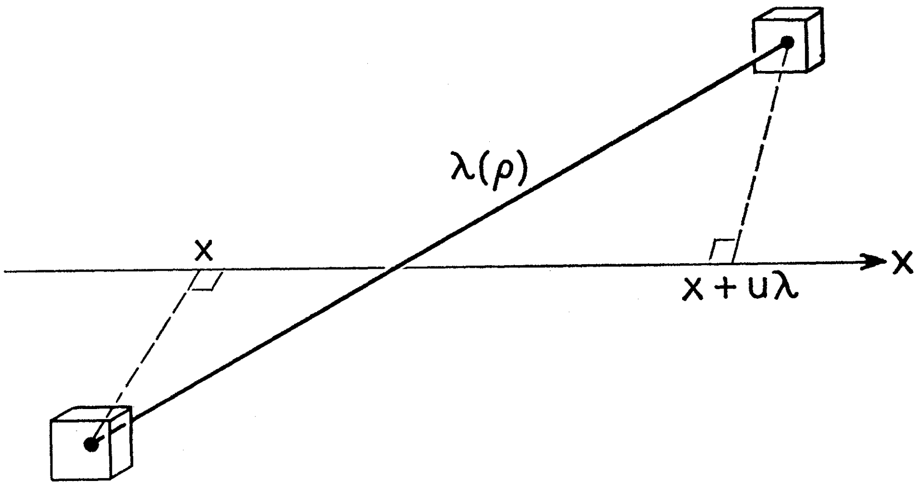

Fig. 6. Schematic diagram illustrating self-diffusion of hard spheres between volume elements separated by a mean free path.

Since the mechanism of mass transfer is the same at all densities, the only density variation in this formula can come from variation of $\lambda(\rho)$.

By definition (*2*, p. 51) the mean free path is

$$\lambda(\rho) = \frac{\bar{c}}{\nu(\rho)} \qquad (20)$$

where $\nu(\rho)$ is the frequency of binary collisions. It is easier to compute first $\nu_f(\rho)$, the frequency of binary collisions with a fixed hard sphere. The number of collisions suffered by such a hard sphere in a time interval dt is given by the number of hard spheres colliding with the fixed sphere (that is, having a separation a between their centers). These must lie within a cylinder of cross section πa^2 and mean length $\bar{c}\ dt$, that is,

$$\nu_f(\rho)dt = \pi a^2 \cdot \bar{c}\ dt \cdot n(a;\rho) \qquad (21)$$

where $n(a;\rho)$ is the effective density given by Eq. 4. To obtain the collision frequency $\nu(\rho)$, we must multiply $\nu_f(\rho)$ by $\sqrt{2}$ to account for the relative motion of the colliding spheres, as is discussed in elementary kinetic theory (2, p. 51), so that (compare Eq. 4)

$$\nu(\rho) = \sqrt{2}\pi a^2 \cdot \bar{c} \cdot n(a;\rho) = \sqrt{2}\pi a^2 \cdot \bar{c} \cdot (p/\rho kT - 1)/\tfrac{2}{3}\pi a^3. \qquad (22)$$

Substituting Eq. 22 into Eq. 20 and the resulting expression into Eq. 18 one finds with $\bar{c}$ given by Eq. 19 that

$$D = \frac{a}{4}\left(\frac{\pi kT}{m}\right)^{\frac{1}{2}} \Big/ \left(\frac{p}{\rho kT} - 1\right) \qquad (23)$$

the well-known Enskog result (*8*, p. 634 ff.; *16*). This equation reduces to the correct Boltzmann limit and agrees within a few percent with machine calculations of D over almost the whole fluid range of densities (*17*).

I shall not discuss the other transport coefficients except to note again that at higher densities the property-transport coefficients contain a nonnegligible collisional (potential) contribution. Thus while the ratio of $D\rho$ to the viscosity is a constant, about 1.2, for the Boltzmann hard-sphere gas, it is the product of D and the viscosity which is more nearly independent of ρ at sufficiently high densities in rough agreement with an often-used empirical correlation for liquids.

Summary and Further Developments

I have noted that the hard-sphere model for a dense, supercritical fluid qualitatively reproduces the observed behavior in that it undergoes a phase transition into a solid phase at a density sufficiently high, yet still below close packing of the spheres (*18*). The analysis of the mechanical basis of the pressure led us naturally to study the spatial correlation in such a fluid. The spatial correlation affects particularly the effective density of hard spheres in contact. This entity was most conveniently examined by focusing attention on density fluctuations which create spherical cavities in the fluid. We thus obtained a very satisfactory approximation to the equation of state. Further analysis of the mean free path and the effect of spatial correlation on it allowed us to deduce the behavior of the self-diffusion coefficient.

I have connected, in passing, our "scaled particle" results with actively evolving theories such as the Percus-Yevick theory (*16*) and have mentioned the knowledge of the first few coefficients in the development in density of the equation of state, the so-called virial series. The nature of the mathematical convergence of this series and certain related questions are currently under investigation and have an important bearing on the phase transition problem as well as on the behavior of the fluid at low density. At very high densities, near to close packing, an (asymptotic) expansion in the reciprocal density has recently been obtained (*19*). This, too, promises to shed light on the elusive mathematical problem of the phase transition and the structure of the "solid" phase.

To further understand real fluids we have to take into account the soft, primarily attractive part of the intermolecular potential. At high enough temperatures the soft (nonhard) core part of the intermolecular potential can be systematically treated as a small perturbing potential acting on a fluid composed of the hard cores of the molecules. Such a perturbation theory has been developed both for the equation of state (*20*) and for the transport coefficients (*21*). The thus corrected equation of state will predict a condensation and the appearance of a liquid phase that ceases beyond the so-called critical point. Space does not permit me to enlarge on these questions or on the bearing they have on phase transitions in general in other many-body problems (*22*).

References and Notes

1. The orientation of this paper is primarily pedagogical. No attempt is made to provide a historical setting or to review all the pertinent literature. The elements of the kinetic theory of gases used are adequately covered in T. G. Cowling, *Molecules in Motion* (Harper, New York, 1960).
2. T. G. Cowling, *Molecules in Motion* (Harper, New York, 1960) p. 43.
3. The hard-sphere model has a venerable history in kinetic theory as a result of the simplicity of the dynamics of these model molecules. Thus the binary collision cross section is independent of the relative velocity of the colliding spheres. Recently Y. Sinai, *Dokl. Akad. Nauk SSSR* **153**, 1261 (1963), has announced a proof of the ergodic theorem for the hard-sphere system in a rectangular box. Thus this system has the distinction of being effectively the only nontrivial many-body system for which the application of statistical mechanics is justified by theory. For a summary of the equilibrium properties of this system see for example, H. L. Frisch, *Advan. Chem. Phys.* **6**, 229 (1964), and references cited therein.
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16. This result has interestingly the form expected from a "free volume" theory of diffusion. This can be seen more explicitly. One notes that the pressure p of a fluid is related to the statistical thermodynamic free volume [see for example T. L. Hill, *Statistical Mechanics* (McGraw-Hill, New York, 1956), p. 360] $v_f(\rho,T)$ through the equation

$$p = kT \int_0^\rho d\rho' \left[\frac{\partial \ln . v_f(\rho',T)}{\partial \ln \rho'} \right]_T$$

Hence, for hard spheres, if this equation is substituted in Eq. 23

$$D = \frac{a\pi\bar{c}\rho}{8} \times \left[\int_0^\rho d\rho' \left[\frac{\partial \ln v_f(\rho',T)}{\partial \ln \rho'} \right]_T - \rho \right]^{-1}$$

which differs though from the usual Doolittle relation used to correlate the behavior of complex fluids.
17. B. J. Alder and T. E. Wainwright, *Transport Processes in Statistical Mechanics*, I. Prigogine, Ed. (Interscience, New York, 1958), p. 121.
18. A more detailed discussion of the nature of the phase transition can be found in F. H. Stillinger, Jr., E. A. diMarzio, R. L. Kornegay, *J. Chem. Phys.* **40**, 1564 (1964).
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The Ethical Basis of Science

Bentley Glass

It has been said that science has no ethical basis, that it is no more than a cold, impersonal way of arriving at the objective truth about natural phenomena. This view I wish to challenge, since it is my belief that by examining critically the nature, origins, and methods of science we may logically arrive at a conclusion that science is ineluctably involved in questions of values, is inescapably committed to standards of right and wrong, and unavoidably moves in the large toward social aims.

Human values have themselves evolved. Man arose after some two billions of years of organic evolution, during which species after species originated, flourished, and fell, or occasionally became the progenitors of species that were new and better adapted, on the basis of the evolutionary scheme of values. Fitness, like it or not, in the long run meant simply the contribution of each trait and its underlying genes to survival. High mortality or sterility led to extinction; good viability and fertility enabled a gene or a trait, an individual or a species, to be perpetuated. Man's own values grew out of his evolutionary origins and his struggle against a hostile environment for survival. His loss of certain unnecessary structures, such as bodily hair once clothing was invented; the homeostatic regulation of his body temperature and blood pressure, breathing, and predominant direction of blood flow; his embryonic and fetal growth inside the mother and his prolonged dependence upon ma-

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