progressively inaccurate as a is raised from 0.2 to 0.8. The net result of these calculations is that for the charged-point and the neutral-point cases, the distribution curves generated by the present theory favor slightly stronger fields than does the theory of BM.

As in I, the method of including noncentral forces through the mechanism of collective coordinates is shown to be highly effective. Exactly how good this method is, is evidenced when the second term in the cluster expansion is calculated; here one finds that the noncentral, two-particle correlations are included, through the use of collective coordinates, to the approximation of the nonlinear Debye-Hückel result. Since this second term is only a small correction to the theory, even in the case of high a values, such an approximation must be considered highly accurate. Furthermore, during the derivation of the general formalism, especially that part relating to the cluster expansion, the fact that it was not necessary to explicitly mention noncentral interactions resulted in much simplification.

Note added in proof. It has recently come to the author's attention that H. Pfenning and E. Trefftz [Z. Naturforsch. **21a**, 697 (1966)] have employed a corrected version of the BM method to generate $P(\epsilon)$ values for neutral point cases. Their results agree quite well with those presented in this paper and in I.

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Dense-Gas Formulation of Self-Diffusion of Liquid Metals*

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An accurate theory for the self-diffusion coefficient of liquid metals is developed in terms of the Van der Waals concept of a dense fluid. Making use of the Enskog hard-sphere formulation we obtain the following results: 1) a relationship for the coefficient of self-diffusion which accurately gives both the magnitude and temperature dependence over the entire liquid range at atmospheric pressure; 2) a relation between the melting point and the coefficient of self-diffusion which is the freezing counterpart of the Lindemann law of melting.

RECENTLY, Dymond and Alder[1] have demonstrated that the Van der Waals concept of a dense fluid yields a simple and accurate description of the transport properties of the rare-gas fluids. The underlying idea in this treatment is that particles move in straight lines between core collisions. The attractive potential energy or cohesive energy term is thought of as a uniform negative potential[2] which does not affect the basically hard-sphere collisions.[3]

In liquid metals, the cohesive energy expressed in units of the melting temperature T_m is an order of magnitude larger than that of rare-gas liquids. However, pseudopotential calculations show that a pair-wise interaction is a valid representation of the interaction energy between electronically screened ions, and that the attractive part of this pair-wise interaction is comparable to that found in rare-gas liquids.[4] Furthermore, the structures of all simple liquids, metallic and nonmetallic, are approximately the same[5,6] when compared at the melting temperature, using as a unit length $r_m=[(3/4\pi)\Omega_m]^{1/3}$, Ω_m being the mean atomic volume at the melting point. This substantiates molecular dynamics calculations[6] which show the insensitiveness of the liquid structure to the details of the pair interaction. Thus, we expect comparable (scaled) effective potentials to be a good approximation for metals and insulators at their melting points. As the Van der Waals concept yields a reasonable description of the rare-gas liquids, we shall here make use of the Van der Waals cohesive-energy-density term as an effective uniform negative potential over the entire temperature range for liquid metals at atmospheric pressure.

In applying this approach to D, the coefficient of self-diffusion of liquid metals, the basic approximations we make are: the use of the Enskog derivation of D for hard-sphere dense fluid, further corrected in accord

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[1] J. H. Dymond and B. J. Alder, J. Chem. Phys. **45**, 2061 (1966).

[2] H. C. Longuet-Higgins and B. Widom, Mol. Phys. **8**, 549 (1964).

[3] H. L. Frisch, Science **150**, 1245 (1965).

[4] W. A. Harrison, *Pseudopotentials in the Theory of Metals* (W. A. Benjamin, Inc., New York, 1966).

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with molecular dynamics calculation, the hard-sphere gas pressure is set equal to the Van der Waals cohesive-energy-density term, which is thought of as a uniform negative potential, and the packing fraction of all simple liquids is 0.45[7] at their melting point. With these assumptions, we obtained the following results: 1) a relationship for D for metals which accurately gives both magnitude and temperature dependence over the entire liquid range at atmospheric pressure, and 2) a relation between the melting point and the coefficient of self-diffusion which is the freezing counterpart of the Lindemann law of melting.

For calculating the transport coefficients of liquid metals, we first make use of the Enskog theory for dense hard-spheres systems.[8] In the Enskog theory, the difference between the collision rate in high density and low density arises mainly because the diameter of hard spheres significantly decreases the distance that two spheres have to travel in order to collide as systems became denser.

We may therefore write the self-diffusion coefficient as

$$D=D_g/\chi, \tag{1}$$

where D_g is the self diffusion of gas of hard spheres and χ is the Enskog high-density correction; making use of the Enskog relation between χ and the hard-sphere pressure we obtain

$$D=\tfrac{1}{2}l\left(\frac{\pi KT}{M}\right)^{1/2}\frac{1}{(P/\rho KT)-1}, \tag{2}$$

where l is the hard-sphere radius, M is the atomic mass, ρ is the mean atomic density, K is the Boltzmann constant, and T is the temperature.

A hard-sphere radius at the melting point can be obtained in a variety of ways. It can be related to a Lennard-Jones potential,[1] or derived by matching an experimental liquid structure with the Percus-Yevick hard-sphere dense-fluids approach,[7] or from the packing fraction which has been obtained at the freezing-phase transition by molecular dynamics calculation of hard-sphere phase transition.[9]

Such a hard-sphere radius is expected to be temperature-dependent and to vary somewhat with the properties it is chosen to match. This is not surprising as the hard-core radius is essentially some average of the repulsive part of the pair interaction. For example, while the structures of liquid sodium and liquid argon are essentially the same at their melting point, implying almost coincident hard-sphere radii, their structure factor at zero wave vector[10] differ by a factor of 2.5, which would imply a change in the packing fraction of 30%, which is an unreasonably large difference.

TABLE I. Comparison of the calculated and experimental self-diffusion coefficient of simple liquid at the melting point.

	$D_{\mathrm{exp}}10^5(\mathrm{cm}^2/\mathrm{sec})$	$D_{\mathrm{cal}}10^5(\mathrm{cm}^2/\mathrm{sec})$	$\Delta D\%$
K	3.90[a]	3.86	−1
Na	4.05[a]	4.2	+4
In	1.66[b]	1.78	+7
Sn	2.05[b]	1.92	−6
Zn	2.02[a]	2.52	+25
Cu	3.96[a]	3.32	−16
Pb	2.19[a]	1.7	−22
Ag	2.55[a]	2.8	+10
Hg	1.17[c]	0.98	−20
Ar	1.53[d]	1.6	+4
Li	6.5[e]	7	+7
Ge	1.67[f]	1.7	+2

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[b] G. Careri, A. Paoletti, and M. Vicentini, Nuovo Cimento **10**, 1088 (1958).
[c] R. E. Meyer, J. Chem. Phys. **65**, 568 (1961).
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We here assume that all simple liquids, metallic and nonmetallic, at their melting point show the same packing fraction, or that the ratio l/r_m is a constant, specifically $\eta(T_m)=l^3/r_m{}^3=0.45$, which has been shown to fit the diffraction data of a number of different liquid metals by the hard-sphere Percus and Yevick (P.Y.) liquid model.[7]

The main contribution to the temperature dependence of the Enskog correction χ is contained in the pressure-dependent term in (2). The hard-sphere equation of state can be obtained in several ways: Dymond and Alder use experimental rare-gas data, from which they derive the hard-core size; or one can follow the approach outlined by Guggenheim[11] which directly relates hard sphere pressure to a Van der Waals attractive term. The basic idea is that at atmosphereic pressure the hard-sphere repulsive pressure has to be balanced almost completely by an attractive Van der Waals term $a\rho/KT$ where a is the usual Van der Waals constant.

We obtain $a\rho/KT$ by using the P.Y. hard-sphere equation of state,[12] namely

$$\frac{a\rho}{KT}=\frac{1+\eta+\eta^2}{(1-\eta)^3}, \tag{3}$$

recalling that all parameters must be related at the melting point where $\eta_m=0.45$, we obtain

$$a\rho_m/KT_m=10. \tag{4}$$

From this argument we arrive at the following form for the Enskog self-diffusion coefficient:

$$D=\frac{0.77}{2}r_m\left(\frac{\pi KT}{M}\right)^{1/2}\frac{1}{[(10T_m\rho/T\rho_m)-1]}. \tag{5}$$

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[7] N. W. Ashcroft and J. Lekner, Phys. Rev. **145**, 83 (1966).

[8] S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, New York, 1939).

[9] B. J. Alder and T. Wainwright, J. Chem. Phys. **31**, 659 (1959); **33**, 1439 (1969), Nuovo Cimento Suppl. **9**, 133 (1952).

[10] The structure factor at zero wave vector $a(0)$ is equal to $KT\times\rho\times C_T$, where C_T is the isothermal compressibility.

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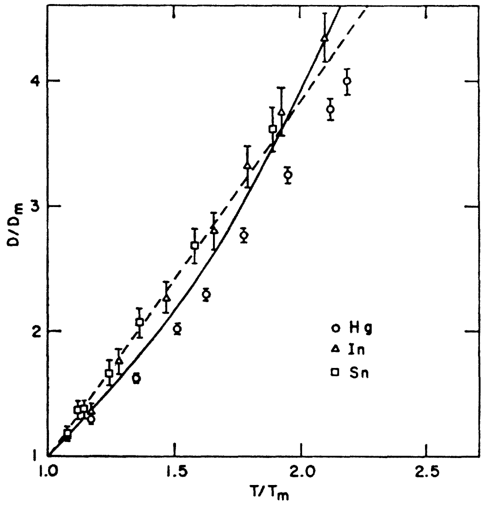

FIG. 1. Comparison of the temperature dependence of D for △ In, □ Sn, and ○ Hg with theory. The full curve is the hard-sphere calculation and the dashed curve is the phenomenological "activated" form $D\propto(T/T_m)^{1/2}e^{-2T_m}/T$. It may be noticed that this last form is also approximated by a linear temperature dependence.

By molecular dynamics calculations of hard spheres,[1] Alder and Wainwright[13] have found that at high density there is a 30% correction to the Enskog formula. For temperatures in the liquid-metal range, the back-scattering correction has been approximated by 0.73 $(\eta_m/\eta)^{1/2}$,[14] and the complete hard-sphere dense-fluids formula becomes

$$D=0.28r_m\left(\frac{\pi KT}{M}\right)^{1/2}\frac{(\eta_m/\eta)^{1/2}}{[(10T_m\rho/T\rho_m)-1]}.\qquad(6)$$

In this formula, while η_m is set equal to 0.45, $\eta(T)$ has been derived at each T by the use of the relation (3) when the constant a is given by (4).

We first demonstrate the validity of (6) by comparing the calculated and observed self-diffusion constants at the melting point, Table I. The agreement between the calculated and observed values for self-diffusion is striking, especially when one considers that the experimental error is generally of the order of 10%.

The temperature dependence of formula (6) is also in good agreement with experiment as shown in Fig. 1. It is worth noticing that the hard-sphere liquid-diffusion process is not an activated one, a point emphasized earlier by Dymond and Alder.

However, the experimental temperature dependence of D for liquid metal is also well fitted by a temperature-dependent coefficient of the form $(T/T_m)^{1/2}e^{-2T_m/T}$. The temperature dependence of this form and of that of Eq. (6) are compared in Fig. 1.

Having found the good agreement for D_m, the coefficient of self-diffusion at the melting point, it is apparent that we have arrived at a relationship which relates the melting point with the self-diffusion, namely,

$$T_m=CMD_m^2/r_m^2,\qquad(7)$$

where C is a dimensional constant equal to 334K^{-1} (deg/erg). At first glance, this relationship might be interpreted as the liquid-state counterpart of the Lindemann formula which relates the melting point to the Debye temperature. It is amusing to recall that Lindemann originally arrived at his relationship by hard-sphere arguments,[15,16] namely, a substance will melt when the shortest distance between the centers of vibrating atoms equals the hard-sphere diameter.

In this note, we have emphasized the coefficient of self-diffusion relationship. Ashcroft and Langreth have recently demonstrated that the structure of alloys is also well approximated by hard-sphere arguments.[17] The transport properties may similarly be treated in terms of hard-sphere arguments and should complement the hard-sphere radii used to fit the structural data. The agreement between experiment and theory for the coefficient of self-diffusion suggests that the hard-sphere dense-gas approach should also be a good description for other mass-transport properties such as viscosity, and it also suggests the extension from pure metals to alloys.

Note added in manuscript. In approximating the back-scattering correction as 0.73 $(\eta_m/\eta)^{1/2}$, we made use of the earlier work of Alder and Wainwright.[13] Since submitting this manuscript, Alder and Wainwright have calculated these corrections in more detail [Private communication and Phys. Rev. Letters **18**, 988 (1967)]. Using their more recent work, a better back-scattering approximation is 0.73 (η_m/η). This would increase our theoretical temperature dependence by 15% at the highest temperature and bring the calculations into closer over-all agreement with the Sn and In data.

ACKNOWLEDGMENTS

It is a real pleasure to thank B. J. Alder for the many stimulating discussions which were directed toward converting us to the hard-sphere approach to understanding liquids.

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[13] B. J. Alder and T. Wainwright, in *The Many Body Problem*, edited by J. K. Percus (Interscience Publishers, Inc., New York, 1963).

[14] We have used the comparison of the diffusion coefficient obtained by the Enskog relation and hard-sphere molecular dynamic calculations to estimate the correction to the Enskog formulation. While the correction of about 30% seems reasonable for packing fractions corresponding to the melting point, the Alder-Wainwright calculations quoted do not seem accurate enough to give the packing fraction at which the correction goes to unity. We have taken the correction to be about 15% in the high-temperature region near the boiling points.

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