Hard-sphere perturbation theory for a model of liquid Ga

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Investigating thermodynamic properties of a model for liquid Ga, we have extended the application of the hard-sphere (HS) perturbation theory to an interatomic pair potential that possesses a soft repulsive core and a long-range oscillatory part. The model is interesting for displaying a discontinuous jump on the main-peak position of the radial distribution function at some critical density. At densities less than this critical value, the effective HS diameter of the model, estimated by the variational HS perturbation theory, has a substantial reduction with increasing density. Thus, the density dependence of the packing fraction of the HS reference fluid has an anomalous behavior, with a negative slope, within a density region below the critical density. By adding a correction term originally proposed by Mon to remedy the inherent deficiency of the HS perturbation theory, the extended Mansoori–Canfield/Rasaiah–Stell theory [J. Chem. Phys. 120, 4844 (2004)] very accurately predicts the Helmholtz free energy and entropy of the model, including an excess entropy anomaly. Almost occurring in the same density region, the excess entropy anomaly is found to be associated with the anomalous packing fraction of the HS fluid. © 2008 American Institute of Physics. [DOI: 10.1063/1.2948950]

I. INTRODUCTION

A general realization about simple liquids is that the liquid structure is primarily determined by the repulsive core of particles, while the attractions between particles determine the cohesion of the liquid.\(^1\) Since the repulsions and attractions in a liquid play different roles in thermodynamics of the liquid, the two portions of interatomic interactions are individually approximated with different strategies. The structure of a liquid can be described by a reference fluid with the repulsive core only, whereas the attractions are treated as a perturbation. This forms the central theme of thermodynamic perturbation theory, which has played an important role in the development of statistical mechanism for simple liquids.\(^2,3\) Some refinements of the theory progress recently, with an aim of applications in soft condensed systems.\(^4–9\)

Owing to the benefit of available analytical expressions of the hard-sphere (HS) fluid in calculating thermodynamic and structural properties, the reference fluid is further approximated to be a HS one with the HS diameter determined by requiring that the two fluids are equivalent in some thermodynamic quantity. For example, in the Weeks–Chandler–Andersen (WCA) theory,\(^10–13\) the HS diameter is determined by the equation of equal compressibility between the two fluids so that their free energies differ in the fourth order of the softness parameter, which is a measure for the difference between the repulsive core and the HS potential. Generally, the WCA theory is accurate for the Lennard-Jones (LJ) fluids at high densities. However, as the repulsive core is very soft, the softness parameter is so large that the inaccuracy of the WCA theory becomes serious. With a different choice for the HS diameter, Lado\(^14\) gave some improvement in the prediction of the WCA theory. Alternatively, according to the Gibbs–Bogolubov inequality, Mansoori–Canfield\(^15\) and Rasaiah–Stell\(^16\) (MCRS) developed independently a variational approach, based on a HS reference system and the first-order perturbation. By treating the HS diameter as a variational parameter, this approach provides an upper bound of the Helmholtz free energy. As the repulsive core is softer than that of the LJ potential, the prediction of this variational approach is found to be more accurate than that of the WCA theory. This variational HS perturbation theory has been applied to calculate the structures and thermodynamics of liquid metals, which can be described by the effective pair potentials with very soft repulsive cores.\(^17–20\)

Pointed out by Mon\(^21–23\) in a few years ago, the inaccuracy of the HS perturbation theory is resulted from an inherent deficiency of the theory: A region in the phase space of a realistic fluid is forbidden by a HS fluid due to the singularity of the HS potential. To make up the deficiency of the HS perturbation theory, Mon proposed a correction term that should be added into the variational function to improve the accuracy of the variational approach. By testing the corrected variational function with the inverted-power fluids and a model of liquid Na,\(^24\) the deficiency of the HS perturbation theory is accounted. Recently, including Mon’s correction term in the two-body approximation, Ben-Amotz and Stell have extended the MCRS theory.\(^25\) Different from other HS perturbation theories, this extended theory needs two effective HS diameters. The cavity distribution function of a HS fluid, which is in the correction term, is evaluated by the HS-diameter value determined by the Lado-WCA method; other HS-diameter parameters, appearing either explicitly or implicitly in the variational function, are still treated as the variational parameter. Also tested with the inverted-power
Relative to a reference fluid of HSs with diameter $\sigma_{\text{HS}}$ at the same temperature and number density, $\tilde{A} = A^{\text{ex}} / Nk_B T$ of a fluid with $N$ particles can be expressed as

$$\tilde{A} = \tilde{A}_{\text{HS}} + \Delta \tilde{A},$$  \hspace{1cm} (1)

where $\tilde{A}_{\text{HS}} = A^{\text{ex}}_{\text{HS}} / Nk_B T$ is the corresponding quantity of the HS fluid and $\Delta \tilde{A}$ is the difference. $\tilde{A}_{\text{HS}}$ is well described by the Carnahan–Starling expression,\(^{32}\)

$$\tilde{A}_{\text{HS}} = \frac{\eta(4 - 3 \eta)}{(1 - \eta)^2},$$  \hspace{1cm} (2)

where $\eta = \pi \rho \sigma_{\text{HS}}^3 / 6$ is the packing fraction of the HS fluid. In the MCRS theory,\(^{15,16}\) $\Delta \tilde{A}$ of a fluid with a pair potential $\phi(r)$ is given as

$$\Delta \tilde{A} = 2 \pi \rho \beta \int_{\sigma_{\text{HS}}}^{\infty} g_{\text{HS}}(r) \phi(r) r^2 dr,$$  \hspace{1cm} (3)

where $g_{\text{HS}}(r)$ is the radial distribution function of the HS fluid and $\beta = (k_B T)^{-1}$. By treating $\sigma_{\text{HS}}$ as a variational parameter, a measured value of $\tilde{A}$ is obtained by minimizing a sum of $\tilde{A}_{\text{HS}}$ and $\Delta \tilde{A}$ given in Eqs. (2) and (3), respectively.

In principle, the entire configuration space $\Omega$ is accessible to a realistic fluid. Because of the singularity of a HS potential, part of $\Omega$ is not available to the HS fluid, which configuration space is denoted as $\Omega_{\text{HS}}$. This is due to the excluded volume effect of the HS particles. Mon pointed out that due to the difference between $\Omega_{\text{HS}}$ and $\Omega$ a correction term that should be added into $\Delta \tilde{A}$ is formulated as\(^{21-23}\)

$$\Delta g = \frac{1}{N} \ln \left[ \frac{\int_{\Omega_{\text{HS}}} e^{-\beta \Phi}}{\int_{\Omega} e^{-\beta \Phi}} \right],$$  \hspace{1cm} (4)

where $\Phi$ is the total interaction energy of the fluid of interest. To the lowest order of fluid density, Ben-Amotz and Stell have shown that the correction term can be approximated to be\(^{25}\)

$$\Delta g = -2 \pi \rho \int_{0}^{\sigma_{\text{HS}}} g(r) r^2 dr,$$  \hspace{1cm} (5)

where $g(r)$ is the radial distribution function of the fluid with $\phi(r)$. As commonly used in the HS perturbation theory, $g(r)$ in the repulsive-core region is approximated as

$$g(r) = y_{\text{HS}}(r) \exp(-\beta \phi(r)),$$  \hspace{1cm} (6)

where $y_{\text{HS}}(r)$ is the cavity distribution function of the HS reference fluid. By using this approximation, a new variational formula of $\Delta \tilde{A}$, refereed as the E-MCRS theory, is given as

$$\Delta \tilde{A} = 2 \pi \rho \beta \int_{\sigma_{\text{HS}}}^{\infty} g_{\text{HS}}(r) \phi(r) r^2 dr,$$

$$-2 \pi \rho \int_{0}^{\sigma_{\text{HS}}} y_{\text{HS}}(r) \exp(-\beta \phi(r)) r^2 dr.$$  \hspace{1cm} (7)

It has been shown that the E-MCRS theory gives better predictions in thermodynamic properties of the inverse-power fluids than other first-order HS perturbation theories. How-
ever, a notice should be given: The HS diameter for describing $\gamma_{\text{HS}}(r)$ in the second integral is determined by the Lado-WCA method and may have a different value from that of the variational parameter $\sigma_{\text{HS}}$, which implicitly determines $g_{\text{HS}}(r)$ in the integrand of the first integral and appears explicitly in the lower and upper limits of the first and second integrals, respectively.

In thermodynamics, $\bar{A}$ of a fluid at density $\rho$ is related to the pressure $P(\rho')$ of the fluid at lower density $\rho'$ via the following integration:

\[
\bar{A} = \int_{0}^{\rho} \left( \frac{P(\rho')}{\rho'} - 1 \right) \frac{d\rho'}{\rho'}.
\]

$P(\rho')$ can be obtained via the pressure equation, in which two inputs are the radial distribution function of the fluid at density $\rho'$ and the first derivative of the pair potential. With the radial distribution functions generated by computer simulation, $\bar{A}$ obtained via the integration in Eq. (8) is recognized as the simulation results, which have no approximations in thermodynamics.

FIG. 2. (Color online) Radial distribution function of the model fluid at the indicated particle number. In each panel, the solid and dashed lines are, respectively, the simulation result and the approximation given by Eq. (6) with $\gamma_{\text{HS}}(r)$ evaluated at the Lado-WCA value of $\sigma_{\text{HS}}$. The dotted line indicates the $\sigma_{\text{HS}}$ value obtained by the E-MCRS theory.

FIG. 3. (Color online) Potential of mean force $w(r)$ of the model fluid at $N=3500$ (dashed line), $2500$ (short-dashed line), $2000$ (dot-dashed line), $1000$ (dot-dot-dashed line), and $100$ (dotted line). The solid line is the interatomic pair potential $\phi(r)$. All potentials are scaled with $\epsilon$ and distance is scaled with $\sigma$.

III. MODEL OF LIQUID Ga AND SIMULATIONS

The interatomic pair potential $\phi(r)$ used in this paper is generated by a first-principles pseudopotential theory for liquid Ga at $T=323$ K. Although the numerical data of $\phi(r)$ are generated at discrete points, the overall shape of $\phi(r)$, shown in Fig. 1, is continuous and smooth. Generally, $\phi(r)$ has a ledge-shape repulsive core and a long-range oscillatory part with a behavior following the Friedel oscillations. Two parameters of $\phi(r)$ are $\sigma$, the depth of the main attractive well, and $\epsilon$, which is the shortest distance at $\phi(r)=0$. The corresponding temperature of $\epsilon$ is about 47 K and $\sigma=4.04$ Å. The repulsive core of $\phi(r)$, denoted as $\phi_0(r)$, is the potential for $r$ smaller than $r_0$, the position of the main attractive well, where $r_0$ is about 1.07$\sigma$. According to the behavior of the repulsive core, $\phi_0(r)$ can be roughly divided into three sections. As $r$ is larger than 0.9$\sigma$, $\phi_0(r)$ with energy less than 6$\epsilon$ behaves like the repulsive core of the LJ potential with the same $\sigma$ and $\epsilon$. In the intermediate region between 0.9$\sigma$ and 0.7$\sigma$, the value of $\phi_0(r)$ varies from 6$\epsilon$ to 30$\epsilon$ and the shape of $\phi_0(r)$ becomes soft and has a ramplike behavior, with a reflection point around 0.8$\sigma$. At $r$ less than 0.7$\sigma$, $\phi_0(r)$ increases almost exponentially with decreasing distance so that the repulsive core changes to be extremely stiff.

With $\phi(r)$, we have carried out a series of molecular dynamics simulations at constant $NVE$ ensemble by using a predictor-corrector algorithm in a time step of 5.45 fs. In each simulation, the temperature is set to be 68.5$\epsilon$, corresponding to $T=323$ K, the box size is fixed at 10.2$\sigma$, and the range of $\phi(r)$ is terminated at half of the box size. All quantities given in this paper are in units of $\sigma$, $\epsilon$, and the mass of Ga atom. The number of simulated particles starts at $N=3500$. Then, in each simulation for a new thermodynamic state, $N$ is reduced by 100, with the lowest $N$ being 100. At $N=3500$, the simulated system has a number density $\rho=0.05$ Å$^{-3}$, with a reduced density $\rho'=\rho\sigma^3$ equal to 3.005, which is close to that of liquid Ga at $T=323$ K and pressure of about 1 bar. At the simulated conditions of $N=3500$, the
static and dynamic structure factors of the system reproduce well the experimentally observed structural and dynamic anomalies of liquid Ga at temperatures close to the melting point \(T_m = 303\) K.\(^{27}\)

The radial distribution functions of our simulated systems at some particle numbers are shown in Fig. 2. At \(N = 3500\), the main peak of the radial distribution function is located at 0.686\(\sigma\), which is in the extremely stiff region of the repulsive core. As \(N\) is decreased, the main peak is lowered and shifts outwardly, while a shoulder near \(\sigma\) appears and then grows. Around \(N = 2100\), corresponding to \(\rho^* = 2\), the roles of the main peak and the shoulder exchange: the main peak changes to occur near \(\sigma\) and the shoulder resides in the inner part of the repulsive core. As \(N\) keeps on decreasing, the inner shoulder gradually disappears, associated with a continuously growing main peak near \(\sigma\) as a compensation. As \(N\) is less than 1000, the number density of the system is rather low and the main peak moves toward the first attractive well, with a final position located at the minimum of the attractive well. A similar density variation of the radial distribution function is also observed for the one-scale and two-scale ramp potentials\(^{31}\) introduced by Jagla\(^{28}\) and the core-softened continuous potential with an attractive well.\(^{36}\)

Another way to manifest the density effect on the radial distribution function of this model is to compare the potential of mean force, which is defined as \(w(r) = -k_B T \ln g(r)\), with \(\phi(r)\). \(w(r)\) is the potential that gives the mean force acting on a particle in the fluid. In concept, the mean force between two neighboring particles in a dense fluid includes the direct force due to the interatomic pair potential and an effective force indirectly intermediated through other particles. In general, the indirect force depends on the fluid density, so the potential of mean force at high density can be quite different from the interatomic pair potential. For our model fluid, the variation of \(w(r)\) with \(N\) is presented in Fig. 3. At \(N = 3500\), \(w(r)\) has a deep attractive well at the first-peak position of \(g(r)\); this attractive well is attributed to the compactness in the fluid at such a high density. As \(N\) is decreased, the depth of this attractive well gradually reduces, while a shoulder near \(\sigma\) appears. At some critical \(N\), corresponding to a critical density, the roles of this attractive well and the shoulder in \(w(r)\) switch with each other. As \(N\) is decreased further, the new attractive well in \(w(r)\) continuously moves out, with its depth becoming deeper first and then attenuated to 0 at final.

In the WCA theory,\(^{11}\) the effective \(\sigma_{\text{HS}}\) of the model is determined by the solution of the following integral equation:

\[
\int_0^{\sigma_{\text{HS}}} y_{\text{HS}}(r) \exp(-\beta \phi_0(r)) r^2 dr = \int_0^{\sigma_{\text{HS}}} y_{\text{HS}}(r) r^2 dr.
\]

This integral equation implies equal compressibility between the reference fluid with the repulsive core \(\phi_0(r)\) and the fluid of HSs with diameter \(\sigma_{\text{HS}}\) at the same temperature and density. In the Lado-WCA method,\(^{14}\) the effective HS diameter is given by the solution of a similar equation, by replacing \(y_{\text{HS}}(r)\) in both integrands in Eq. (9) with \(\partial y_{\text{HS}}(r)/\partial \sigma_{\text{HS}}\). To solve these equations efficiently, we have replaced \(y_{\text{HS}}(r)\) and \(\partial y_{\text{HS}}(r)/\partial \sigma_{\text{HS}}\) with their analytical expressions in the hard-fluid (HF) approximation,\(^{37,38}\) which can be simply evaluated in terms of the packing fraction \(\eta\) of the HS fluid.

By using the discrete data of \(\phi_0(r)\) and \(\eta\) evaluated at the simulated density, we have solved these equations to obtain the WCA and Lado-WCA values of HS diameter, and their density variations are shown in Fig. 4. For each method, our results are consistent with the general understanding that the effective HS diameter of a fluid is decreased with increasing the fluid density.\(^{25}\) At each density, the HS diameters obtained by the two methods are close, with the WCA value larger. At high densities, both WCA and Lado-WCA \(\sigma_{\text{HS}}\) values are larger than the main-peak position of \(g(r)\), which is located in the exponential region of the repulsive core. But, the HS diameters estimated at low densities becomes smaller than the main-peak position of \(g(r)\), which has a sudden jump to a larger distance in the repulsive core with a LJ-type behavior around \(\rho^* = 2\). With the results shown in Fig. 2 for some particle numbers, we have examined the approximated \(g(r)\) given in Eq. (6) for our model, with \(y_{\text{HS}}(r)\) evaluated in the HF approximation at the Lado-WCA value of HS diameter. For our model at high densities, Eq. (6) is a good approximation of \(g(r)\) for distances less than the main-peak position, while at low densities the validity of the approximation extends over the main peak of \(g(r)\).

**IV. THERMODYNAMIC PROPERTIES**

Through the pressure equation with \(g(r)\) generated by our simulations as an input, we have calculated the compressibility factor \(Z = \beta P(\rho)/\rho\) of our model and the results are shown by the symbols in Fig. 5. Theoretically, \(Z(\rho)\) as a function of density can be expanded into a series with the leading term to be one.

\[
Z(\rho) = 1 + b_2 \rho + b_3 \rho^2 + b_4 \rho^3 + b_5 \rho^4 + \cdots.
\]

Here, \(b_i\) is the \(i\)th Virial coefficient, which is associated with \(\phi(r)\) via some diagrams.\(^{5}\) In the second Virial approximation, \(Z(\rho)\) is approximated to be \(1 + b_2 \rho\) and the calculation of \(b_2\) is
prediction on the excess Helmholtz free energy than the MCRS theory does, and the value of the HS diameter obtained by the E-MCRS theory is larger than that by the MCRS theory. These results are expected to be true for all kinds of fluid.\(^{25}\)

In order to investigate the effect of the approximation in Eq. (6) on the values predicted by the E-MCRS theory, we also evaluate the variational \(\overline{A}\) with Mon’s correction term \(\Delta_p\) given in Eq. (5) with the simulated \(g(r)\) used. As shown in Fig. 6, the corresponding variational curve of \(\overline{A}\) generally shifts upward relative to the one obtained by the E-MCRS theory, except that at very low densities the curves of the two methods are found to be almost the same. Therefore, our results lead to the conclusion that the approximation in Eq. (6) makes the prediction of the E-MCRS theory better.

In Fig. 4, the density variations of the effective HS diameters obtained by the MCRS and E-MCRS theories are compared to those obtained by the WCA and Lado-WCA theories. Similar as the results of the WCA and Lado-WCA theories, the \(\sigma_{\text{HS}}\) values estimated by the MCRS and E-MCRS theories also increase with decreasing density. For \(\rho^*\) larger than 2, the \(\sigma_{\text{HS}}\) values of the MCRS and E-MCRS theories are limited by the main-peak position of \(g(r)\), with the density dependence of the E-MCRS value almost along the track of the peak position. For \(\rho^*\) less than 2 around which the main-peak position of \(g(r)\) makes a jump to a larger value, the MCRS and E-MCRS values are apparently released from the restriction due to the main-peak position of \(g(r)\) and ascend manifestly as \(\rho^*\) varies from 2 to 1. For \(\rho^*\) less than 1, the MCRS value becomes saturated roughly to 0.9\(\sigma\) as density approaches to zero, but the E-MCRS value continuously increases at very low densities and even passes over the values of the WCA and Lado-WCA theories.

The comparison of the excess Helmholtz free energies estimated by various HS perturbation theories is shown in Fig. 7. Apparently, the variational approaches do a better job than the WCA and Lado-WCA theories, which are only good for \(\rho^*\) less than 1. For all calculated densities, the predicted value of the E-MCRS theory is the one closest to the simulation data.

The excess entropy \(S^{\text{ex}}\) of a realistic fluid is defined as the difference between the entropy of the fluid and that of an ideal gas at the same density and temperature. In thermodynamics,

\[
S^{\text{ex}} = -(\partial A^{\text{ex}}/\partial T)_{N,V}.
\]

\(\overline{S}\) is defined as \(S^{\text{ex}}/Nk_B\). In the MCRS theory, the excess entropy \(\overline{S}_{\text{MCRS}}\) is equal to \(-\overline{A}_{\text{HS}}\), which is the excess entropy of a HS fluid with the HS diameter of the MCRS value.\(^{19}\) In the E-MCRS theory, Mon’s correction term gives an extra contribution to \(\overline{S}\). In order to derive the extra contribution, we use the formula of \(\Delta_p\) in Eq. (5), rather than the approximated one in Eq. (7). After substituting \(g(r) = \exp(-\beta w(r))\) into Eq. (5), \(\overline{S}\) in the E-MCRS theory can be expressed as

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**TABLE I.** The fitting coefficients of \(Z(\rho)\) for \(\rho^* < 1\) and \(\rho^* > 1\). The data are given in unit of \(\sigma\).

<table>
<thead>
<tr>
<th>(Z(\rho))</th>
<th>(b_2)</th>
<th>(b_3)</th>
<th>(b_4)</th>
<th>(b_5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\rho^* &lt; 1)</td>
<td>0.995</td>
<td>4.129</td>
<td>-4.969</td>
<td>4.670</td>
</tr>
<tr>
<td>(\rho^* &gt; 1)</td>
<td>-0.323</td>
<td>5.228</td>
<td>-0.523</td>
<td>0.055</td>
</tr>
</tbody>
</table>

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![Figure 5](image-url)  
**FIG. 5.** (Color online) Compressibility factor, \(Z = \beta P/\rho\), as a function of density. The circles are calculated by the pressure equation with the simulated \(g(r)\) as an input. The solid line is the fitting function as described in the text with the fitting parameters given in Table I. The inset shows \(Z\) at low densities and the second Virial approximation (dashed line).
correction term. Then, after using the approximation in Eq. Here, the second term on the right-hand side is due to Mon’s 
modynamic integration in Eq. Then, the second term on the right-hand side is due to Mon’s 

\[ \tilde{S}_{\text{EMCRS}} = -\tilde{A}_{\text{HS}} + 2\pi \rho \int_0^{\sigma_{\text{HS}}} g(r)[1 + \beta w(r)]r^2 \, dr. \]  

(12)

Here, the second term on the right-hand side is due to Mon’s correction term. Then, after using the approximation in Eq. (6) for \( g(r) \),

\[ \tilde{S}_{\text{EMCRS}} = -\tilde{A}_{\text{HS}} + 2\pi \rho \int_0^{\sigma_{\text{HS}}} y_{\text{HS}}(r) \exp(-\beta \phi(r)) \times [1 + \beta \phi(r) - \ln y_{\text{HS}}(r)]^2 \, dr. \]  

(13)

To evaluate \( \tilde{S}_{\text{EMCRS}} \), the HS diameter is required in three places in the above equation: the packing fraction in \( \tilde{A}_{\text{HS}} \), the upper limit of the integral in the second term, and \( y_{\text{HS}}(r) \), which is approximated to be the analytical expression of the HF approximation.\(^{37,38}\) Care must be taken for that the value of \( \sigma_{\text{HS}} \) in the first and second places should be the one obtained by the minimization of variational \( \tilde{A} \) in the E-MCRS theory but the Lado-WCA value of \( \sigma_{\text{HS}} \) should be used in the third place. Also, we have calculated Eq. (12) in terms of the simulated \( g(r) \) and \( w(r) \), and no significant difference is found between the results calculated by Eqs. (12) and (13). Thus, for our model, the two equations give almost identical results.

On the other hand, \( \tilde{S} \) can be evaluated by the difference between the excess internal energy \( \tilde{U} \) and the \( \tilde{A} \) obtained by Eq. (8). By using \( \phi(r) \) and the simulated \( g(r) \), the calculation of \( \tilde{U} \) is straightforward\(^2\) and the result of \( \tilde{S} \) is shown by the symbols in Fig. 8. The value of \( \tilde{S} \) at \( \rho^* = 3.305 \) is estimated to be \(-4.10\), which is reasonably comparable to the experimental value of \(-4.62\) of the excess entropy of liquid Ga at a higher temperature.\(^{19}\) At low densities, \( \tilde{S} \) decreases almost linearly with density; this decrease arises from the excluded volume effect due to the repulsive core of \( \phi(r) \). Intriguingly, in the intermediate range of density, roughly from \( \rho^* = 1.4 \) to 1.8, the density curve of \( \tilde{S} \) has an anomalous behavior, which has a positive slope of a small value. Beyond this anomalous region, \( \tilde{S} \) decreases again in a slower rate with increasing density. Observed also in the two-scale ramp potential,\(^{40}\) the

![Figure 6](https://jcp.aip.org/jcp/024503-6.png)

**FIG. 6.** (Color online) Variational \( \tilde{A} \) as a function of \( \sigma_{\text{HS}} \) at the indicated particle number. In each panel, the solid and dashed lines are the E-MCRS and MCRS \( \tilde{A} \), respectively. The dot-dashed line is the variational \( \tilde{A} \) with Mon’s correction term given in Eq. (5). For \( N = 500 \), the solid and dot-dashed lines are almost the same.

![Figure 7](https://jcp.aip.org/jcp/024503-6.png)

**FIG. 7.** (Color online) The excess Helmholtz free energy \( \tilde{A} = A^e / N k_B T \) predicted by the E-MCRS (solid line), MCRS (dash line), WCA (dotted line), and Lado-WCA (dot-dashed line) theories and the results calculated by thermodynamic integration in Eq. (8) (symbols).

![Figure 8](https://jcp.aip.org/jcp/024503-6.png)

**FIG. 8.** (Color online) Density dependence of the excess entropy \( S^e / N k_B \). The solid and dashed lines are the predictions of the E-MCRS and MCRS theories, respectively. The dot-dashed line is the excess entropy of the HS fluid with the HS diameter estimated by the E-MCRS theory. The symbols are the simulated results as described in the text.
anomalous behavior of $\bar{S}$ is associated with the density anomaly, where the density increases with increasing temperature at constant pressure.²⁴

For our model, the comparison between $\bar{S}$ calculated by simulation and those obtained by the MCRS and E-MCRS theories is shown in Fig. 8; the three results of $\bar{S}$ give similar density behavior. The predictions of the MCRS theory agree with the simulation results only at low densities and produce an excess entropy anomaly in a range shifting a little toward smaller density, but are deviated from the simulation data at densities beyond the anomalous region. The E-MCRS theory has a triumph over the MCRS theory for a perfect agreement with the simulation results in the entire range of density we have calculated. We also present the excess entropy of the HS fluid with the E-MCRS HS diameter, which shows a manifested anomaly with a larger positive slope. The absolute value of the excess entropy of this HS fluid is larger than that estimated by the E-MCRS theory. This implies that because part of the phase space is inaccessible by the HS fluid, in which the free volume of each particle is reduced, the difference between the entropy of the HS fluid and that of the ideal gas is, therefore, enhanced. Mon’s correction makes a compensation for the excluded volume effect so that the predictions of the E-MCRS theory for all densities agree well with the simulation results. As indicated in Fig. 8, the larger the fluid density is, the more significant the compensation due to Mon’s correction term. Thus, Mon’s correction fundamentally improves the prediction of the HS variational approach for the excess entropy of a fluid.

To address the reason why the anomaly in $\bar{S}$ predicted by the MCRS and E-MCRS theories occurs in our model, we have plotted in Fig. 9 the density dependence of the packing fractions of the reference HS fluids in various perturbation theories. In the WCA or the Lado-WCA theories, the packing fraction $\eta$ increases monotonically with the increase in density. At $\rho^*=3.3$, which is close to that of realistic liquid Ga, the $\eta$ values estimated by the two theories are over 0.7, which is in the solid phase of a HS system. This indicates that because of the overestimation in the effective HS diameter, the reference HS fluids in the two theories are too much deviated from our model. On the other hand, with the $\sigma_{\text{HS}}$ values estimated by the MCRS and E-MCRS theories, the density curve of the packing fraction apparently has a negative slope in the intermediate region, roughly from $\rho^*=1.3$ to 1.7, which corresponds to the substantial shrinkage in the size of the effective HS with increasing density, as shown in Fig. 4. Thus, the packing fraction of the HS fluid is reduced with increasing density in this density region. This anomaly in the packing fraction is the origin for the excess entropy anomaly predicted by the two theories. Beyond this anomalous region in packing fraction, the size of the effective HS is limited by the exponentially increasing repulsion in the inner core of the pair potential so that the packing fraction increases again with density at a smaller rate. At $\rho^*=3.3$, the packing fractions estimated by the MCRS and E-MCRS theories are, respectively, 0.473 and 0.5, which are in the fluid-solid coexistence region of the HS system, and the reference HS system is physically reasonable.

V. CONCLUSIONS

In terms of various HS perturbation theories, we have investigated thermodynamic behaviors of a model fluid, with which the structure and dynamic properties of liquid Ga close to the triple point are reproduced.²⁶,²⁷ The interatomic pair potential of the model has two features: a ledge-shape repulsive core and a long-range oscillatory part. Somewhat like the two-scale ramp potential, the repulsive core of the pair potential varies continuously from an exponential-decay inner core, through a ramplike intermediate region, to a LJ-type outer core. The model has been simulated at constant NVE conditions from low to high densities; at the highest density the simulated system corresponds to realistic liquid Ga at $T=323$ K. The radial distribution function of the model has an interesting variation with number density: At high density, the main peak of the radial distribution function is located in the inner region of the repulsive core with an exponential decay. At some critical density, the position of the main peak makes a discontinuous jump to the outer core of the LJ-type region. As the density is further decreased, the main peak moves toward the minimum of the first attractive well of the pair potential.

We have used the WCA, Lado-WCA, MCRS, and E-MCRS methods to estimate the effective HS diameter of the model. With the HS diameter estimated by the WCA or Lado-WCA method, the packing fraction of the HS system monotonically increases with density and, therefore, the packing fractions at high densities are over the freezing point of the HS system, which makes the WCA and Lado-WCA theories breakdown for our model at high densities. In the MCRS and E-MCRS theories, the packing fraction increases again with density at a smaller rate. At $\rho^*=3.3$, the packing fractions estimated by the MCRS and E-MCRS theories are, respectively, 0.473 and 0.5, which are in the fluid-solid coexistence region of the HS system, and the reference HS system is physically reasonable.
HS reference system increases again with density and has a physically reasonable value at high densities.

By including Mon’s correction term to compensate the deficiency of the HS perturbation theory, the E-MCRS theory indeed gives better predictions than the MCRS theory does; the predictions of the E-MERS theory for the excess Helmholtz free energy and entropy agree well with the simulation results from low to high densities. The excess entropy of our model is found to have an anomalous behavior, which has a density function with a positive slope. This excess entropy anomaly also occurs in the two-scale ramp potential, with which the waterlike thermodynamic properties are investigated recently. The excess entropy anomaly in our model can be described by the E-MCRS and MCRS theories, and the anomaly is associated with the substantial reduction of the effective HS diameter estimated by the two variational theories. Our results indicate that the E-MCRS theory is superior to other first-order HS perturbation theories for investigating thermodynamics of core-softened potentials.

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