

**Application of hard sphere perturbation theory for thermodynamics of model liquid metals**

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Hard sphere perturbation theory (HSPT) has contributed toward the fundamental understanding of dense fluids for over 30 years. In recent decades, other techniques have been more popular. In this paper, we argue for the revival of hard sphere perturbation theory for the study of thermodynamics of dense liquid in general, and in liquid metal in particular. The weakness of HSPT is now well understood, and can be easily overcome by using a simple convenient Monte Carlo method to calculate the intrinsic error of HSPT free energy density. To demonstrate this approach, we consider models of liquid aluminum and sodium. We obtain the intrinsic error of HSPT with the Monte Carlo method. HSPT is shown to provide a lower free energy upper bound than one-component plasma (OCP) for alkali metals and polyvalent metals. We are thus able to provide insight into the long standing observation that a OCP is a better reference system than a HS for alkali metals.

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**I. INTRODUCTION**

The configurations of dense simple fluids with strongly repulsive interactions at small separations are known to be well described by the packing of hard spheres [1–4]. This provided the basis for the extensive application of hard sphere perturbation theory (HSPT) over many decades for a wide range of liquids [1–4]. In particular, HSPT has played an important pioneering role in the study of liquid metals [5]. Since then, advances in numerical simulation methods and the availability of inexpensive computers have somewhat diminished the use of HSPT. Molecular dynamics or Monte Carlo simulations allow one to obtain numerically exact results for equilibrium and nonequilibrium properties of model liquids, and is limited only by the speed and memory of the computer [6]. In recent decades, the integral-equation method has also been popular, and demonstrated approximate results which are very accurate (when compared to computer simulations) for many liquid metals [7].

In spite of these significant developments, one is still not able to find a replacement for HSPT in the important role of quickly and efficiently calculating the thermodynamic free energy for liquid metals [5]. This goal remains elusive, in part because a calculation of the free energy for dense fluids by computer simulation or integral equation methods is non-trivial and tedious [1–7]. In contrast, the two factors which have made it very convenient to apply first-order HSPT remain valid today. First, the structure factor of hard sphere fluids has been evaluated analytically in the Percus-Yevick approximation [8–11]. Second, the free energy of the hard sphere reference system is available analytically as fits to accurate machine calculation [12]. By using the hard sphere diameter as a variational parameter, first order HSPT, in principle, becomes a rigorous upper bound to the true free energy [13].

The deficiencies of HSPT for liquid metals are well known [14–16]. Initial applications indicate that hard sphere

fluids do not provide an adequate description of the experimental liquid alkali metal structure factor [14–16]. Later calculations were able to overcome this difficulty [17,7]. The free energy bound from variational HSPT was also inferior when compared to the bound using a one-component plasma (OCP) reference system [14,15]. These difficulties were attributed to the relatively softer core of the effective ion-ion potentials of the alkali metals [16]. In contrast, the HS reference system was argued to be the preferred reference system for polyvalent metals with stiffer core potentials. Implicit in these arguments is that although first-order variational perturbation theory is not exact, the magnitude of the error is small if the structure of the reference HS fluids is able to provide an adequate description of the model liquid metals. The assumption is that the error is rooted in the truncation of HSPT to first order; if the perturbation is carried out to all orders, then the result will be exact.

The possibility that HSPT, when applied to a continuous model potential, actually represents an application with singular perturbation was not fully appreciated until recently. This is important, because singular perturbation may produce a free energy density with an intrinsic error. In a recent paper [18], the application of HSPT to dense fluids with a singular perturbation was rigorously shown not to be exact, even when perturbation to all orders is included. A region of phase space was systematically neglected, and produced error in the thermodynamic estimates. In this paper, we propose that a simple Monte Carlo method can be used to study this intrinsic error of the HSPT free energy density, and we apply this technique to model liquid aluminum and sodium. We find that the intrinsic error is strongly dependent on the hard sphere diameter  $\sigma_{hs}$  of the reference system, and appears to increase rapidly for larger  $\sigma_{hs}$ . The magnitude of the error also depends on the stiffness of the repulsive part of the effective ion-ion potential. The error is smaller for model liquid aluminum and larger for liquid sodium, corresponding to the potential for aluminum being stiffer than that for sodium. Since the intrinsic error of HSPT does not have an analog for the OCP reference system, our results provide an explanation for the long standing observation that an OCP is

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a better reference system than a HS for the alkali metals with softer core potentials.

We argue for a revival of HSPT by combining HSPT with a simple convenient Monte Carlo method to calculate the intrinsic error. The corrected HSPT is shown to provide a lower free energy bound than an OCP for both alkali metals and polyvalent metals. In Sec. II, we recall the origin of the intrinsic error. In Sec. III, the Monte Carlo method and results for model liquid aluminum and sodium will be considered. The paper concludes with discussions in Sec. IV.

## II. HARD SPHERE PERTURBATION THEORY WITH SINGULAR PERTURBATION

Thermodynamic perturbation theory provides a systematic approach to calculating all thermodynamic properties of a model system of particles interacting with a potential  $v$  in terms of ensemble averages over configurations in phase space, distributed according to the Boltzmann distribution of the reference system [1]. Consider a system of  $N$  classical particles interacting with a potential  $v$  in a volume  $V$  at temperature  $T$  in the canonical ensemble. The Helmholtz free energy per particle for the system with potential  $v$  is

$$\beta f_v = -(1/N) \ln \left( \int_{\Omega} e^{-\beta\Phi} \right), \quad (1)$$

where the partition integral over all configuration phase-space ( $\Omega$ ) is denoted by  $\int_{\Omega}$  and  $\Phi$  is equal to the total energy of interactions from summation of  $v(r)$  over all possible pairs of particles.  $\beta = 1/k_B T$ . The Helmholtz free energy per particle for the hard sphere reference system, with the same  $N$  and  $V$ , is

$$\beta f_{\text{hs}} = -(1/N) \ln \left( \int_{\Omega} e^{-\beta\Phi_{\text{hs}}} \right). \quad (2)$$

The difference in free energy density follows:

$$\begin{aligned} \delta\beta f &\equiv \beta(f_v - f_{\text{hs}}) \\ &= -(1/N) \ln \left[ \left( \int_{\Omega} e^{-\beta\Phi} \right) / \left( \int_{\Omega} e^{-\beta\Phi_{\text{hs}}} \right) \right]. \end{aligned} \quad (3)$$

This difference can be evaluated in two different ensembles. The first is the ensemble sampled by the continuous model potential  $v$  and denoted by  $\langle \rangle_v$ ,

$$\begin{aligned} \langle \delta\beta f \rangle_v &= +(1/N) \ln \left[ \left( \int_{\Omega} e^{-\beta\Phi_{\text{hs}}} \right) / \left( \int_{\Omega} e^{-\beta\Phi} \right) \right] \\ &= (1/N) \ln \langle e^{-\beta(\Phi_{\text{hs}} - \Phi)} \rangle_v. \end{aligned} \quad (4)$$

The second is given by HSPT as an ensemble average over configurations sampled by the hard sphere reference system. For this, we need to divide the total configuration phase space  $\Omega$  into two parts:

$$\Omega = \Omega_{\text{hs}} \oplus \Delta. \quad (5)$$

The two parts have no overlaps.  $\Omega_{\text{hs}}$  is defined to be the total phase space sampled by the hard sphere reference ensemble  $\langle \rangle_{\text{hs}}$ , and thus contains no configuration with hard sphere overlap.  $\Delta$  is the remainder of the phase space, with at least one pair of hard sphere overlaps. With these definitions, Eq. (3) can be rewritten within HSPT as,

$$\begin{aligned} \langle \beta \delta f \rangle_{\text{hs}} &= -(1/N) \ln \left[ \left( \int_{\Omega_{\text{hs}}} e^{-\beta\Phi} \right) / \left( \int_{\Omega_{\text{hs}}} e^{-\beta\Phi_{\text{hs}}} \right) \right] \\ &= -(1/N) \ln \langle e^{-\beta(\Phi - \Phi_{\text{hs}})} \rangle_{\text{hs}}. \end{aligned} \quad (6)$$

We stress that Eq. (6) represents the HSPT prediction to all orders in the perturbation  $\beta(\Phi - \Phi_{\text{hs}})$ , and thus should be considered as an exact HSPT.

The difference of the two ensembles is the intrinsic error of HSPT,

$$\begin{aligned} \langle \beta \delta f \rangle_{\text{hs}} - \langle \beta \delta f \rangle_v &= -(1/N) \ln \left[ \left( \int_{\Omega_{\text{hs}}} e^{-\beta\Phi} \right) / \left( \int_{\Omega} e^{-\beta\Phi} \right) \right] \\ &= -(1/N) \ln \epsilon_{\eta}, \end{aligned} \quad (7)$$

with  $\epsilon_{\eta} = [(\int_{\Omega_{\text{hs}}} e^{-\beta\Phi}) / (\int_{\Omega} e^{-\beta\Phi})]$ . Observe that the error is a simple consequence of the exclusion of phase space with overlaps of hard spheres in the hard sphere reference ensemble. One needs the fraction of configurations sampled by the Boltzmann distribution for a model liquid interacting with a potential  $v$  which has no hard sphere overlaps. This is denoted by  $\epsilon_{\eta}$  for hard sphere reference fluids with packing fractions of  $\eta$ . Although, in general,  $\epsilon_{\eta}$  cannot be evaluated analytically for an arbitrary potential  $v$ , it can be estimated by the numerical Monte Carlo method [6]. In Sec. III, we will consider our Monte Carlo methods and results for model liquid aluminum and sodium.

## III. MONTE CARLO STUDY OF MODEL LIQUID ALUMINUM AND SODIUM

Using the Monte Carlo method, we study the intrinsic error of HSPT for typical models of liquid aluminum and sodium at densities near freezing. The particles of the model liquid metals interact with standard pseudopotentials, calculated using the empty core pseudopotential [19] and Lindhard dielectric function [20] with exchange and correlation corrections [21]. Such effective ion-ion potentials have been used for many years, and are well documented in the literatures [5]. The potential is given in Figs. 1 and 2 for sodium and aluminum at densities ( $\rho$ ) of 0.02435 and 0.05315 ions/ $\text{\AA}^3$ , respectively. We consider standard constant volume Monte Carlo sampling [6] in the canonical ensemble. A fixed number of particles in a cubic box is used at temperatures of 379 K for sodium and 933 K for aluminum. A periodic boundary condition is implemented. A range of particle sizes is used to probe empirically for systematic errors using only a finite-size system. Since we are far away from any critical point with an infinite correlation length [22], we do not expect, and indeed find no, significant evidence of

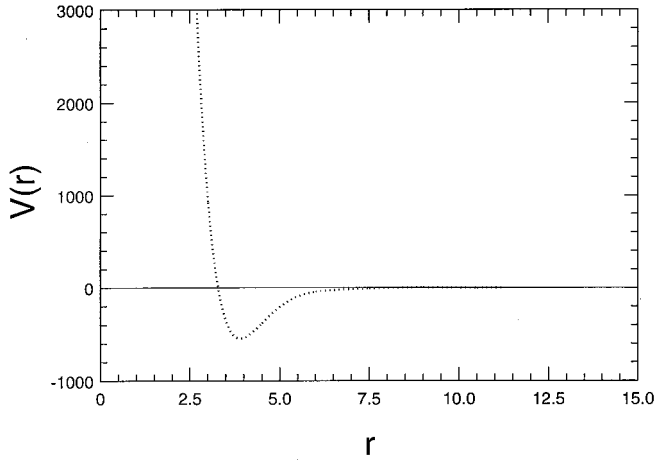


FIG. 1. Pseudopotential pair interaction in units of  $K$  for Na with an empty core radius of  $0.89 \text{ \AA}$  at an ion density of  $0.02435/\text{\AA}^3$  vs separations in units of  $\text{\AA}$ . See the text.

finite-size effects within our sampling error. Statistical errors are estimated by considering different runs and standard block averaging (see Ref. [6]).

The fraction of configurations sampled by the Boltzmann distribution for the model liquid interacting with  $v$ , which have no hard sphere overlaps, is denoted in Eq. (7) by  $\epsilon_\eta$ . This is a function of the hard sphere diameter [ $\sigma_{\text{hs}} = (6\eta/\pi\rho)^{1/3}$ ]. For small  $\eta$  and  $\sigma_{\text{hs}}$ , the fraction of configurations with no overlaps is large, and approaches 1 in the small  $\eta$  limits. The HSPT intrinsic error, given by  $\ln$  of the fraction, will approach zero rapidly in the small  $\eta$  limits. As  $\eta$  increases, the fraction with no overlaps decreases rapidly, producing an increasing intrinsic error for HSPT (see Figs. 3 and 4). It is useful to note that the simulation depends only on  $v$ , and the minimum pair separation of the configurations from the Monte Carlo is stored and analyzed for a range of values of  $\eta$ . This approach is very fast and efficient.

We have considered two different ways of sampling  $\epsilon_\eta$ . First,  $\epsilon_\eta$  is calculated as the fraction of configurations gen-

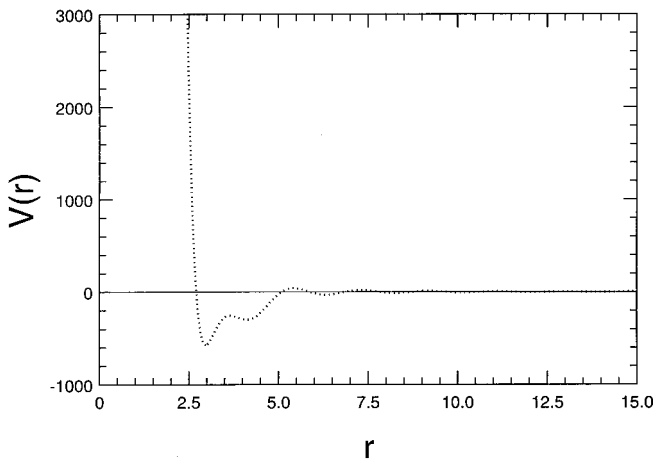


FIG. 2. Pseudopotential pair interaction in units of  $K$  for Al with an empty core radius of  $0.591 \text{ \AA}$  at an ion density of  $0.05315/\text{\AA}^3$  vs separations in units of  $\text{\AA}$ . See the text.

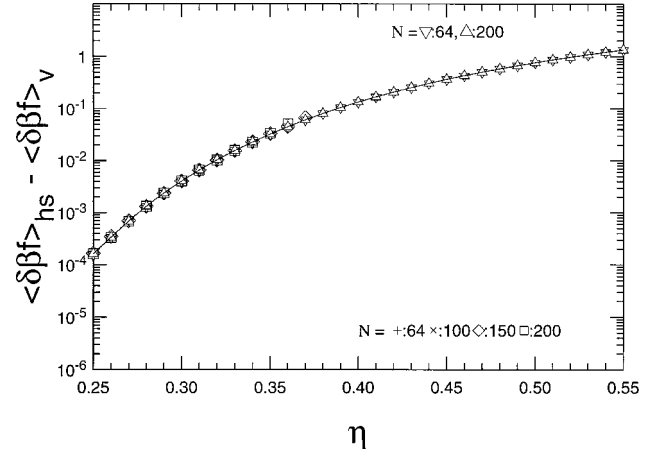


FIG. 3. Intrinsic error of the HSPT free energy density for liquid sodium at 379 K vs the packing fraction of the hard sphere reference system for different system sizes. The inverted triangles and triangles are results of the  $(p_o)^N$  approximate estimate. The dotted and solid lines are guides for the eye for 64 and 200 particles, respectively. The other symbols are results of the exact numerical estimate. The estimated errors are about the same as or smaller than the size of the symbols. See the text.

erated by a Boltzmann distribution with no hard sphere overlaps. This method is numerically exact, but is limited to a small number of particles and/or small  $\eta$ . The limitation is a consequence of  $\epsilon_\eta \sim e^{-N(\langle \beta\delta f \rangle_{\text{hs}} - \langle \beta\delta f \rangle_v)}$ , and  $\epsilon_\eta$  will decrease rapidly toward zero for large  $N$ . The number of total configurations needed to be sampled for an accurate estimate grows exponentially with the number of particles, which can be much larger than 1. We have used up to 2.5 million Monte Carlo steps per particle to sample  $\epsilon_\eta$  directly for up to  $\eta \sim 0.40$  with 64 particles and  $\eta \sim 0.37$  with 200 particles.

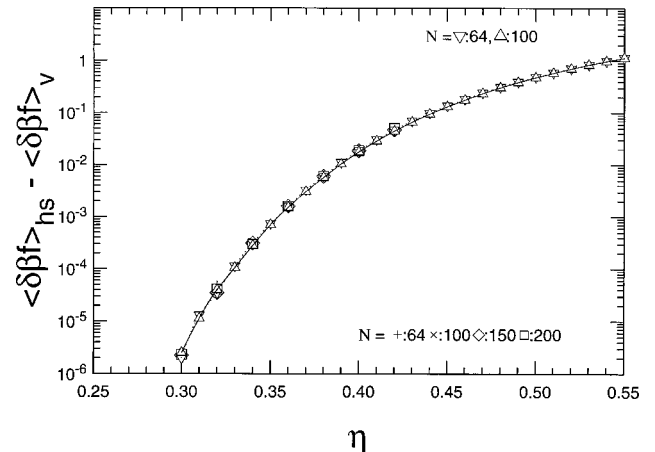


FIG. 4. Intrinsic error of the HSPT free energy density for liquid aluminum at 933 K vs the packing fraction of the hard sphere reference system for different system sizes. The inverted triangles and triangles are results of the  $(p_o)^N$  approximate estimate. The dotted and solid lines are guides for the eye for 64 and 100 particles, respectively. The other symbols are results of the exact numerical estimate. The estimated errors are about the same as or smaller than the size of the symbols. See the text.

To explore larger values of the packing fraction  $\eta$ , we observe that the fraction of configurations generated by the Boltzmann distribution with no hard sphere overlaps can be approximated by  $(p_o)^N$ .  $p_o$  is the square root of the normalized probability that any given particle has no hard sphere overlap with another particle. This is the single pair approximation, and ignores a possible correlation between two or more particles having no simultaneous hard sphere overlap with their neighbors. The  $(p_o)^N$  approximation allow us to study larger systems and large  $\eta$ . We can estimate the error introduced by the  $(p_o)^N$  approximation by comparing them to the exact estimate for  $\eta \leq 0.38$ . This is  $\sim 0.0001$  for liquid aluminum. For liquid sodium, the  $(p_o)^N$  approximation is statistically indistinguishable from the numerically exact sampling results, (see Figs. 3 and 4).

#### IV. REMARKS

Our Monte Carlo results provide, for the first time to our knowledge, an estimate for the error introduced by HSPT in a calculation of the free energy density. This can be as large as  $\sim 1.0k_B T$  for liquid sodium for  $\eta \sim 0.45$  and  $\sim 0.1k_B T$  for liquid aluminum. Such differences between the two metals can be traced to  $p_o$ .  $p_o$  is the square root of the normalized probability that a particle has no hard sphere overlap with another particle. This is related to the small  $r$  dependence of the pair correlation function  $[g(r)]$ , and depends on the stiffness of the potential.

Observe that the presence of the intrinsic error in HSPT does not invalidate the rigorous upper bound character of first order variational HSPT. Since  $\epsilon_\eta \leq 1.0$  in Eq. (7),  $\langle \beta \delta f \rangle_{\text{hs}} \geq \langle \beta \delta f \rangle_v$ . We also have

$$\langle \beta \delta f \rangle_{\text{vhs}} \geq \langle \beta \delta f \rangle_{\text{hs}} \geq \langle \beta \delta f \rangle_v, \quad (8)$$

where  $\langle \rangle_{\text{vhs}}$  denotes the first order variational HSPT results. By correcting  $\langle \beta \delta f \rangle_{\text{vhs}}$  with the Monte Carlo calculated correction, one obtains an improved first order HSPT upper bound without an intrinsic error.

Since the intrinsic error can be conveniently calculated with Monte Carlo technique, we propose that future HSPT applications be corrected using our simple algorithm. The two examples of liquid sodium and aluminum used here were studied with variational perturbation theories many years ago with the OCP and uncorrected HSPT reference systems [15]. It was shown that the OCP has a lower free energy bound than HSPT for sodium at  $\eta \sim 0.44$  by  $0.17k_B T$ . Our Monte Carlo estimate for the correction is  $\sim 0.3k_B T$  (see Fig. 3). Thus the bound of the corrected HSPT is lower than that if the OCP by  $\sim 0.13k_B T$ . For the model liquid aluminum, the correction for HSPT at  $\eta \sim 0.48$  is  $\sim 0.3k_B T$  (see Fig. 4). This implies that the corrected HSPT is lower than the OCP by  $\sim 0.7k_B T$ . These results demonstrate that the corrected HSPT provides a lower free energy bound than the OCP for both alkali and polyvalent metals. Since the computational effort for calculating the correction for HSPT with our Monte Carlo method is very small (a few hours of CPU on fast work stations or a few days on a very inexpensive PC), the corrected HSPT should again be a useful tool to study the thermodynamic properties of liquid metals.

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