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Entropy of a model for liquid Ga: Contribution due to Friedel oscillations

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ABSTRACT

In terms of an interatomic pair potential, possessing a soft repulsive core and the long-range Friedel oscillations, we have recently reproduced the anomalous structures and dynamic properties of liquid Ga just above the melting point. In this paper, evaluating separately for the model and the corresponding repulsive core by numerical simulation and the hard-sphere perturbation theory, we investigate the contribution due to the Friedel oscillations to the excess entropy of the model fluid. For the two model fluids, the density variations of the pair-correlation and residual-multiparticle entropies are also presented.

1. Introduction

The structures of liquid Ga just above the melting point are well known for an anomalous shoulder on the high-q side of the first peak in the static structure factor. Recently, we have reproduced the anomalous structures with an interatomic pair potential $\phi(r)$ generated from a first-principles pseudopotential theory [1,2]. Besides the anomalous structures, the dynamic properties of liquid Ga, including dynamic structure factor, dispersion relation and the damping factor of collective excitations at low q as well as the linewidth of dynamic structure factor at high q, are also well described by this model. However, the anomalous structures are not produced by the repulsive core $\phi_0(r)$ of the model, but appear as the range of the pair potential extends up to including the third attractive well, within a range of nanoscale, in Friedel oscillations. Thus, we conclude that the anomalous structures are associated with some medium-range order due to the Friedel oscillations.

Motivated from the aforementioned results, we investigate in this paper the excess entropy contributed by the Friedel oscillations in $\phi(r)$. Arising from particle interactions, the excess entropy of a simple fluid is a thermodynamic quantity related to the degree of structural disorder of particles [3]. As far as we know, there are only few papers studying the role of the attractive particle interactions in the thermodynamic properties of polyvalent liquid metals [4]. For simple fluids, the structures are primarily determined by the repulsive core of particles and the attractions between particles act as a perturbation [5]. Based on this general picture, the contribution due to the Friedel oscillations can be obtained by the difference of the excess entropies of $\phi(r)$ and $\phi_0(r)$ at the same NVT conditions; the excess entropies are evaluated separately with both numerical simulation and the hard-sphere (HS) perturbation theory [6]. We also examine the density variations of the excess entropy and its pair-correlation and residual-multiparticle parts for the model fluid with $\phi(r)$ or $\phi_0(r)$ [7].

2. Model and the HS perturbation theory

Presented in [2,6], $\phi(r)$ is characterized by a ledge-shape repulsive core and a long-range oscillatory part, with the first zero of $\phi(r)$ at $\sigma = 4.04$ Å. The repulsive core $\phi_0(r)$ is obtained by truncating $\phi(r)$ at $\sigma_0 = 4.32$ Å, the location of the first minimum, and shifting upwardly by an amount of the first-attractive-well depth ϵ, which corresponds to a temperature about 47 K. Like the two-scale Jagla potential [8], $\phi_0(r)$ possesses an extremely stiff region following by a ramp.

We performed a series of molecular dynamics simulations for particles interacting with $\phi(r)$ in a cubic box of length $L = 41.21$ Å at $T = 323$ K [6]. The particle number N in the simulation starts at 3500 and, then, is reduced by 100 in each new simulation, down to the lowest $N = 100$. Two notices should be given here. First, at $N = 3500$, with $\rho\sigma^3 = 3.3$, the simulated system mimics the equilibrium state of liquid Ga at pressure of about 1 bar and $T = 323$ K; however, the systems at other particle numbers have nothing to do with real Ga. Secondly, both the radial distribution function $g(r)$ generated by the simulation and the compressibility factor $Z = PV/Nk_BT$, where pressure P is evaluated from the pressure equation with an input of $g(r)$, change smoothly with density [6], indicating that the simulated system does not undergo a gas–liquid phase transition as N is reduced. The temperature of our simulations is about seven times of ϵ so that the simulated systems are expected to be supercritical. Similarly, we also performed the simulations with the repulsive core $\phi_0(r)$ at the same NVT conditions.

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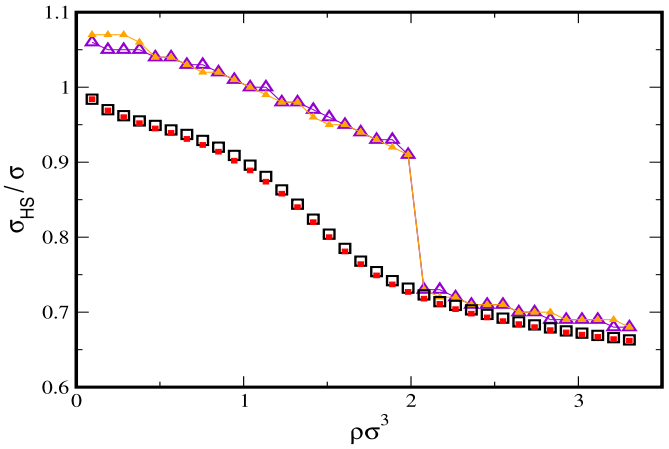

Fig. 1. Density variation of σ_{HS} estimated by the HS perturbation theory (squares) [9] and the main-peak position of $g(r)$ (triangles). $\rho = N/L^3$ is the number density. The large open symbols are for $\phi(r)$ and the small filled ones are for $\phi_0(r)$.

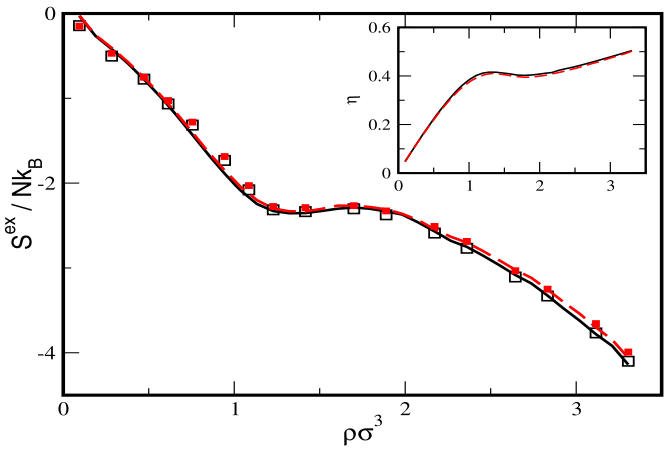

Fig. 2. Excess entropy S^{ex} as a function of density. The open and filled symbols are the simulation results for $\phi(r)$ and $\phi_0(r)$, respectively. The solid line is estimated by the HS perturbation theory for $\phi(r)$ and the dashed line is for $\phi_0(r)$. The inset shows the packing fraction η of the HS fluid with σ_{HS} shown in Fig. 1.

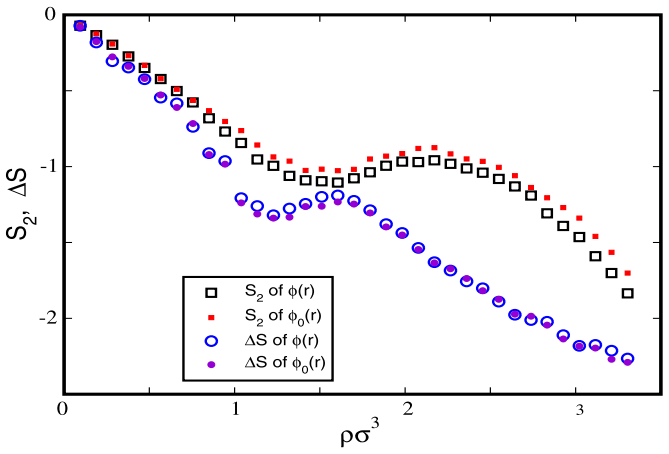

Fig. 3. Density dependence of pair-correlation entropy S_2 (squares) and RMPE ΔS (circles) in unit of k_B. The large open symbols are for $\phi(r)$ and the small filled ones are for $\phi_0(r)$.

In thermodynamics, the excess entropy S^{ex} of a fluid is given as $(A^{ex} - U^{ex})/T$, where A^{ex} and U^{ex} are the excess Helmholtz free energy and the internal energy of the fluid, respectively [3]. The calculation for U^{ex} is straightforward and A^{ex} can be obtained by an integration on the density function of Z [6]. Without any approximation in thermodynamics, S^{ex} obtained in this method are considered as the simulation results. Alternatively, A^{ex} can be estimated by an HS perturbation theory, which accurately predicts the thermodynamic quantities of fluids with very soft repulsive-core potentials [9].

The HS perturbation theory estimates an effective diameter σ_{HS} of particles in a fluid. Shown in Fig. 1, the σ_{HS} values of the two models are almost the same for all densities, and so are the main-peak positions of $g(r)$. At low densities, the main-peak position of $g(r)$ is located around the first attractive well of $\phi(r)$. But, at high-enough densities, the jam in the system pushes more particles into the extremely stiff region of $\phi_0(r)$, which causes the main-peak position of $g(r)$ near $\rho\sigma^3 = 2$ a discontinuous jump to a smaller distance of r. At densities above $\rho\sigma^3 = 2$, the density dependence of σ_{HS} is almost along the track of the main-peak position of $g(r)$.

3. Excess entropy

For both models, a good agreement between the S^{ex} obtained by simulation and that estimated by the HS perturbation theory is shown in Fig. 2. Generally, S^{ex} of $\phi(r)$ is slightly less than that of $\phi_0(r)$ at high densities, indicating that the Friedel oscillations in $\phi(r)$ cause a small decrease in the excess entropy. At low densities, S^{ex} decreases almost linearly with density, due to the excluded volume effect of the repulsive core. More interestingly, the density function of S^{ex} shows an anomalous behavior, with a small positive slope in the intermediate region, and then changes back to decreasing at higher densities. The anomaly in the density function of S^{ex} also occurs to a model fluid with the two-scale Jagla potential [10]. Owing to the appearance of a similar anomaly in the packing-fraction curve of the HS fluid with σ_{HS}, the S^{ex} anomaly can be explained by the shrinkage of σ_{HS} at the intermediate densities shown in Fig. 1.

The difference in S^{ex} between the two models is too small to be noticeable. To manifest clearly the difference, we separate S^{ex} per particle into the pair-correlation entropy S_2 and the residual multiparticle entropy (RMPE) $\Delta S = S^{ex} - S_2$ [7], where S_2 is related to $g(r)$ via the equation

$$S_2 = -\frac{\rho k_B}{2} \int d\mathbf{r} \left[g(r) \ln g(r) - g(r) + 1 \right]. \tag{1}$$

S_2 is associated with the pair correlation in a fluid and ΔS is related to the three-particle and higher order correlations. The density variations of S_2 and ΔS for the two models are shown in Fig. 3. Evidenced by our data, ΔS of the two models are almost the same from low to high densities. S_2 of $\phi_0(r)$ is larger than that of $\phi(r)$, with a noticeable difference in Fig. 3. Thus, we conclude that the Friedel oscillations in $\phi(r)$ cause a decrease in S_2.

4. Conclusions

In this paper, we have investigated the excess entropy of a model fluid with $\phi(r)$, which possesses a soft repulsive core $\phi_0(r)$ and the long-range Friedel oscillations. At some specific density, the model fluid describes well the structural and dynamic properties of liquid Ga at $T = 323$ K. By simulation and the HS perturbation theory, we have calculated separately the excess entropy of the model fluid and that of the fluid with $\phi_0(r)$. For both models, the predictions of the HS perturbation theory agree well with the simulation results. By the difference between the excess entropies of the two model fluids, we obtain the contribution due to the Friedel oscillations. Indicated by our results, from low to high densities, the Friedel oscillations always cause a decrease in the excess entropy of the model fluid with $\phi(r)$ at $T = 323$ K.

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