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High-temperature free-energy expansion for metal fluids

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The cluster expansion of the Helmholtz free energy is based on two-body interactions through a central potential $\phi(r)$. For a fluid at fixed density, it is shown that the cluster expansion provides a convergent high-temperature expansion of the free energy. Because $\phi(r)$ for a liquid metal depends explicitly on the density, the corresponding cluster expansion of the pressure differs from the ordinary virial series. For a physically realistic interaction, $\phi(r)$ is integrable at small r. From this it follows that the two-body-interaction contributions to thermodynamic functions for realistic fluids are bounded at high temperatures. In contrast, for potentials such as Lennard-Jones which are not integrable at small r, these thermodynamic contributions increase without limit as the temperature increases.

I. INTRODUCTION

In computer simulation techniques, e.g., Monte Carlo and molecular dynamics, it is not possible to determine directly the entropy S of a dense fluid at moderate temperatures; it is necessary to begin at some limiting state, where the constant of integration is known, and then integrate dS along a thermodynamic equilibrium path to the dense-fluid state. Two such limits have been established, and have been used to determine the entropy of a dense fluid. When the interatomic forces are of sufficiently short range, the cluster expansion of the Helmholtz free energy F exists, and the expansion converges at low density. From this result, Hoover and Ree[1] calculated F for a hard-sphere fluid, by evaluating F for the dilute gas, and then integrating dF to the dense-fluid phase. Hansen and Verlet[2] used the same procedure for the Lennard-Jones system. For Coulomb forces, the cluster expansion does not exist, but a resummation leads to a Debye-Hückel limit at high temperatures.[3] Brush, Sahlin, and Teller[4] used the Debye-Hückel limit to determine the entropy of the fluid phase of the one-component plasma.

In the present work we are interested in liquid metals at moderate temperatures, i.e., at temperatures where thermal excitation of electrons from their ground state is weak (a perturbation). For this system, neither of the above methods gives us a straightforward way to evaluate the entropy constant of integration. If we think of going to the dilute gas limit, difficulties arise because of the volume-dependent term in the total energy of the metal, and the volume dependence of the effective ion-ion potential [see, e.g., Eq. (1)]. On the other hand, the ion-ion interactions in a metal at moderate temperatures are of shorter range than Coulomb, due to electronic screening, so the metal is not a plasma, and the Debye-Hückel limit is not the correct high-temperature limit. In fact, the cluster expansion provides a suitable high-temperature limit for liquid metals, as shown in Secs. II and III below. Some unusual properties of the cluster expansion are found from its application to metals; specifically, the pressure expansion is different from the ordinary virial series, and the potential-energy contribution to any thermodynamic function is bounded in the high-temperature limit. The qualitative temperature dependence of the heat capacity from melting to the high-temperature limit, due to motion of the ions but neglecting electronic excitations, is discussed in Sec. IV, and our calculations for liquid Na are found to display the expected behavior.

II. THE CLUSTER EXPANSION

We consider a neutral system of N ions plus their associated electrons, representing a monatomic liquid metal, in a volume V at a temperature T. In first approximation the electrons are in their ground state, and the total system energy is the kinetic energy of the ions plus the total adiabatic potential Φ, where

$$\Phi=\Omega(V)+\sum\phi(r;V) . \tag{1}$$

Here $\phi(r;V)$ is a central potential between two ions separated by a distance r, and the sum is over all distinct pairs of ions. The dependence of ϕ on V arises through the electrons. Thermal excitation of the electrons, as long as it is weak, is accounted for by an additive term in the free energy[5]; this term should be kept for accurate thermodynamics, but we omit it in the following because it is not relevant to our discussion. At very high temperatures, electronic excitation becomes a large effect, and the potentials in (1) will change. In the present work, we simply pretend that this does not happen. The theory will then be physically correct for temperatures where electronic excitation is weak, and the liquid-metal entropy constant will be correctly determined by the high-temperature limit of the theory.

From the classical partition function for a fluid, based on the potential (1), the cluster expansion of the Helmholtz free energy is[6]

$$F=\Omega(V)+NkT\left[\ln(\rho\Lambda^3)-1+\sum_{n=2}^{\infty}\frac{B_n\rho^{n-1}}{n-1}\right], \tag{2}$$

where $k=$ Boltzmann's constant, $\rho=N/V=$ the atomic density, and Λ is the thermal de Broglie wavelength, given in terms of the ion mass M by $\Lambda^2=2\pi\hbar^2/MkT$. The first B_n coefficient is

$$B_2=2\pi\int_0^{\infty}(1-e^{-\beta\phi(r;V)})r^2\,dr\ , \tag{3}$$

where $\beta=1/kT$. In general, $B_n=B_n(T;V)$. Equations for the internal energy U and the pressure P follow from (2):

$$U=\Omega+NkT\left[\frac{3}{2}-\sum_{n=2}^{\infty}\left[\frac{\partial B_n}{\partial\ln T}\right]_V\frac{\rho^{n-1}}{n-1}\right], \tag{4}$$

$$P=-\frac{d\Omega}{dV}+kT\rho+kT\sum_{n=2}^{\infty}\left[B_n-\frac{1}{n-1}\left[\frac{\partial B_n}{\partial\ln V}\right]_T\right]\rho^n\ . \tag{5}$$

III. CONVERGENCE AS A HIGH-T EXPANSION

If $\phi(r)$ is a constant potential, in particular if $\phi(r)$ does not depend on V, then B_n are the usual virial coefficients, and $B_n=B_n(T)$. The virial expansion of P is, from (5),

$$P=-\frac{d\Omega}{dV}+kT\sum_{n=1}^{\infty}B_n\rho^n\ , \tag{6}$$

where $B_1=1$. This is generally considered as an expansion in ρ at a fixed T. Results on the convergence of (6) are collected by Ruelle.[7] The following conditions are required of the potential $\phi(r)$: $\sum\phi(r)$ is bounded below, i.e., $\sum\phi(r)\geq -NB$, where $B\geq 0$; and $C(\beta)$ is finite, where

$$C(\beta)=4\pi\int_0^{\infty}|e^{-\beta\phi(r)}-1|\,r^2\,dr\ . \tag{7}$$

Then the radius of convergence of (6) is at least $\sigma=[e(e^{2\beta B}+1)C(\beta)]^{-1}$, and the virial coefficients are bounded in magnitude by

$$|B_n|\leq\frac{1}{n}[e(e^{2\beta B}+1)]^{n-2}C(\beta)^{n-1}\ . \tag{8}$$

In the general case where $\phi=\phi(r;V)$, we consider a fixed density ρ_a, and indicate this condition by subscripting a on functions which depend on density, as $\phi=\phi_a(r)$. We again require $\sum\phi_a(r)\geq -NB_a$, where $B_a\geq 0$; and $C_a(\beta)$ is finite. Then the series (2) for F has a radius of convergence at least as large as σ_a. We have $\sigma_a>0$, σ_a is a monotone increasing function of T, and σ_a is not bounded. Hence for the fixed density ρ_a, there exists a T_a such that the series (2) converges for all $T\geq T_a$, and T_a is not greater than the solution of $\sigma_a(T_a)=\rho_a$. The series (2) is therefore a convergent high-temperature expansion for the free energy of a monatomic dense fluid.

Let us drop the subscript a, with the understanding that we are considering high-temperature behavior at a fixed density. The spatial average of $\phi(r)$ is defined by

$$\langle\phi\rangle=4\pi\rho\int_0^{\infty}\phi(r)r^2\,dr\ . \tag{9}$$

There are two classes of potentials, according to whether or not $\langle\phi\rangle$ exists. Since $C(\beta)$ is assumed to exist, $\phi(r)$ is integrable at large r, and we can restrict our consideration to a possible singularity in $\phi(r)$ at small r.

$\langle|\phi|\rangle$ *exists*. This is true for any bounded potential. It is also true for any physically realistic potential. In this case we have the limits, as $T\to\infty$,

$$\rho B_2\to\tfrac{1}{2}\beta\langle\phi\rangle\ , \tag{10a}$$

$$\rho C(\beta)\to\beta\langle|\phi|\rangle\ . \tag{10b}$$

From the bounds (8), it follows that for $n\geq 3$, $TB_n\to 0$ as $T\to\infty$; hence the limiting contribution of the two-body potential $\phi(r)$ to each thermodynamic function F, U, and P is a (density-dependent) constant, arising from the term in B_2. The internal energy, for example, has the high-temperature limit

$$U\to\Omega+\tfrac{3}{2}NkT+\tfrac{1}{2}N\langle\phi\rangle\ . \tag{11}$$

From the mathematical point of view, convergence of F to the high-T limit can be arbitrarily slow. However, for a real metal, $\phi(r)$ should be approximately a screened Coulomb potential at small r, and in general for any material we expect the limiting singularity in $\phi(r)$ to be of the form r^{-1}. In this case each $|B_n|$ is bounded by a power series in β, whose lowest order is β^{n-1}, and the free energy series will converge rapidly for sufficiently high temperature.

$\langle\phi\rangle$ does not exist. We illustrate this case with a specific form of $\phi(r)$ at small r, namely, $\phi(r)=r^{-\alpha}$, $\alpha\geq 3$. Define b: $\phi(b)=kT$. Then in the high-T limit, the leading term in $C(\beta)$ is $\frac{4}{3}\pi b^3=\frac{4}{3}\pi\beta^{3/\alpha}$, and the leading term in B_2 is $\frac{1}{2}C(\beta)$. The leading term in F arises from B_2 and goes as $T^{1-(3/\alpha)}$, so this term is either constant, or else it is monotone increasing with T and unbounded. The same is true of the corresponding terms in the energy U and the pressure P.

There is a question as to whether the potentials that have finite $\langle|\phi|\rangle$ satisfy $\sum\phi(r)\geq -NB$. In fact, for potentials with a central repulsion like $\phi(r)\sim r^{-\alpha}$, $\alpha<3$, and with an attractive region, if the attraction is strong enough, not only is there no virial series, there is no thermodynamics.[8] For the potentials of interest to us,[9] we have satisfied ourselves that $\sum\phi(r)\geq -NB$ is true. In these cases the attractive well is not strong enough to cause trouble.

IV. HIGH-TEMPERATURE HEAT CAPACITY

We consider the heat capacity $C_V=(\partial U/\partial T)_V$ for classical fluids at high temperatures, and we exclude specifically the contribution from critical phenomena, so that C_V is well behaved at the critical temperature T_c. Experimental evidence suggests that C_V decreases from around $3k$ per atom at melting, to about $2k$ at T_c. Grimvall[10] has shown that the data for liquid Na, K, and Hg, which are available for T up to about $\frac{1}{2}T_c$, are consistent with this decrease. To explain this behavior, Brillouin[11] suggested that as T increases, potential energy is gradually lost from the transverse motions of the atoms, until at the critical point, the motional energy is only $2kT$ per atom. Following Brillouin's suggestion, Wannier and Piroué[12] constructed a model in which the fluid has a Debye distribution of atomic vibrations of frequencies ω, and potential energy is attributed only to those modes for which $\omega\tau\gtrsim 1$, where τ is approximately the macroscopic shear relaxation time. Actually, Brillouin's picture should be corrected by noting that transverse potential energy is not lost, but saturates, so the motional energy near the critical point is $2kT+\text{const}$; the presence of the constant affects the shape of the entire $U(T)$ curve. A description of our picture of the mean potential energy of dense fluids follows.

Let us fix the positions of all the ions but one, the probe ion, and consider its potential, due only to the two-body interactions $\phi(r)$, as a function of position throughout the volume V. To visualize the potential surface, let the volume be a horizontal plane, with energy measured vertically. The potential surface is characterized by valleys in the open spaces between ions, and by ridges between the valleys, and positive poles at the ion positions. The mean potential of the probe ion is a statistically weighted average over this surface, and it qualitatively reflects the mean potential per ion of the entire system. First take a fixed volume. At temperatures near melting, the probe ion is statistically confined to the valleys, and its mean potential contributes $\frac{3}{2}k$ to the heat capacity. As the temperature increases, the probe ion steadily climbs (in the mean) the potential surface. When the probe ion moves freely over the ridges, its potential contributes only about $\frac{1}{2}k$ to the heat capacity, and finally when the probe ion moves freely over the entire plane, except for arbitrarily small excluded areas at the locations of the fixed ions, its mean potential no longer increases with T. Hence at a fixed volume, the mean potential of the system continually increases with T, and approaches the limit $\frac{1}{2}\langle\phi\rangle$ per ion.

If we fix T instead, and increase the volume, the

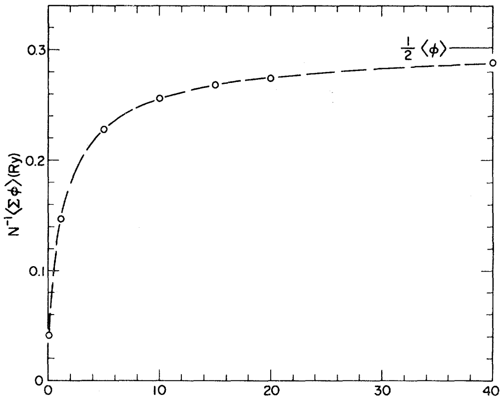

FIG. 1. The circles show molecular-dynamics calculations of the mean potential per atom for fluid sodium at a fixed volume. The high-temperature limit $\frac{1}{2}\langle\phi\rangle$ is also shown. Temperature-induced ionization has been neglected, as explained in the text.

potential surface of the probe ion diminishes, and the mean potential decreases in trend (if not in detail) and approaches zero as $\rho \rightarrow 0$. This property is explicitly apparent in the high-T value of the mean potential, $\frac{1}{2}\langle\phi\rangle$, which according to (9) is proportional to ρ.

Molecular-dynamics calculations of the thermodynamic properties of solid sodium, based on a pseudopotential model for the potentials in Φ, were reported recently.[9] We have evaluated the mean potential energy for this same model in the fluid phase at high temperatures, for the volume of $256a_0^3$ per atom. The mean potential is $\langle \sum \phi(r;V) \rangle$, and is precisely the contribution to U from the cluster expansion, the sum for $n \geq 2$ in Eq. (4). As shown in Fig. 1, the mean potential per atom increases with T and approaches the limit $\frac{1}{2}\langle\phi\rangle$, in agreement with Eq. (11) and with the description sketched above.

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