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Two-order-parameter description of liquid Al under five different pressures

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In the present work, using the *glue* potential, the constant pressure molecular-dynamics simulations of liquid Al under five various pressures and a systematic analysis of the local atomic structures have been performed in order to test the two-order-parameter model proposed by Tanaka [Phys. Rev. Lett. **80**, 5750 (1998)] originally for explaining the unusual behaviors of liquid water. The temperature dependence of the bond order parameter Q_6 in liquid Al under five different pressures can be well fitted by the functional expression $\frac{Q_6}{1-Q_6}=Q_{60}\exp(\frac{\Delta E-P\Delta V}{k_BT})$ which produces the energy gain ΔE and the volume change upon the formation of a locally favored structure: $\Delta E=0.025$ eV and $\Delta V=-0.27$ (Å)^3. ΔE is nearly equal to the difference between the average bond energy of the other type I bonds and the average bond energy of 1551 bonds (characterizing the icosahedronlike local structure); ΔV could be explained as the average volume occupied by one atom in icosahedra minus that occupied by one atom in other structures. With the obtained ΔE and ΔV, it is satisfactorily explained that the density of liquid Al displays a much weaker nonlinear dependence on temperature under lower pressures. So it is demonstrated that the behavior of liquid Al can be well described by the two-order-parameter model.

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I. INTRODUCTION

As well known, both gas and liquid phases are isotropic and homogeneous and have complete translational and rotational symmetries. Moreover, there is no loss of symmetry in going from the gas to the liquid phase. The isotropy and homogeneity mean that the average environment of any point is identical to that of any other point. The principal physical quantity distinguishing the liquid phase from the gas phase is the density. Because of these features, it has been widely believed that a liquid can be described by just one order parameter, density ρ. Although the density of liquid phase is uniform, the correlation between the positions of neighboring atom is strong; i.e., there is a strong peak at the near-neighbor spacing and less pronounced peaks at next-near and further neighbor separations in pair distribution functions. The strong correlations (local order) become increasingly more important as temperature is decreased.[1] There are number of studies that have tried to improve the theory of liquids by including many-body effects or higher-order density correlation. Despite numerous experimental and theoretical attempts to determine the structural nature of liquids, no satisfactory understanding has been attained because of the complexity of the structure. The most important is the concept of local bond-orientational order, which is based on the fact that even spherical molecules locally favor a tetrahedral configuration in a liquid phase. For example, Frank[2] pointed out that icosahedral clusters, composed of 13 particles, have a significantly lower energy than the more obvious crystallographic arrangements of the corresponding fcc or hcp structures. But it is impossible to fill space by packing icosahedra. There is a competition between a local preference for icosahedral structure and the global requirement of filling space. Hence, contrary to the one-order-parameter description of liquids, Tanaka[3–10] recently proposed a two-order-parameter model, density, and bond order parameters. The density order parameter maximizes the (globe) density (or packing) and leads to the crystallization representing the long-range ordering. At the same time, however, the bond order parameter maximizes the quality of local bonds and leads to the formation of the locally favored structures representing the short-range order, which can be viewed as a consequence of specific many-body interactions. Note that the symmetry of locally favored structures is generally inconsistent with the crystallographic symmetry. As mentioned above, the spherical atoms locally favor icosahedral arrangements, which are in a lower-energy state than that of the corresponding fcc, hcp, or bcc (most stable or metastable) crystalline units. Therefore, the following physical picture of liquid was proposed by Tanaka:[3] (i) in any liquids there exist well-defined and unique locally favored structures (which is in the lower-energy state) and (ii) such local structures are excited in a sea of another disordered background structure (normal-liquid structure, being in a higher-energy state). For the simple liquid metals the disordered background structures could be a mixture of some characteristic pairs/units, which can be thought as crystal (fcc, hcp, and bcc or most stable and metastable) basic units (for example, 1421, 1422, and 1441 and 1661 pairs are related to fcc, hcp, and bcc structures, respectively[11]). Since these pairs/units are present substantively in liquid metals and during the cooling process, besides the competition between glass formation and crystallization, there are other competitions among all kinds of crystalline structures.[12–16] The relevance of the two-order-parameter model of liquid is supported by the successful description of water's anomalies[3,7,8] and by the well explanation of the temperature dependence of the structure factor and the thermodynamic anomalies of density and heat capacity in liquid Si in a coherent manner.[10] But little is known of the applicability of the two-order-parameter model to the properties of liquid metals. It is interesting to see whether or not the two-order-parameter model is successful in understanding the temperature dependence of liquid metals properties.

It is found experimentally that the temperature dependence of density for liquid metals and alloys is linear. However, for Al, there are sufficient data to indicate that the density does not change linearly with temperature over the whole liquid range.[17] In the present work, we have carried out molecular-dynamics (MD) simulations by using a many-body potential in order to describe the evolution of some locally favored structures during the cooling process and the effect of high pressure on the local structural order in liquid Al in hope of performing a test of the two-order-parameter model on the properties of liquid Al. The rest of the paper is organized as follows: in Sec. II, we describe the method of our simulations; the results of our simulations and the corresponding discussion are reported in Sec. III; and a short summary is given in Sec. IV.

II. COMPUTATIONAL METHODS

The glue potential developed by Ercolessi and Adams[18] can correctly reproduce many basic properties of Al in crystalline and noncrystalline phases.[19–22] In our present work, the glue potential is employed to model the Al atomic interaction. The MD simulations of the cooling of Al system are performed under constant pressure conditions including 0.0, 0.1, 1.0, 2.0, and 3.0 GPa. The simulated system consists of 4000 atoms in a cubic cell with periodic boundary conditions. The Newtonian equations of motion were integrated using the velocity-Verlet algorithm with a time step of 5.3 $\times 10^{-16}$ s. The well-equilibrated initial system was prepared by heating the perfect crystal gradually. Then this system was cooled down with a sequentially cooling model, which means that after a period of temperature drop it experienced a relaxation process with 20 000 steps. During the later 6000 steps of relaxation process, 20 configurations were saved to collect data for analyzing the microstructures by another program. According to Abraham's suggestion,[23] the glass transition temperature T_g can be obtained using intersection of two lines with different slopes in the enthalpy versus temperature curves. In the meantime, the time-dependent mean-square displacement (MSD) was calculated. Here we only present and discuss the results of liquid Al, that is, the temperature ranges are above T_g, and the MSD is linear with time. All the results of structural analysis are obtained by averaging over 20 configurations.

To analyze the bond orientational order in noncrystalline states, Steinhardt *et al.*[24] proposed the bond order parameter Q_{lm}, $Q_{lm}(\mathbf{R})=Y_{lm}[\theta(\mathbf{R}),\phi(\mathbf{R})]$. Here $Y_{lm}(\theta,\phi)$ denotes the spherical harmonic function, θ and ϕ refer to the polar angles of the bond measured with respect to the reference coordinate system, and $\mathbf{R}$ is the midpoint of a bond. The average of their rotationally invariant combination can be calculated,

$$Q_l = \left[\frac{4\pi}{2l+1} \sum_{m=-l}^{l} |\bar{Q}_{lm}|^2 \right]^{1/2}. \tag{1}$$

In the present work, we use Q_6 as the bond order parameter of the two-order-parameter model since there exist a great of icosahedral units in liquid Al.

The pair analysis technique proposed by Honeycutt and Andersen[11] has been widely used to monitor liquid, glass, and crystalline structures. In this technique, pairs of atoms can be classified by the relationship among their near neighbors with four indices of integer. A pair of atoms are said to be near neighbors or, equivalently, are considered to form a bond (a root pair) if they are within this cut-off distance, chosen to equal the position of the first minimum in the pair distribution function. The first index is 1 if the pair is bonded and 2 otherwise; these are denoted as type I and II pairs/bonds. The second index represents the number of near neighbors shared by the root pair. The third index represents the number of the bonds among the shared neighbors. The fourth index is introduced to resolve the ambiguity about the arrangement of the bonds. The 1551 pair/bond corresponds to two near-neighboring atoms with five common near neighbors forming a pentagon of near-neighbor contacts and thus characterizes the icosahedronlike local structure. An icosahedron has 12 pairs of 1551 bonds between the central atom and its near neighbors. Because in the two-order-parameter model the bond order parameter maximizes the quality of local bonds, the difference ($\Delta\bar{E}_b$) between the average bond energy of 1551 bond and the average bond energy of the other type I bonds may be related to ΔE (the energy gain upon the formation of a locally favored structures) in the two-order-parameter model. Here the bond energy for two atoms i and j connected by a bond of type l is defined by

$$E_l = \frac{1}{2}\phi(r_{ij}) + \frac{1}{2}\left[\sum_k U(r_{ik}) + \sum_m U(r_{jm})\right], \tag{2}$$

where $\phi(r)$ is a pair potential and $U(r)$ is a "glue function" for many-body potential (for more details, see Ref. 18).

An icosahedron is a compact cluster of 20 tetrahedra. There are eight tetrahedra formed by the near-neighboring atoms in a unit cell of fcc structure, indicating one atom occupies the volume of two tetrahedra, and for hcp structures, there also exist two tetrahedra for one atom. Thus, we calculate the volume of tetrahedra in the icosahedra and their average volume ($\bar{V}_{t,\mathrm{ico}}$). We also calculate the volume V_{i1} and V_{i2} of two smallest tetrahedra among the tetrahedra (except those have counted in the icosahedra) formed by any atom i and its near neighbors. Then we obtain the average volume ($\bar{V}_{t,\mathrm{other}}$) of the other tetrahedra for all atoms in the simulated system and the average volume difference $\Delta\bar{V}_t=\bar{V}_{t,\mathrm{ico}}-\bar{V}_{t,\mathrm{other}}$, which may be related to the volume increase/decrease upon the formation of locally favored structures in the two-order-parameter model. In order to define the fine difference of the related structure units in energy and volume, we employed the inherent structure mechanism proposed by Stillinger and Weber.[25] That is, we first relax the simulated system at a certain temperature to its closest local

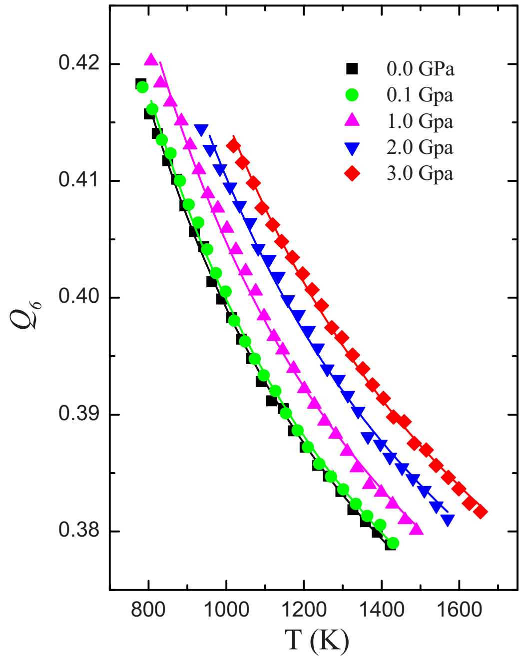

FIG. 1. (Color online) The bond order parameter Q_6 as a function of temperature. The solid lines are best fits to the data using $\frac{Q_6}{1-Q_6}=Q_{60}\exp(E_f/k_BT)$.

minimum by a conjugate gradient energy minimization, then analyze the inherent structure, and finally calculate $\Delta\bar{E}_b$ and $\Delta\bar{V}_t$ as described above.

III. RESULTS AND DISCUSSIONS

In the two-order-parameter model, one is for the state of normal-liquid structures ($j=\rho$) and another is for the state of locally favored structures ($j=S$). The equilibrium average of the fraction of locally favored structures $\bar{S}$ can be straightforwardly obtained as

$$\frac{\bar{S}}{1-\bar{S}}=\frac{g_s}{g_\rho}\exp\left(\frac{\Delta E-P\Delta V}{k_BT}\right), \tag{3}$$

where g_ρ and g_s are the degeneracy of normal-liquid structures and locally favored structures, respectively, and ΔE ($=E_\rho-E_s$) and ΔV ($=V_s-V_\rho$) are the energy gain and the volume change upon the formation of a locally favored structure, respectively. Figure 1 shows the bond order parameter Q_6 as a function of temperature for five different pressures. A glance of these data shows that there exists the similar dependence for all studied pressures: as temperature is lowered, Q_6 increases exponentially. At high temperatures, locally favored structures are created randomly in space and time. At low temperatures, on the other hand, locally favored structures are created at higher probability. Now we quantitatively analyze the temperature dependence of Q_6 (which represents $\bar{S}$) and the pressure effect. As shown in Fig. 1, the temperature dependence of Q_6 can be well fitted by the functional expression $\frac{Q_6}{1-Q_6}=Q_{60}\exp(E_f/k_BT)$ for five studied pressures.

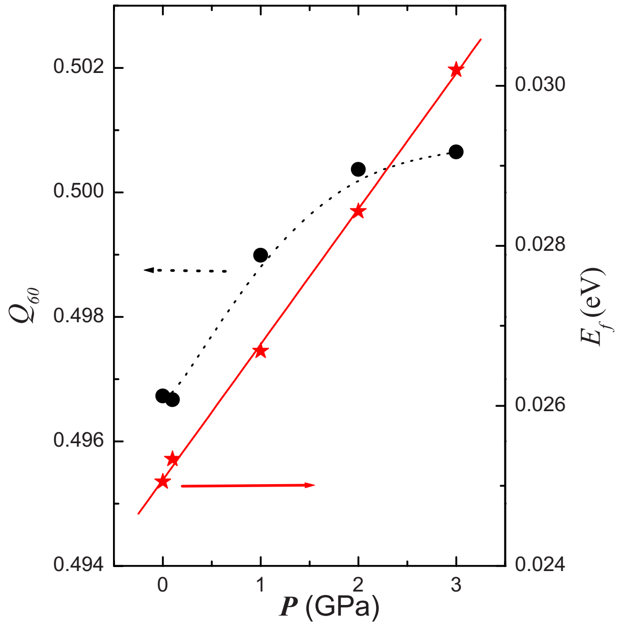

FIG. 2. (Color online) The pre-exponential factor Q_{60} (solid circle) and the favorable energy E_f (star) versus the pressure. The dotted line is a guide to the eyes, and the solid line is a curve fit obtained assuming a linear behavior, $E_f=\Delta E-P\Delta V$.

These fits of data yield the pre-exponential factor Q_{60} and E_f. Here E_f is defined as the *favorable* energy representing the energy gain originated from the formation of a locally favored structure. We plotted Q_{60} and E_f as a function of pressure in Fig. 2. The pre-exponential factor Q_{60} is about 0.5 and smaller than 1 indicating $g_S<g_\rho$, which is reasonable. Moreover it first increases with pressure and then levels off but the whole increment is much small, indicating the effect of pressure on Q_{60} is insignificant. As can be seen from Fig. 2, the linear fit of the pressure dependence of E_f is quite satisfactory and produces ΔE and ΔV: $\Delta E=0.025$ eV and $\Delta V=-0.27$ (Å)^3. What is the meaning of these two constants, 0.025 eV and -0.27 (Å)^3? ΔE is much smaller compared to 0.155 eV in water.[7] It should be stressed that here ΔV is *negative*, forming a striking contrast to the positive value [$\Delta V=16.6$ (Å)^3] in water.[7] No doubt, the reasonable explanation for both ΔE and ΔV will give a strong support to the two-order-parameter model. Keep this key question in mind, we first calculate the bond energy of all kinds of bonds using Eq. (2) and then the average volume of tetrahedra in the icosahedra ($\bar{V}_{t,\text{ico}}$) and the average volume ($\bar{V}_{t,\text{other}}$) for the other tetrahedra described in Sec. II.

Figure 3 displays the temperature dependence of average bond energy for 1551 bonds E_{1551} and the other type I bonds E_{other} and their difference $\Delta E_b=E_{\text{other}}-E_{1551}$. Note that E_{other} and E_{1551} are calculated from the inherent structures. It is obvious that both E_{other} and E_{1551} decrease with the temperature, but ΔE_b nearly keeps a constant of 0.022 eV. If we assume that E_s is represented by the average bond energy of 1551 bonds and E_ρ is represented by the average bond energy of the other type I bonds, $E_\rho-E_s=0.022$ eV, which is in good agreement with the above-obtained energy gain ΔE $=0.025$ eV. This implies that the locally favored structures

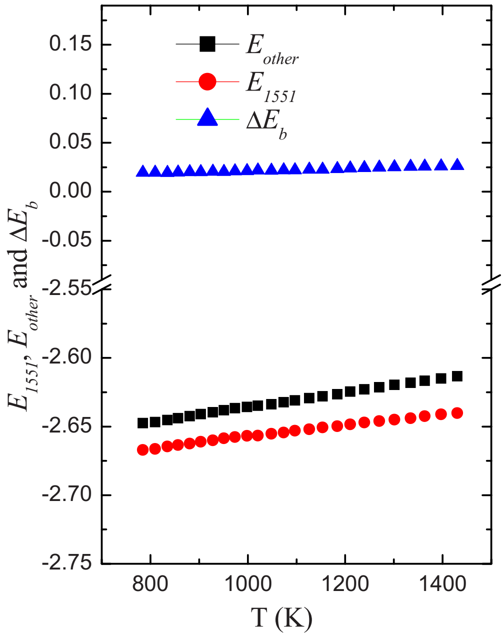

FIG. 3. (Color online) The average bond energy for 1551 bonds E_{1551} and for other type I bonds (all non-1551 bonds) E_{other} and their difference $\Delta E_b(=E_{\mathrm{other}}-E_{1551})$ as a function of temperature at 0.1 GPa.

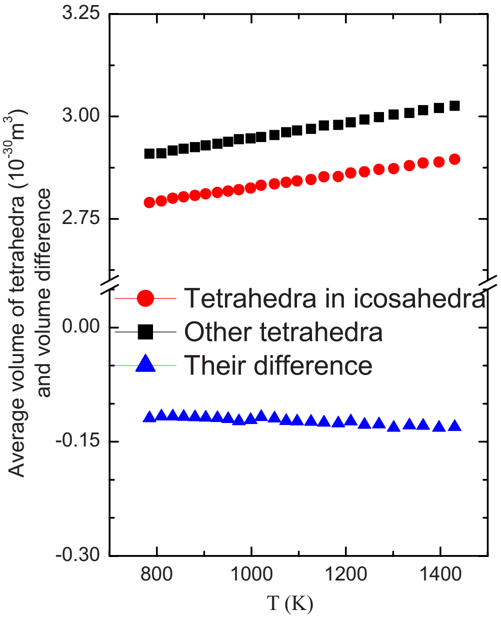

FIG. 4. (Color online) The average volume of the tetrahedra in icosahedra and the others and their difference as a function of temperature.

in liquid Al is related to icosahedronlike units, also undoubtedly provide a positive support to the two-order-parameter model. The small ΔE indicates that the difference between locally favored structures and normal structures is much small; so in high temperature, there are many kinds of bonds such as 1551, 1541, 1431, 1421, and 1422 binds in liquid Al. The population of 1551 bonds is not obviously larger than other bonds, but as the temperature is lowered the 1551 bonds increase faster than other bonds and become the largest among all type I bonds.

Figure 4 presents the temperature dependence of average volume for the tetrahedra in icosahedra ($\bar{V}_{t,\mathrm{ico}}$) and the other tetrahedra ($\bar{V}_{t,\mathrm{other}}$) along with their difference ($\Delta\bar{V}_t=\bar{V}_{t,\mathrm{ico}}-\bar{V}_{t,\mathrm{other}}$). Note that, $\bar{V}_{t,\mathrm{ico}}$ and $\bar{V}_{t,\mathrm{other}}$ are also calculated from the inherent structures. Both $\bar{V}_{t,\mathrm{ico}}$ and $\bar{V}_{t,\mathrm{other}}$ linearly decrease with lowering temperature, but their difference $\Delta\bar{V}_t$ nearly keep a constant of $\Delta\bar{V}_t=-0.123\ (\text{Å})^3$. The illustration in Sec. II indicates that one atom occupies two tetrahedra volume. The above-obtained $\Delta V[=-0.27\ (\text{Å})^3]$ is about two times $\Delta\bar{V}_t[=-0.123\ (\text{Å})^3]$. Therefore, in liquid Al the volume decrease upon the formation of a locally favored structure could be explained as the average volume occupied by one atom in icosahedra minus that occupied by one atom in other structures.

Thus, we make a reasonable explanation for the obtained ΔE and ΔV. Now we extend our study on the temperature dependence of density ρ under various pressures. Figure 5 shows the density as a function of temperature under five different pressures. Note that in melting point the experimental density of liquid is 2.38×10^3 kg m^{-3},[17] our result is in good agreement with it. From this figure, we can see that under lower pressures such as 0.0 and 0.1 GPa there exists a noticeable nonlinear dependence of the density on the temperature. Moreover this nonlinear dependence weakens and becomes linear with increasing pressure. In the light of the two-order-parameter model, the temperature and pressure dependences of the density can be expressed as

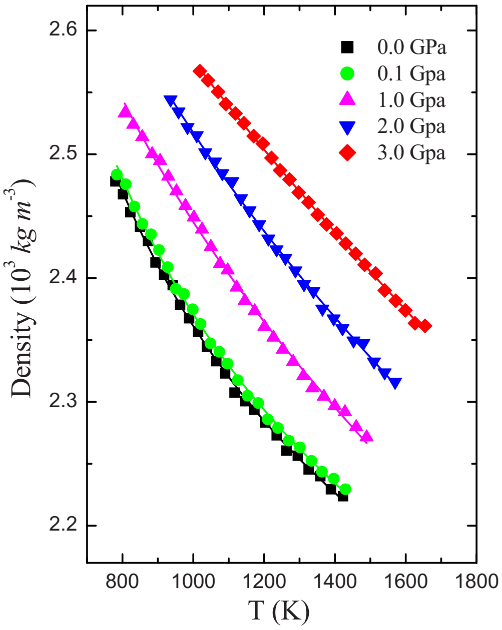

FIG. 5. (Color online) The temperature dependence of the density ρ under five different pressures. The solid lines are fits obtained assuming $\rho=a(P)+b(P)T-c(P)\frac{Q_6}{1-Q_6}$, where a, b, and c are the fitting parameters.

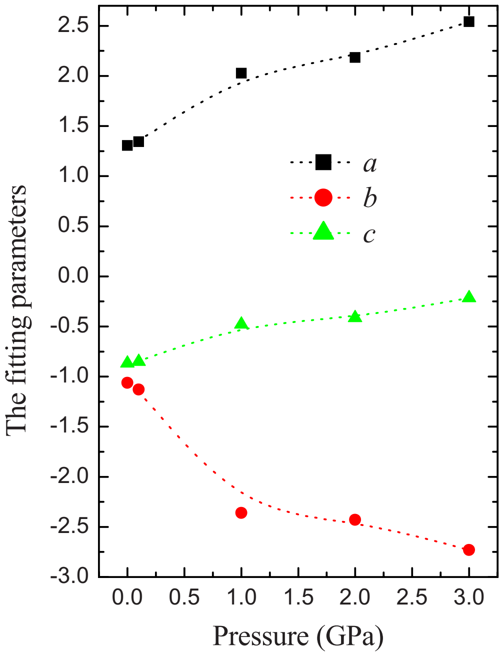

FIG. 6. (Color online) The fitting parameters a, b, and c as a function of pressure: a and c is in units of 10^3 kg m^{-3} and b is in units of 10^{-1} kg m^{-3} K^{-1}. The dotted lines are guides to the eyes.

$$\rho(T,P) = a(P) + b(P)T - c(P)\frac{Q_6}{1-Q_6}, \qquad (4)$$

where the background part is assumed as the linear-temperature dependence, $a(P)+b(P)T$, similar in liquid water[3,7] and in liquid Si;[10] a, b, and c are the fitting parameters. So in our present work, using the above-obtained value of ΔE and ΔV, we make the fits of Eq. (4) to all data shown in Fig. 5. These fits are shown by solid lines in Fig. 5 and quite satisfactory indicating that with the obtained ΔE and ΔV the two-order-parameter model can well describe the temperature and pressure dependences of the density in liquid Al. For making the discussion more quantitatively, the fitting parameters a, b, and c are presented in Fig. 6 as a function of pressure. a ranges from 1.31×10^3 to 2.54×10^3 kg m^{-3} and b ranges between -1.06×10^{-1} and -2.73×10^{-1} kg m^{-3} K^{-1}, The former increases with increasing pressure, and the later decreases with increasing pressure, which is in agreement with the background part being increased with the pressure as shown in Fig. 5. c is a key parameter which together with the bond order parameter controls the anomalous temperature dependence of some quantities. In our simulated liquid Al c is negative and in the range of $-1.74\sim-0.43\times10^3$ kg m^{-3} for various pressures, in contrast with the relatively large positive values in liquid water[3] and liquid Si.[10] So it is reasonable that the nonlinearity of the temperature dependence of density (see Fig. 5) in liquid Al is opposite in the curvature to that (Fig. 2 of Ref. 3 and Fig. 3 of Ref. 10) in liquid water and liquid Si. With increasing pressure the magnitude of c becomes small, which weakens the nonlinear temperature dependence of density; i.e., the curvature of the curves is close to zero. So it is observed that under higher pressures such as 3.0 GPa the density shows a linear dependence on the temperature.

IV. CONCLUSION

Using the glue potential we have performed constant-pressure molecular-dynamic simulations of liquid Al under five various pressures in order to test the two-order-parameter model proposed by Tanaka[3] originally for explaining the unusual behaviors of liquid water. The temperature dependence of the bond order parameter Q_6 in liquid Al under five different pressures can be well fitted by the functional expression $\frac{Q_6}{1-Q_6}=Q_{60}\exp(\frac{\Delta E-P\Delta V}{k_BT})$. The fits yield the energy gain ΔE and the volume change upon the formation of a locally favored structure; $\Delta E=0.025$ eV and $\Delta V=-0.27$ (Å)^3. We found that ΔE approximates to the difference between the average bond energy of other type I bonds and the average bond energy of 1551 bonds; ΔV could be explained as the average volume occupied by one atom in icosahedra minus that occupied by one atom in other structures. Using the obtained ΔE and ΔV, we have well described the temperature and pressure dependences of the density of liquid Al. Hence, it is demonstrated that the behavior of liquid can be described by the two-order-parameter model. It should be stressed that in liquid Al the energy gain is greatly smaller than that in liquid water. Moreover in liquid Al the volume does decrease a little because of the formation of the locally favored structure, whereas in water the volume does increase quite a little. Thus, for example, the density of liquid water shows a strongly abnormal behavior; however the density of liquid Al displays a much weakly nonlinear dependence on temperature only under lower pressures.

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