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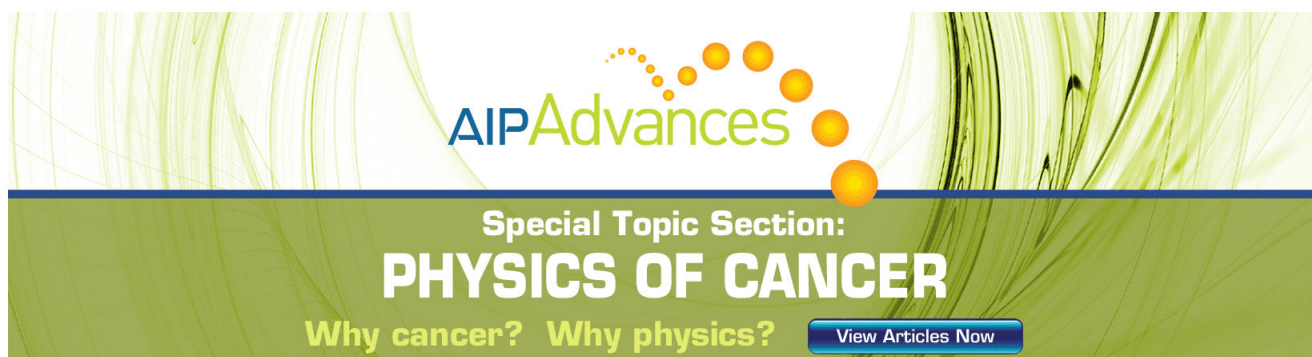
Correlations among residual multiparticle entropy, local atomic-level pressure, free volume and the phase-ordering rule in several liquids

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A modified Wang-Landau density-of-states sampling approach has been performed to calculate the excess entropy of liquid metals, Lennard-Jones (LJ) system and liquid Si under NVT conditions; and it is then the residual multiparticle entropy (S_{RMPE}) is obtained by subtraction of the pair correlation entropy. The temperature dependence of S_{RMPE} has been investigated along with the temperature dependence of the local atomic-level pressure and the pair correlation functions. Our results suggest that the temperature dependence of the pair correlation entropy is well described by T^{-1} scaling while $T^{-0.4}$ scaling well describes the relationship between the excess entropy and temperature. For liquid metals and LJ system, the $-S_{RMPE}$ versus temperature curves show positive correlations and the $-S_{RMPE}$ of liquid Si is shown to have a negative correlation with temperature, the phase-ordering criterion (based on the S_{RMPE}) for predicting freezing transition works in liquid metals and LJ but fails in liquid Si. The local atomic-level pressure scaled with the virial pressure (σ_{al}/σ_{av}) exhibits the much similar temperature dependence as $-S_{RMPE}$ for all studied systems, even though simple liquid metals and liquid Si exhibit opposite temperature dependence in both σ_{al}/σ_{av} and $-S_{RMPE}$. The further analysis shows that the competing properties of the two effects due to localization and free volume on the S_{RMPE} exist in simple liquid metals and LJ system but disappear in liquid Si, which may be the critical reason of the failure of the phase-ordering criterion in liquid Si. © *2011 American Institute of Physics*. [doi:10.1063/1.3524206]

I. INTRODUCTION

The phase transition from a disordered liquid into an ordered solid is a widely studied phenomenon. But even for some simple model systems it still represents a major challenge locating the phase boundaries accurately. Molecular simulations can be effectively used to this end and the accuracy of the estimated fluid-solid coexistence boundaries has significantly improved with the advent of advanced numerical-simulation methods for the calculation of free energies. However, calculating the free energy of either a dense liquid or a hot solid still remains a demanding computational task that requires intensive simulations to be carried out at several state points as well as some preliminary selection of the most likely candidate solid structures. For such reasons, several semiempirical rules have been proposed with the aim of locating the liquid-solid transition, without resorting to the knowledge of the free energy of liquid and solid phases. The first famous proposals of melting criterion was made by Lindemann,[1] which states that the ratio of the root-mean-square displacement of a particle to the average nearest neighbor distance is about 0.15 when the crystal melts. The second freezing criterion was due to Hansen and Verlet[2] who observed that the peak value of the first maximum of the structure factor, $S_{\max}(Q)$, is about 2.85 along the freezing curve

of simple fluids. Indeed, it has been found that the value of $S_{\max}(Q)$ at freezing depends on the softness of the potential as well as on the dimensionality of the hosting space.[3] Another empirical rule proposed by Raveché *et al.*[4] states that the ratio between the values of the pair correlation function at distances corresponding to the first nonzero minimum and to the largest maximum is around 0.20 ± 0.02 at freezing. More recently, based on the observation that the residual multiparticle entropy (S_{RMPE}) of the fluid changes sign when the fluid is close to the thermodynamic freezing transition, Giaquinta and Giunta[5] proposed a phase-ordering rule on the S_{RMPE}, i.e., the zero residual multiparticle entropy (zero-S_{RMPE}) freezing criterion. Here, the S_{RMPE} is defined as the contribution to the entropy of a fluid due to three-body and higher order correlations, and is thus the difference between the excess entropy per particle (S_e) and the pair correlation entropy (S_2). The zero-S_{RMPE} freezing criterion provides a quasiuniversal "one-phase" rule for the location of the liquid-solid transition and has been argued to be more general than other phenomenological freezing rules because the criterion does not hinge on system-dependent parameters. This criterion has been examined extensively and found to be valid for a number of phase transitions where a disordered or partially ordered fluid transforms to a more structured phase, such as freezing, fluid-fluid phase separation, isotropic-nematic transition and the infinite-order Kosterlitz and Thouless phase transition.[6–9] However, some results suggest that a change in sign of the S_{RMPE} of the fluid is not always a reliable locator of the freezing

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transition. For example, the zero-S_{RMPE} criterion is a less accurate predictor of freezing for systems with a finite short-range repulsion than for systems with a strong short-range repulsive core.[10] The zero-S_{RMPE} criterion works in two and three-dimensions fluids but it fails in other spatial dimensions for *d*-dimensional hard-sphere ($d = 1$–5).[11] For the majority of the isochors studied in a two-dimension square-shoulder fluid by Singh *et al.*[12] the zero-S_{RMPE} prediction and the thermodynamic evidence for a phase transition were consistent, but this criterion fails along isochors that are in regions of two coexisting ordered phases, thus they concluded that the zero-S_{RMPE} rule may be only likely to be approximately predictive in systems with small phase coexistence regimes, e.g., in the case of liquid crystal forming systems.

As mentioned above, although there have been a number of tests of the zero-S_{RMPE} freezing criterion, it has not been clarified how universal this criterion is or what is the condition for it, i.e., establishing the range of validity of the zero-S_{RMPE} criterion remains an open question. So it needs us to perform further studies in order to confidently label the zero-S_{RMPE} freezing criterion and use it. In the present work, simple liquid metals characterized by central force potentials with isotropic many-body interactions and liquid Si with anisotropic interatomic interactions are studied under NVT conditions to critically examine the usefulness of the zero-S_{RMPE} criterion. It is important to point out that the structure of Si strongly differs from that in the examined metallic liquids: the coordination number of simple liquid metals is about 12 while in liquid Si it is about 6, indicating that liquid Si appears not to be a "free-electron" metal but contains "covalent character". In liquid Si, besides the first peak in g(r) (the pair correlation function) there exists a small peak on the high-*r* side; in simple liquid metals characterized by central force potentials the first peak in g(r) is very sharp. Thus, for simple liquid metals the pair correlation entropy contribute ~85% to excess entropy,[13] implying the S_{RMPE} makes very less contribution to the excess entropy; while in liquid Si the pair correlation entropy contributes less to excess entropy compared to liquid metals, the contribution of the S_{RMPE} to excess entropy turns out to be very important. These are why in the present work simple liquid metals and liquid Si are selected to be the studied systems for further studying the zero-S_{RMPE} criterion through exploring the correlation among S_{RMPE}, the atomic-level pressure, the free volume of a atom and the zero-S_{RMPE} criterion.

The S_{RMPE} is a cumulative "measure" of the statistical weight associated with correlations involving at least three particles, and it can be obtained by subtraction of the pair correlation entropy from the excess entropy of the fluid. The pair correlation entropy is expressed as

$$S_2 = -2\pi\rho \int_0^\infty \{g(r)\ln g(r) - [g(r)-1]\}r^2\, dr, \quad (1)$$

where ρ is number density. So the precision in calculation of S_{RMPE} is mainly dependent on the accurate calculation of excess entropy.

As a well known fact, the entropy, the number of accessible configurations, is calculated by

$$S(N,V,E) = -k_B \ln \Omega(N,V,E), \quad (2)$$

where k_B is the Boltzmann constant and $\Omega(N, V, E)$ is the density of states. A novel Monte Carlo method (WL method) has been proposed by Wang and Landau[14] for direct calculation of the density of states of systems as a function of one or more macroscopic observables like energy, temperature and volume. This method has drawn wide attention of researchers due to its straightforward implementation and wide applicability. Also, it has been generalized for off-lattice simulations.[15] Shell *et al.*,[16] in 2003, proposed a modified Wang-Landau density-of-states sampling approach (WLTM) which combines the good statistical accuracy of Transition Matrix Monte Carlo algorithm (TM) with the rapid broad sampling of space generated by the WL method. With this method, the entropy over a significant range of temperatures can be obtained easily. In the present work, the WLTM method is used to accurately calculate the excess entropy of LJ system, liquid metals and liquid Si under NVT conditions.

The rest of the paper is organized as follows: in Sec. II, the computational methods and details are described; in Sec. III, the results are presented and discussed; finally, the conclusions are given in Sec. IV.

II. COMPUTATIONAL METHODS AND DETAILS

The interparticle interactions of simple metals including Al, Cu, Ti and Pb were described by the second-moment approximation of the tight-binding scheme,[17] which has been widely used in numerical simulation studies in metals and alloys.[17–20] According to this formalism, the potential energy *U* of a system can be written as

$$U = \sum_i \left\{ \sum_j A e^{-p(r_{ij}/r_0-1)} - \left(\sum_j \xi^2 e^{-2q(r_{ij}/r_0-1)} \right)^{1/2} \right\},$$
$$(3)$$

where the sum is over all atoms in the system, r_{ij} represents the distance between atom *i* and *j*, and r_0 is the first-neighbors distance of the bulk crystal. The repulsive portion is a Born-Mayer pair-wise interaction. The attractive term mimics the form of the square root of the second moment of local density of states, and hence has a many-body character. In this paper, we use the value of parameters **A**, ξ, *p* and *q* as given by Cleri and Rosato.[17] The Tersoff potential[21] is employed to model the Si atomic interaction. It is found that this potential is very useful for the structural analysis of liquid Si though it overestimates greatly the melting temperature.[22,23] Tersoff gives his potential as

$$V_{\text{Tersoff}} = (1/2) \sum_{i \neq j} f_c(r_{ij})\left(A e^{-\lambda r_{ij}} - b_{ij} B e^{-\mu r_{ij}}\right), \quad (4)$$

where r_{ij} represents the distance between atom *i* and *j*; f_c is a smooth cutoff function; *A, B, λ, μ* are parameters; and b_{ij} is the bond-order term, which depends on the local environment and gives the many-body character to the potential. The potential was described in detail in Ref. 21 and the parameter values were taken from this paper.

In the standard WL algorithm the probability of observing a particular atomic configuration is inversely proportional

to the density of states ($\Omega(E)$) corresponding to the given energy, that is to say, the new state is accepted with probability:

$$p(E_I \rightarrow E_J) = \min\left[\frac{\Omega(E_I)}{\Omega(E_J)}, 1\right], \quad (5)$$

where E_I and E_J are the energies of the initial and final states, respectively. The density of states is initially set so $\Omega(E) = 1$, and is modified at every simulation step. For each of the visited states, the corresponding $\Omega(E)$ is updated according to $\Omega(E) = f \times \Omega(E)$, where f is an arbitrary convergence factor which can be as large as $f = f_0 = e^1 \approx 2.71828$ initially and tends to unify as the calculation proceeds. We also keep track of the histogram $H(E)$, counting the number of times each energy is visited. Once the histogram is sufficiently flat, f is reduced and $H(E)$ is reset to zero. These steps are repeated until f has become close to unity. However, it has been noted that the WL algorithm reaches a limiting accuracy, after which the statistical quality of data no longer improves, no matter how much additional computer time is invested. Hence, Shell *et al.*[16] propose to measure the transition matrix (TM) elements $C(E_I \rightarrow E_J)$. From the TM elements one can estimate the probability $T(E_I \rightarrow E_J)$ that being in state with energy E_I, a move to a state with energy E_J is proposed,

$$T(E_I \rightarrow E_J) = \frac{C(E_I \rightarrow E_J)}{\sum_K C(E_I \rightarrow E_K)}, \quad (6)$$

and this is related to the density of states via

$$\frac{\Omega(E_I)}{\Omega(E_J)} = \frac{T(E_J \rightarrow E_I)}{T(E_I \rightarrow E_J)}. \quad (7)$$

Hence, by recording TM elements, the density of states can also be constructed. In the present work (following Ref. [16]) we combine WL sampling with the TM method. With an accurate density of states, the partition function or the averages of other important thermodynamic quantities can be calculated directly; for example entropy can be computed by Eq. (2). Reweighing techniques[24] is employed for transforming $S(N,V,E)$ as function of temperature. Since the density of states is modified every time the state is visited, a relative density of states and a relative entropy are obtained only at the end of the simulation.[14] The difference between the relative entropy and the absolute entropy is a constant. In order to get the value of the constant, we select the LJ system as a reference system whose equation of states is known and then the absolute entropy is easy to obtain. Once the constant has been obtained, we can obtain the absolute entropy over the range of studied temperatures. Then the excess entropy is calculated by subtracting the entropy of an equivalent ideal gas from the absolute entropy of the system.

Monte Carlo simulations for all the systems are carried out in the canonical (NVT) ensemble under cubic periodic boundary conditions. First, we run short simulations in the canonical ensemble for both the low temperature and high temperature phases to get the energy range. The energy range is then divided into a number of bins and in which we then run the WLTM algorithm for 1×10^8 MC steps. We reduce the modification factor $\ln f \rightarrow 0.1 \ln f$, and finally postpone the refreshing of the density of states using the transi-
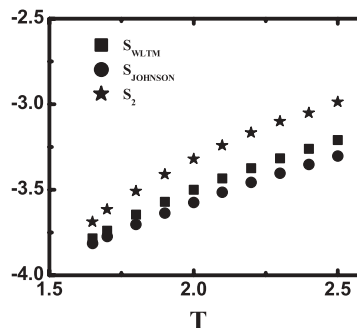

FIG. 1. The temperature dependences of the excess entropy obtained with WLTM method (S_{WLTM}) and calculated by the LJ equation of state ($S_{JOHNSON}$) as well as the pair correlation entropy (S_2) of LJ liquid.

tion matrix until the first few stages of the modification factor schedule have passed, during which $f \gg 1$. The system is run for 500 000 cycles at the given temperature to guarantee an equilibrium liquid state; a cycle consisted of one attempt to change all particle positions. The maximum displacement of a particle was adjusted along the run so as to keep the acceptance ratio of the MC moves as close to 0.5 as possible. After achieving equilibrium in the system, 50 000 MC steps were applied to calculate thermodynamic averages. The $g(r)$ are obtained by averaging 50 configurations sampled during another run of 25 000 steps, the integral in the Eq. (1) was evaluated using $g(r)$ data with a cutoff distance equal to the half of the box length.

In our simulation we have used systems consisting of 1000 particles for liquid Si, and of 1372 particle for simple liquid metals and LJ system. We have conducted test to establish the sensitivity of the calculated excess entropy, pair correlation entropy and pair distribution function on the size of the system and found that the sizes of the systems used in our work are sufficient for the present purpose. In order to judge the accuracy of the WLTM method used in the present paper, the excess entropy obtained with WLTM method were compared with that calculated by the LJ equation of state.[25] Both methods give results that are very close to each other, as shown in Fig. 1.

III. RESULTS AND DISCUSSIONS

Figure 2 shows the temperature dependences of the pair correlation entropy (S_2) and the excess entropy (S_e) under NVT conditions, for several simple liquid metals, liquid Si and LJ system. Note that S_2 and S_e are in the units of K_B per atom. We also use the reduced temperature $T^* = k_B T/\varepsilon$ and density $\rho^* = \rho\sigma^3$ for LJ system. As expected, both S_2 and S_e increase with increasing temperature for all studied systems. S_2 is always larger than S_e, indicating that the residual multiparticle entropy S_{RMPE} is negative. The S_{RMPE} contributes about 20% or less to the S_e for LJ system and liquid metals, while for liquid Si the contribution of the S_{RMPE} to the S_e can be as large as 50% which is evidenced by the large distances between solid and open pentacles shown in this figure. So it is unreasonable the estimation of excess entropy by pair correlation entropy for liquid Si. In addition, this figure tells us that S_2 increases more strongly than S_e for liquid
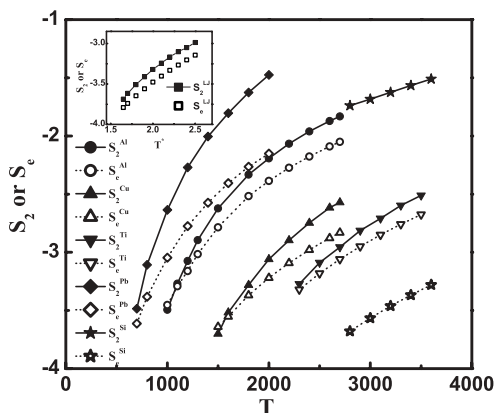
FIG. 2. The pair correlation entropy (S_2) and excess entropy (S_e) as functions of temperature (T) for several simple liquid metals and liquid Si. The inset shows the S_2 and S_e of LJ liquid also plotted as a function of the reduced temperature (T^*). Lines are guides for the eyes.

metals and LJ system, emphasizing that the difference between S_2 and S_e is not a constant, thus the best fit expression to the temperature dependence of S_2 is different from that of S_e. Earlier density functional studies on inverse power and repulsive Yukawa potentials[26] suggest that the excess entropy S_e can be well represented by the form

$$S_e \propto T^{-0.4}, \tag{8}$$

as it happens in many cases. A few years ago, employing realistic many-body potential for a series of simple liquid metals, Li *et al.*[20] approximated the excess entropy by the pair correlation entropy as in Ref. [27] and found that S_e, i.e., S_2, universally scales with temperature as:

$$S_2 \propto T^{-1}. \tag{9}$$

We fit Eqs. (8) and (9) to the temperature dependence of S_e and S_2, respectively, and find that the temperature dependence of S_2 is well described by T^{-1} scaling and $T^{-0.4}$ scaling describes the relationship between the excess entropy and temperature accurately, for all the liquid metals, liquid Si and LJ system as shown in Fig. 3.

The phase-ordering rule of S_{RMPE} for predicting transitions from disordered to ordered phases is tested by plotting -S_{RMPE} as a function of temperature along isochors for various systems as shown in Fig. 4. A glance of this figure shows that over the studied temperature range liquid Si exhibits a different temperature dependence of -S_{RMPE} from other studied liquid systems: as temperature is lowered, for liquid Si -S_{RMPE} increases, whereas for other simulated liquid systems it decreases and the decrease trend becomes rapid with the decrease of temperature. These indicate that with the increase of temperature in liquid metals and LJ system the multiparticle (three-body and higher order) correlation is enhanced, whereas in liquid Si the multiparticle correlation is weakened, which is in agreement with the fact that in liquid Si the covalent bonds decrease and the floating bonds increase with temperature. Therefore, for all studied systems except liquid Si the freezing temperatures can be obtained using the phase-ordering rule of S_{RMPE}, the change sign of -S_{RMPE} from positive to negative, which are summarized in Table I. In order
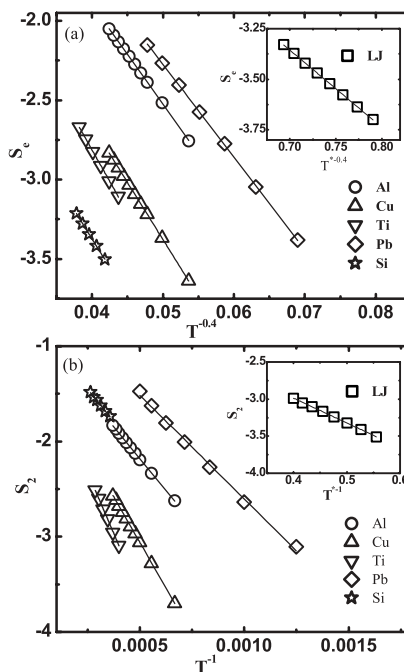

FIG. 3. $T^{-0.4}$ dependence (a) of excess entropy (S_e) and T^{-1} dependence (b) of the pair correlation entropy (S_2) for several simple liquid metals, liquid Si. The inset in panel (a) shows $T^{*-0.4}$ dependence of S_e of LJ system, the inset panel (b) shows T^{*-1} dependence of S_e of LJ system. Lines are the best to present the data.

to make a comparison, we also present in Table I the experimental values (T_E), the theoretical estimates (T_{HV}) from the freezing criterion proposed by Hansen and Verlet,[2] theoretical values (T_C) obtained using the thermodynamic condition for two-phase coexistence with the same model potential. As a result, the extrapolated freezing temperatures on the basis of the zero-S_{RMPE} criterion are in reasonable agreement with experimental values or results calculated by other methods. In contrast, the failure of liquid Si in obtaining freezing temperature clearly indicates that the zero-S_{RMPE} criterion does not hold for liquid Si. Only based on the present results we may not conclude which one of these two semiempirical freezing rules is better. But it should be pointed out that the first-peak value of $S(Q)$ of liquid Si close to melting temperature is much
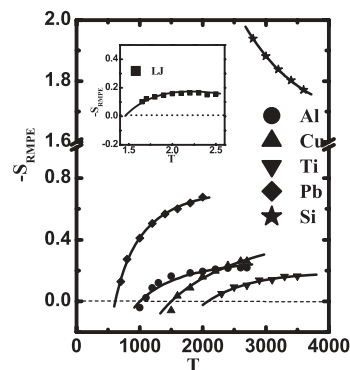

FIG. 4. Dependence of residual multiparticle entropy (S_{RMPE}) on temperature (T) for several simple liquid metals and liquid Si. The inset shows the -S_{RMPE} of LJ liquid also plotted as a function of the reduced temperature (T^*).

TABLE I. Obtained freezing temperatures using the phase-ordering rule of S_{RMPE} (T_{RMPE}) and using the freezing criterion proposed by Hansen and Verlet Ref. 2 (T_{HV}) for liquid LJ, liquid metals and liquid Si. Freezing temperature T_C is theoretical value obtained using the thermodynamic condition for two-phase coexistence, and T_E is the experimental freezing temperature. ρ is number density. For LJ liquid, number density in units of σ^{-3}, temperature in units of ε/k_B (ε and σ are LJ parameters, k_B is Boltzmann constant). For liquid metals, number density in units of $\mathring{A}^{-3}$, temperature in units of K.

	LJ	Al	Cu	Pb	Ti	Si
ρ	1.0130	0.0531	0.0760	0.0310	0.0517	0.0551
T_{RMPE}	1.46	1006.45	1503.46	614.59	2070.51	
T_{HV}	1.54	770.8	1355.8	683.0	1834.7	
T_C	1.59[a]	870 ± 5[b]	1237 ± 7[b]	466 ± 5[b]		2750[c],2547[d]
T_E		933.25[e]	1357.6[e]	600.6[e]	1943[e]	1683[f]

[a]Reference 34.
[b]Reference 18.
[c]Reference 23.
[d]Reference 16.
[e]Reference 35.
[f]Reference 36.

lower than the value given by the Hansen-Verlet freezing criterion, therefore the freezing criterion proposed by Hansen and Verlet[2] also fails in liquid Si. In addition, the results of pair correlation entropy at freezing point of liquids except Si are shown in Fig. 5, which is in good agreement with the work of Chakraborty[28] and Yokoyama,[29] where the S_2 value at freezing is $-3.5(\pm 0.3)$ for LJ, soft-sphere, and Morse liquids, also in agreement with the work of Rosenfeld,[26] where the excess entropy at freezing is -4.0 for all soft inverse power potential and Yukawa potentials. Why does the phase-ordering rule of S_{RMPE} hold for liquid LJ systems and simple liquid metals but not hold for liquid Si? Keep this question in mind while we discuss the following.

The variations in the residual multiparticle entropy as a function of the temperature must not only be related to the behavior of different order metrics charactering the nature as well as the extent of structural disorder, but also reflect the atomic dynamics. In order to obtain some information about the connections among the residual multiparticle entropy, dynamics and local order in liquids we use the concept of atomic-level stresses, which is introduced to describe the local structure of metallic glass systems and has been successfully used in describing the atomistic nature of defects in crystalline, the glass transition and atomistic structures of liquids.[30–32] The atomic-level stresses reflect the topology and symmetr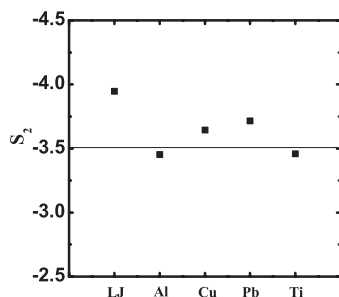y of the environment of each atom as well as the interaction of this atom with its surrounding atoms. Thus, the atomic-level stresses together with the atomic-level volume may approximately describe the atomic dynamics and could be used as the basis for the statistic mechanics of liquids.

The expression for local atomic-level stresses σ^{ab} is given by[30–32]

$$\sigma_i^{ab} = -\frac{1}{\Omega_i}\left[\frac{1}{2}\sum_j F_{ij}^a r_{ij}^b + M_i v_i^a v_i^b\right], \qquad (10)$$

where a and b are the Cartesian coordinates, F_{ij} is the force on atom i due to atom j, M_i is the mass of atom i, v_i is the velocity of atom i, r_{ij} is the separation of atoms i and j, Ω_i is local atomic volume of atom i. The kinetic contribution [the second term in Eq. (10)] associated with the flow of particles across a fixed spatial surface is trivial compared to the configurational contribution (the first term) associated with the interatomic forces acting between particles.[32] Here, the stress is thus calculated using the following form:

$$\sigma_i^{ab} = -\frac{1}{2\Omega_i}\sum_j F_{ij}^a r_{ij}^b. \qquad (11)$$

The local atomic volume (Ω_i) can be calculated using the volume of Voronoi-polyhedron of atom i.[32] For the sake of simplicity, as in Ref. 32 we used an essentially equivalent but simpler approach, calculating Ω_i using a weighted average near-neighbor distance for atom i,

$$\Omega_i = \frac{4}{3}\pi a_i^3, \qquad (12)$$

and

$$a_i = \frac{\sum_j r_{ij}^{-1}}{2\sum_j r_{ij}^{-2}}, \qquad (13)$$

where r_{ij} is the distance between atom i and its near-neighbor atom j. a_i is average radius of the near-neighbor shell around atom i. In our present calculations, the cutoff distance for defining near-neighbor atoms of atom i correspond to the first minimum of the pair correlation function. Liquids are macroscopically isotropic, so it is natural to use spherical representation of stresses or equivalently the cubic representation. One of the local stress components in the cubic representation is:

$$\sigma_i^\alpha = \sqrt{\frac{1}{3}\left[\sigma_i^{xx} + \sigma_i^{yy} + \sigma_i^{zz}\right]}. \qquad (14)$$

The local atomic-level stress corresponds to the atomic-level pressure by

$$\sigma_{al} = \left(\frac{1}{\sqrt{3}}\right)\sigma_i^\alpha. \qquad (15)$$

Atomic-level pressure fluctuation leads to a rearrangement in the nearest neighbor atomic configuration and changes the local density. In order to make comparison, here the atomic-level pressure is scaled by the average virial pressure of corresponding system. Therefore, we display the ratio of the average values of the atomic-level pressure (σ_{al}) to the average virial pressure of systems (σ_{av}) as a function of temperature for several simple liquid metals, liquid Si and LJ system
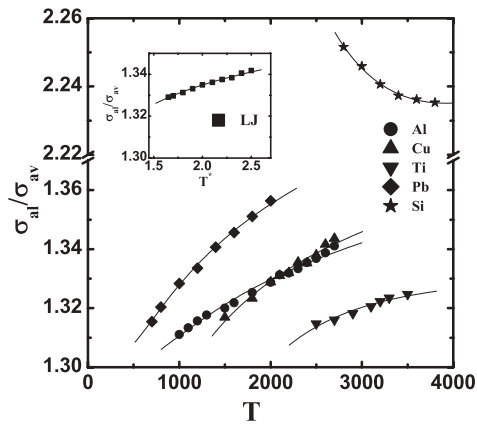

FIG. 5. The pair correlation entropy (S_2) of liquids at freezing.

FIG. 6. The ratio of the average values of the atomic-level pressure (σ_{al}) to the average virial pressure of systems (σ_{av}) as a function of temperature (T) for several simple liquid metals and liquid Si. The inset shows the corresponding quantity of LJ liquid also plotted as a function of the reduced temperature (T^*).
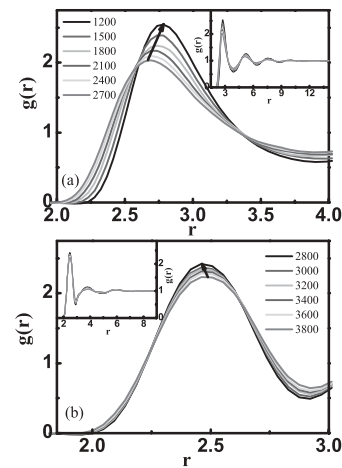

FIG. 7. The pair correlation function at different temperature in the region around the main peak: (a), liquid Al; (b), liquid Si. The insets show the long-range behavior of the pair correlation functions.

under NVT conditions in Fig. 6. As can be seen from this figure, the σ_{al}/σ_{av} of liquid metals and LJ system is positively correlated with temperature, however, for liquid Si it is negatively correlated with temperature. That is, when temperature is increased the local density around an atom increases under NVT conditions for liquid metals and LJ system while for liquid Si it decreases. The comparison between Fig. 4 and Fig. 6 clearly indicates that, σ_{al}/σ_{av} and -S_{RMPE} have much similar temperature dependence for all studied systems, even though simple liquid metals and liquid Si exhibit opposite temperature dependence of both σ_{al}/σ_{av} and -S_{RMPE}. Thus, there exists the positive correlation between σ_{al}/σ_{av} and -S_{RMPE}: when the local density around an atom increases/decreases the multiparticle correlations becomes strong/weak, i.e., the absolute value of the residual multiparticle entropy becomes large/small.

It has been argued that the *zero-S_{RMPE}* criterion is the outcome of two competing effects[12,33] of multiparticle correlations on the excess entropy of a fluid: one is that the increase of localization tends to lower S_{RMPE}, another is that an increase in the free volume as a consequence of local ordering results in a positive contribution to S_{RMPE}. As the temperature is lowered the localization is always increased. So the change behavior of the free volume of atoms with temperature may play a critical role in the temperature dependence of S_{RMPE}, it turns out to be the critical factor of the zero-S_{RMPE} criterion. The change behavior of free volume with temperature can be obtained quantitatively from the pair correlation function. In Fig. 7 we plot the pair correlation function $g(r)$ of liquid Al (as an example of simple liquid metals and LJ system) and liquid Si at different temperatures. From Fig. 7(a) we can see that the first peak in the $g(r)$ of liquid Al shifts to a longer distance and the inner portion of the first peak shifts the weight to the outer portion with the decrease of temperature. But as shown in Fig. 7(b) the first peak in the $g(r)$ of liquid Si shifts to a shorter distance and the outer portion of the first peak shifts the weight to the inner portion with lowering temperature, which is in agreement with the fact that the floating binds decrease and the covalent bonds increase with

the decrease of temperature in liquid Si. Thus, in simple liquid metals the free volume increases with the decrease of temperature, which makes a positive contribution to S_{RMPE}. And the greater free volume afforded by the more efficient structural packing overcomes the effect of increased positional ordering in determining the S_{RMPE} at freezing temperatures. But in liquid Si the free volume decreases with the decrease of temperature, which makes a negative contribution to S_{RMPE}. The competing properties of the above-mentioned two effects on the S_{RMPE}, which exist in simple liquid metals, disappear in liquid Si. Therefore, the phase-ordering criterion based on the residual multiparticle entropy works in simple liquid metals and LJ system but fails for liquid Si.

IV. CONCLUSIONS

Employing realistic many-body potential for a series of liquid metals, LJ potential and Tersoff potential for liquid Si, a modified Wang-Landau density-of-states sampling approach has been performed to calculate the excess entropy under NVT conditions. Our results suggest that the temperature dependence of the pair correlation entropy is well described by T^{-1} scaling while $T^{-0.4}$ scaling well describes the relationship between the excess entropy and temperature. Liquid Si exhibits a different temperature dependence of -S_{RMPE} from liquid metals and LJ system: as temperature is lowered, for liquid Si -S_{RMPE} increases, whereas for other liquid systems it decreases. This is in agreement with the fact that in simple liquid metals and LJ system, the local atomic-level pressure decreases with decreasing temperature, while in liquid Si, the atomic-level pressure increases with the decrease of temperature. The phase-ordering criterion based on the residual multiparticle entropy work on simple liquid metals, but fails in liquid Si. Our further analysis shows that the competing properties of the two effects due to localization and free volume on the S_{RMPE} exist in simple liquid metals and LJ system but disappear in liquid Si, which may be the critical reason of the failure of the phase-ordering criterion in liquid Si.

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