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 total N-particle interaction can be considered to be the sum of independent pair-wise contributions. At least for one class of systems, the rare gases, this approximation is known to be rather accurate.[1] For other cases important many-body effects arise and this assumption becomes questionable. However it is sometimes possible to include 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 implicit 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 reflecting the screening of the ionic charges by the electron gas have been suggested and used successfully 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

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

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

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

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

$$p/\rho k_{\mathrm{B}}T=1+4\eta g(\eta)\Gamma, \qquad (3)$$

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,

$$(\rho k_{\mathrm{B}}T\chi_T)^{-1}=1+4\eta g\Gamma[1+\Gamma+\eta(g'/g)\Gamma+\eta\Gamma'], \qquad (4)$$

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 $\Gamma^{-1}=\underset{\wedge}{-}4\eta g(\eta)$. 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 $\Gamma^{-1}=\underset{\wedge}{-}4\eta g(\eta)$. 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-