$+ \int_0^T S_0(\theta)d\theta]$ vs T, so that the slope of the curve
is $\bar{S}$. We observe that $\bar{S}$ falls to a minimum
which is equal to zero within experimental uncer-
tainty at the onset in both of these curves. This
behavior of $\bar{S}$ accounts for the disappearance of
third sound and other thermally excited super-
flow at the transition, without requiring that $\rho_S/$
ρ vanish.[11]

We believe these results throw new light on the
nature of the film. For the first time the onset
curve may be related directly to an independent
measurement of a thermodynamic property of
the film. On the other hand, there is apparently
another transition curve to the right of the onset
curve in Fig. 1 where ρ_S really goes to zero.
The nature of the film between these curves,
with finite ρ_S but without macroscopic flow, pre-
sents an interesting problem for the future.[12]

A more detailed report on the adsorption prop-
erties of the film is in preparation.

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DENSITY-DEPENDENT POTENTIALS AND THE HARD-SPHERE MODEL FOR LIQUID METALS

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It has been found that various properties of liquid metals are interpretable in terms of
a hard-sphere model. Since electronic screening of pair interactions in metals leads to
density-dependent hard-sphere diameters, we have examined the effect that this has on
the thermodynamic equations. The virial equation is shown to contain extra contributions
to the pressure and compressiblity which are quite relevant for metallic systems. The
behavior of alkali metals is discussed.

In many treatments of the condensed state the
simplifying assumption often is made that the to-
tal N-particle interaction can be considered to be
the sum of independent pair-wise contributions.
At least for one class of systems, the rare gas-
es, this approximation is known to be rather ac-
curate.[1] For other cases important many-body
effects arise and this assumption becomes ques-
tionable. However it is sometimes possible to in-
clude the most important part of the contribution
of the many-body forces in a self-consistent
treatment in which pair interactions alone are
formally retained, but in which these become im-
plicit functions of the thermodynamic variables.

In metals this reduction is also complicated by
the two-component nature of the system of ions
and electrons. Nevertheless pair potentials re-
flecting the screening of the ionic charges by the
electron gas have been suggested and used suc-
cessfully in a variety of problems.[2,3] These
screened potentials are always implicit functions
of the electron density, and by neutrality, of the
ion number density. The temperature dependence
of potentials which have been used is negligible.

The purpose of the present paper is to discuss
the contributions to pressure and compressibility
in liquid metals arising from the explicit density
dependence of these effective pair interactions in
the liquid state. We point out that the hard-sphere
model of liquids can be encompassed within this

formalism by considering the hard-sphere diameter to be density dependent. Since it has become increasingly evident that the hard-sphere fluid may be considered a reasonable limit case for the description of the liquid state[4] and can be successfully applied to the case of liquid metals,[5,6] we have chosen to formulate our discussion in this Letter specifically for the hard-sphere model, leaving the treatment of general potentials to a more detailed article.

The virial equation for the case of a density-dependent central pair potential $\Phi(r_{ij};\rho)$ can be written

$$\frac{p}{\rho k_B T} = 1 - \frac{\rho^2}{2k_B T}\int d^3r \left[\frac{r}{3\rho}\frac{\partial \Phi}{\partial r} - \frac{\partial \Phi}{\partial \rho}\right] g(r;\rho); \qquad (1)$$

p is the pressure, T is the temperature, and k_B is Boltzmann's constant. $g(r;\rho)$ is the pair distribution function at number density ρ for a pair of particles separated at distance r and by definition is taken here to be that which would result in a system at fixed density ρ; that is, it is defined in the canonical ensemble. Equation (1) differs from the usual virial equation only in the additional term in $(\partial \Phi/\partial \rho)$.[7] In order to apply Eq. (1) to a hard-sphere model in which the hard-sphere diameter d is a function of number density ρ, the derivatives of the pair potential must be replaced in the usual way[8] by a delta function of appropriate strength. The resulting virial equation for the hard sphere is

$$\frac{p}{\rho k_B T} = 1 + g(d,\rho)\frac{2\pi}{3}\rho d^3\left[1 + 3\frac{\rho}{d}\frac{\partial d}{\partial \rho}\right]. \qquad (2)$$

Again one can verify that for the case of constant diameter this reduces to the standard form.[9] It is convenient to rewrite Eq. (2) in terms of the packing fraction $\eta = \frac{1}{6}\pi\rho d^3$ and the quantity $\Gamma = (\partial \ln\eta/\partial \ln\rho)$. It becomes

$$p/\rho k_B T = 1 + 4\eta g(\eta)\Gamma, \qquad (3)$$

where $g(\eta)$ is written for $g(d;\rho)$ since this is a function of η alone. By differentiating at constant temperature one can easily obtain an expression involving the isothermal compressibility,

$$(\rho k_B T\chi_T)^{-1} = 1 + 4\eta g\Gamma[1 + \Gamma$$

$$+ \eta(g'/g)\Gamma + \eta\Gamma'], \qquad (4)$$

where the primes denote differentiation with respect to η at constant T. Equation (4) will reduce to the result obtained without volume dependence

when $\Gamma = 1, \Gamma' = 0$. In general it will be different from this value except for fortuitous circumstances involving relationships between g, g', Γ, and Γ'.

It is interesting at this point to discuss the effect of some hypothetical functional relationships between d and ρ. First, if d varies as the nth power of ρ, the value of Γ will be $1 + 3n$, while $\Gamma' = 0$. The particular case that $n = -\frac{1}{3}$, for which $\Gamma = 0$, is of special interest. According to Eq. (4) this case will result in the perfect gas equation of state! The value $n = -\frac{1}{3}$ implies that the packing fraction η remains constant as the volume is changed. Therefore the radial distribution function will exactly scale with d, and it is plausible that the "excess entropy" does not change. Thus the thermodynamic relationship $(\partial S/\partial V)_T = (\partial p/\partial T)_V$, which in particular for hard spheres can be written simply as $(\partial S/\partial V)_T = p/T$, then shows that p/T must be identical with that of a perfect gas, although the entropy is not.[10]

A second case having striking consequences is when $\Gamma^{-1} = 4\eta g(\eta)$. Just as the volume dependence of the diameter can compensate for the nonideality correction of the virial, it can go further and compensate for the kinetic pressure as well. The condition for zero pressure is just $\Gamma^{-1} = 4\eta g(\eta)$. Recalling that $\Gamma = \partial \ln\eta/\partial \ln\rho$, this condition is a first-order differential equation determining ρ as a function of the packing fraction η, and hence implicitly d as a function of ρ. For example, one may obtain $\rho(\eta)$ for the particular form of $g(\eta)$ given by the Percus-Yevick equation. This condition of zero pressure is of course a stability condition, illustrating that particular volume dependencies may in fact lead to phase transitions. We shall not go further into this here.

Hard-sphere model of metals. — The hard-sphere model applied to liquid metals has recently been shown to be quite successful in explaining various properties.[5,6] Because the volume dependence of the pair interaction is likely to be considerably more important in metals than in nonconducting condensed systems,[3] it would appear necessary for the further development of this model to explicitly consider a volume dependence of hard-sphere diameter.[11] We shall briefly review the essentials of the hard-sphere model and its foundations in the more general theory of pair potentials in metals.

While discussion of the energy of a metal in terms of pair interactions was implicit in many formulations, a more modern treatment, which attempts to relate this decomposition into pair in-

teractions to a rigorous formulation of the elec-
tronic theory of metals, was initially given by
Cohen.[12,13] For present purposes, staying within
that approximation which assumes that a separa-
tion of structural and nonstructural contributions
to energy can be made, and taking the kinetic en-
ergy of the ions in the liquid state to be $\frac{3}{2}Nk_BT$
and volume independent, and neglecting as well
the broadening of the Fermi-Dirac distribution
of electronic momentum, the expression for the
energy[12] can be written as

$$E = E_0(V) + \tfrac{1}{2}\sum_{i \neq j} \Phi(r_{ij};\rho) + \tfrac{3}{2}Nk_BT. \tag{5}$$

The term E_0 includes the reference zero for the

bottom of the conduction band together with the
total energy of electrons in the conduction band.
It thus depends explicitly upon volume as well as
upon number density. Any structural dependence
of the bottom of the band is assumed to be includ-
ed in the pair terms.

Consistent with the expression given for ener-
gy, the pressure can be obtained and it is obvious
that in addition to the pressure arising from the
pair interaction terms, there is also the contri-
bution $-(dE_0/dV)$. Because of the assumption of
complete degeneracy of the electron gas it is not
necessary to specify that this derivative is isen-
tropic. For reference we will write the complete
formula for pressure p as

$$p = -\frac{\partial E_0}{\partial V} + \rho k_B T \left\{ 1 - \frac{\rho^2}{2k_B T} \int d^3r \left[\frac{r}{3\rho} \frac{\partial \Phi}{\partial r} - \frac{\partial \Phi}{\partial \rho} \right] g(r;\rho) \right\}. \tag{6}$$

To relate this to experimental quantities, not on-
ly does one need to know the specific forms of E_0
and of the pair interactions but one needs to know
the pair distribution function corresponding to the
assumed pair interactions. To obtain this latter
function requires either extensive numerical cal-
culations by molecular dynamics techniques or
else approximate analytic calculations.[3] Since,
as has been discussed previously, a hard-sphere
model for liquid metals provides a qualitatively
correct description of the short-range order in
liquid metals and successfully predicts various
properties, we choose to consider the approxima-
tion that the pair potential $\Phi(r_{ij};\rho)$ be replaced
by a hard-core pair interaction. The success of
this admittedly crude simplification is probably
due to the fact that in the liquid state of metals
the contribution of the attractive part of the pair
interaction is as small, either with respect to
the total energy which is essentially determined
by E_0 (consistently with a perturbation treatment
of the electron gas), or with regard to the con-
figurational entropy and its volume derivative.
The observation that the experimentally deter-
mined structures of all simple liquids, metallic
and nonmetallic, can with a good approximation
be understood only as a result of packing of hard
spheres, indicates the prevailing role that short-
range repulsive forces play in determining the
structure and hence the configurational entropy
of liquids.

Thus in the density-dependent hard-core ap-
proximation the pressure expression can be giv-
en as

$$p = -\frac{\partial E_0}{\partial V} + \rho k_B T[1 + 4\eta g\Gamma]. \tag{7}$$

At this point it is useful to try to estimate the
nature of the correction arising from the density
dependence of the pair interaction.

First, a Thomas-Fermi model[14] of screening
of a point ion leads to a screening distance that
varies as the inverse $\frac{1}{6}$ power of the number den-
sity of electrons, and hence of ions, in a neutral
system with metallic densities. If we assume for
the sake of argument that the hard-sphere radius
varies as the screening length, the quantity Γ de-
fined previously would be equal to $\frac{1}{2}$, while its de-
rivative is zero. Thus the hard-sphere correc-
tion is reduced by a factor of 2.

Second, an alternate plausibility argument can
be given to justify a choice of hard-sphere radius
varying inversely as the Fermi momentum k_F,
hence as the inverse $\frac{1}{3}$ power of number density,
giving $\Gamma = 0$. This might be expected to be reason-
able when the potential is well represented by the
asymptotic form varying as $\cos(2k_F r)/r^3$.[2]

Third, recently Dickey et al.[15] have calculated
the dependence of the resistivity of alkali metals
under volume changes in the framework of a
phase-shift analysis. For this purpose they de-
fined a hard-sphere diameter and a corresponding
packing fraction, and calculated the density de-
pendence of these quantities. Because of the dif-
ferent character of the screening charges in the
various alkali metals differing results were ob-
tained. For Li the packing fraction remained
fairly constant with change in volume, while for
K and Rb the diameters remained approximately
constant. Thus according to these results the
value $\Gamma = 0$ is appropriate for Li, and therefore

the pressure is given for Li by

$$p = -\frac{\partial E_0}{\partial V} + \rho k_B T,$$ (8)

while for K and Rb, the value $\Gamma = 1$ is appropriate
and the pairing forces give the usual hard-sphere
contribution to the total pressure.

In summary we wish to stress that apart from
the question as to which form of volume-depen-
dent potential is to be used in any given situation,
the fact that these volume-dependent forces exist
means that important corrections to the pressure
and to the compressibility arise. We can specu-
late that in higher approximation, as the volume-
dependent forces are replaced by ones on local
density, corrections to the radial distribution
function will arise which in momentum space
amount to corrections at very small momentum
vectors.

In this work we have discussed some of the con-
sequences that a volume-dependent pair interac-
tion has on the behavior of classical systems of
particles. Most important, we feel that these
corrections affect properties of metals and are
especially relevant when the behavior of insulat-
ing and metallic systems are compared not only
with respect to properties of a single phase but
also in characterizing the trend at a first-order
phase-phase transition when volume changes oc-
cur, and also when diffusion at constant volume
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We thank Professor E. Lieb and Professor I.
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that corrections due to an "excluded volume" would
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to volume, since the volume then simply is renormal-
ized. A consideration of entropy such as we have giv-
en is however necessary to understand quantitatively
why the full volume is retained in the perfect-gas equa-
tion.

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through the volume dependence of potential together
with the thermal expansion is expected to be small due
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The temperature dependence deriving from the finite
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