Diffusion activation energy versus the favourable energy in two-order-parameter model: A molecular dynamics study of liquid Al*

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In the present work, we find that both diffusion activation energy $E_{\mathrm{a}(D)}$ and $E_{\mathrm{a}(S^{\mathrm{ex}})}$ increase linearly with pressure and have the same slope (0.022±0.001 eV/GPa) for liquid Al. The temperature and pressure dependence of excess entropy is well fitted by the expression $-S^{\mathrm{ex}}(T,P)/k_{\mathrm{B}} = a(P)+b(P)T+c(P)\exp(E_{\mathrm{f}}/k_{\mathrm{B}}T)$, which together with the small ratio of $E_{\mathrm{f}}/k_{\mathrm{B}}T$ leads to the relationship of excess entropy to temperature and pressure, i.e. $S^{\mathrm{ex}} \simeq -cE_{\mathrm{f}}/T$, where c is about 12 and E_{f} $(= \Delta E - P\Delta V)$ is the favourable energy. Therefore, there exists a simple relation between $E_{\mathrm{a}(S^{\mathrm{ex}})}$ and E_{f}, i.e. $E_{\mathrm{a}(S^{\mathrm{ex}})} \simeq cE_{\mathrm{f}}$.

Keywords: activation energy, favourable energy, molecular dynamics simulation

PACC: 6125M, 6550, 7115Q

1. Introduction

It has been independently demonstrated that the self-diffusivity D of several simple liquids, when cast in an appropriately reduced form, shows an approximate scaling with S^{ex}, the excess entropy per particle of the fluid (relative to an ideal gas with the same number density).[1−4] This type of empirical scaling behaviour has great practical significance because it relates dynamic quantity, D, that can be difficult to predict or measure, to experimentally accessible thermodynamic quantity, S^{ex}, which can be calculated directly by computer simulation[5−7] or estimated on the basis of knowledge of the pair-correlation function $g(r)$.[8−10] Most simple liquids obey the more exact Dzugutov scaling law, which is stated as $D^* = D/(\sigma^2\Gamma) = 0.049\,\mathrm{e}^{S^{\mathrm{ex}}}$, where σ is the location of the first maximum of $g(r)$ and Γ is the collision frequency according to Enskog theory. S^{ex} is approximated by the two-body contribution which is denoted by S_2 and given by

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

Notwithstanding the frequent use of these entropy scaling laws [11−18] and the various attempts to place them on firmer theoretical ground by using either mode coupling theory or cell-theory models,[19] the exact origin of this apparent connection between thermodynamics and dynamics of fluids is still uncertain. The excess-entropy scaling relation is only a semi-quantitative model (like the van der Waals equation of state), rather than a theory.[1−3] In our previous work, we have made some active progress in exploring the origin of excess entropy scaling relation.[15] Our results showed that the scaling laws for the diffusion coefficient and the Arrhenius-type relationship $D = D_0\exp(-E_{\mathrm{a}(D)}/k_{\mathrm{B}}T)$ are linked via the relationship connecting the excess entropy and the temperature as $S^{\mathrm{ex}} = -E_{\mathrm{a}(S^{\mathrm{ex}})}/T$. Obviously, the activation energy $E_{\mathrm{a}(D)}$ (pertaining to the diffusion coefficient) and $E_{\mathrm{a}(S^{\mathrm{ex}})}$ (pertaining to the excess entropy) are therein two important quantities.[17,18,20,21] It is natural that the activation energy is dependent on liquid species.[22] But the values of the ratio of $E_{\mathrm{a}(D)}$ to $E_{\mathrm{a}(S^{\mathrm{ex}})}$ for various metallic liquids are found to exhibit the element-independent behaviour.[15] Besides

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the dependence of the activation energy on the element, the activation energy should be related to the thermodynamic condition, but until now it remains unclear that how the activation energy depends on thermodynamic condition. How do we characterize the pressure dependences of both $E_{a(S^{ex})}$ and $E_{a(D)}$? And are their pressure dependences different or identical?

In our recent work,[23] in simulated liquid Al we successfully tested the two-order-parameter model of liquids proposed by Tanaka originally for explaining the unusual behaviour of a liquid, water.[24] The model is based on the idea that in any liquid there always exist two competing orderings: density ordering (ρ) and bond ordering (ϕ), which lead two types of local structures: normal-liquid structures and locally favoured structures, to compete with each other. The temperature- and pressure-dependent bond order parameter $\overline{\phi}$ is given by

$$\overline{\phi}/(1-\overline{\phi}) = \phi_0 \exp(E_f/k_B T), \tag{2}$$

and $E_f = \Delta E - P\Delta V$ with ΔE ($= E_\rho - E_\phi$) and ΔV ($= V_\phi - V_\rho$) being the energy gain and the volume change upon the formation of a locally favoured structure, respectively. Accordingly, the thermodynamic or dynamic quantities such as density, entropy (S), isothermal compressibility and heat capacity at constant pressure can commonly be expressed as

$$X(T,P) = X_B(T,P) + \Delta X\overline{\phi}/(1-\overline{\phi}). \tag{3}$$

Our recent work has shown that the density of liquid Al is well described by Eq. (3) in both temperature and pressure dependences.[23] Is the entropy of liquid Al also well described by Eq. (3)? If so, what is the relation between E_f and $E_{a(S^{ex})}$? And how is the pressure dependence of E_f related to the pressure dependence of $E_{a(S^{ex})}$ or $E_{a(D)}$?

In the present work, using a realistic many-body potential for liquid Al, we first examine the scaling law proposed by Dzugutov for different pressures, and then clarify the above-mentioned issues on the basis of the two-order-parameter model, which may provide new insights into the activation energy. Specifically, the rest of the present paper is organized as follows: in Section 2, we describe the method of our simulations; the results of our simulations and the corresponding discussion are reported in Section 3; a short summary is given in Section 4.

2. Computational methods

Using many-body potentials, computer simulations have been successfully performed to study the structural properties of liquid metals and alloys.[25−27] The many-body glue potential developed by Ercolessi and Adams[28] can correctly reproduce many basic properties of Al in the crystalline and noncrystalline phase.[29−34] In our present work, the glue potential is employed to model the Al atomic interaction. The molecular dynamics (MD) simulations of the cooling of Al system are performed under different pressures: 0.0, 0.1, 1.0, 2.0, and 3.0 GPa. The simulated system consists of 4000 atoms in a cubic cell with a periodic boundary condition. The Newtonian equations of motion are integrated by using the velocity-Verlet algorithm in time-steps of 5.3×10^{-16} s. The well-equilibrated initial system is prepared by heating the perfect crystal at a rate of 1.9×10^{14} K$\cdot$s^{-1} and experiencing a relaxation process of 6×10^5 time steps. Then this system is cooled down at a rate of 1.9×10^{13} K$\cdot$s^{-1} in a sequentially cooling manner, which means that after a period of temperature drop it experiences a relaxation process with 20000 steps. During the later 6000 steps of the relaxation process, 20 configurations are saved to collect data for analysing the microstructures by another program. At the same time, the time-dependent mean-square displacement (MSD) is calculated. According to Abraham's suggestion,[35] glass transition temperature T_g can be obtained by using the intersection of two lines with different slopes on the curves for enthalpy versus temperature. Here we present and discuss only the results of liquid or shallowly supercooled-liquid Al, that is, the temperature ranges are above T_g, specifically, the temperatures are higher than 780, 784, 806, 935, 1018 K for five different pressures (0, 0.1, 1.0, 2.0, and 3.0 GPa), respectively; and the MSD varies linearly with time. The diffusion coefficient is calculated from the MSD and the excess entropy, S^{ex}, is approximately calculated from Eq. (1). Note that our obtained diffusion coefficient at 1015 K and 0 GPa is 4.73×10^{-9} m$^2\cdot$s^{-1}, which is in good agreement with the reported result 4.87×10^{-9} m$^2\cdot$s^{-1}.[36] Hence, the glue potential can describe well the dynamic properties of liquid Al. All the results of structural analysis are obtained by averaging over 20 configurations. Here we use Q_6[37] as a bond order parameter of the two-order-parameter model, since there exist a great number of icosahedral units in liquid Al. And the pair analysis technique proposed by Honeycutt and Andersen[38] has been used to

quantitatively calculate $E_{\rm f}(=\Delta E - P\Delta V)$. ΔE approximates to the difference in average bond energy between type I bonds and 1551 bonds characterizing the icosahedron-like local structure; ΔV could be explained as an average volume occupied by one atom in icosahedra minus that occupied by one atom in other structures. For details see our recent work.[23]

3. Results and discussion

Figure 1 shows the reduced diffusion coefficients as a function of the excess entropy in liquid Al under five different pressures. We find that the scaling law of diffusion coefficient holds rather well for five different pressures, i.e. $D^* = 0.04\,{\rm e}^{0.96S^{\rm ex}}$. This relationship is independent of pressure, indicating that the scaling law holds very well no matter in what thermodynamic conditions.

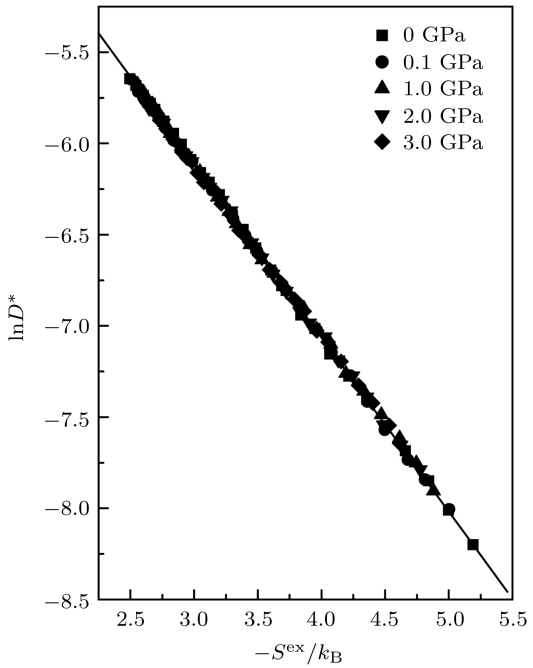


Fig. 1. Reduced diffusion coefficients D^* as a function of excess entropy $S^{\rm ex}$, where solid lines, being the best fits to the data, represent the present scaling law $D^* = 0.04\,{\rm e}^{0.96S^{\rm ex}}$.

As is well known, the temperature dependence of diffusion coefficient in liquid phase exhibits Arrhenius-type relationship $D = D_0 \exp(-E_{{\rm a}(D)}/k_{\rm B}T)$, where D_0 and $E_{{\rm a}(D)}$ are constants: D_0 is the diffusion pre-exponential factor and $E_{{\rm a}(D)}$ is called the activation energy. Excess entropy $S^{\rm ex}$ and the natural logarithm of reduced diffusion coefficient D^* against reciprocal temperature at five different pressures are plotted in Figs. 2(a) and 2(b) respectively. As expected, the diffusion coefficient increases with temperature increasing, decreases under isothermal compression with pressure increasing, and so does the excess entropy. Not only the reduced diffusion coefficient but also the excess entropy can be linearly fitted in a high accuracy. These linear fits of semilog curves of $D^* \sim 1/T$ and $S^{\rm ex} \sim 1/T$ yield the intercepts (I_D and I_S) and the slopes ($E_{{\rm a}(D)}$ and $E_{{\rm a}(S^{\rm ex})}$), which are shown in Fig. 3. As can be seen from Fig. 3(a), for different pressures I_S fluctuates around zero and is close to zero, indicating that the expression ($S^{\rm ex} = -E_{{\rm a}(S^{\rm ex})}/T$) provides a universal relation between $S^{\rm ex}$ and $1/T$. I_S and I_D for various pressures fluctuate slightly around 0.22 and -3.24, respectively. That is to say, I_S and I_D are nearly independent of pressure. A glance of Fig. 3(b) shows that both $E_{{\rm a}(D)}$ and $E_{{\rm a}(S^{\rm ex})}$, with the same slope (0.022 ± 0.001 eV/GPa), increase linearly with pressure increasing. The ratio of $E_{{\rm a}(D)}$ to $E_{{\rm a}(S^{\rm ex})}$ keeps constant (about 0.96) for various pressures, just like that for various liquids in our previous work.[15] Our present results show again that the scaling law for diffusion coefficient and the Arrhenius law are related via expression $S^{\rm ex} = -E_{{\rm a}(S^{\rm ex})}/T$. In the following we turn our attention to the temperature and pressure dependence of excess entropy in the light of the two-order-parameter model.

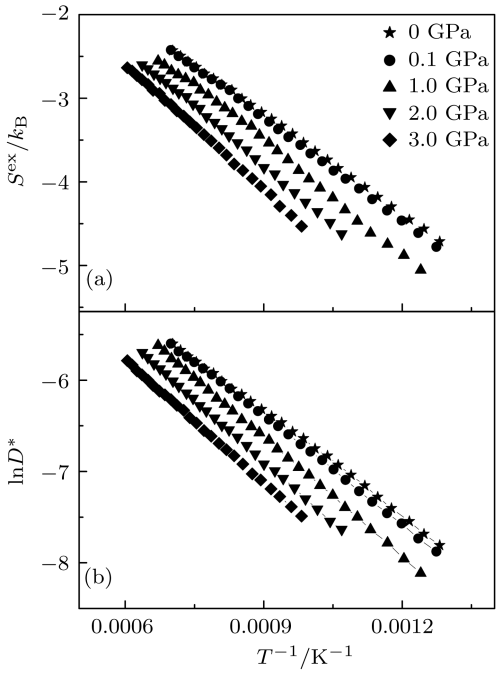


Fig. 2. Reduced diffusion coefficients and excess entropies versus reciprocal temperature under different pressures.

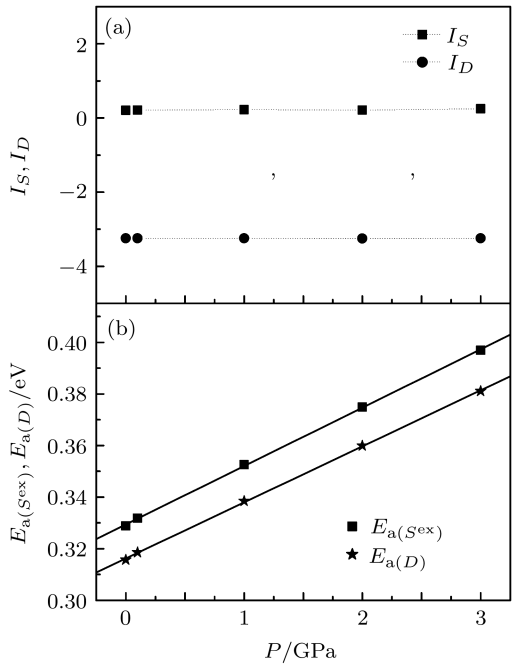


Fig. 3. Intercepts (I_D, I_S) and the slopes $(E_{a(D)}, E_{a(S^{ex})})$ each as a function of pressure. These linear fits of semilog curves of reduced diffusion coefficients and excess entropies (D^*, S^{ex}) yield the intercepts and the slopes.

As mentioned above, according to the two-order-parameter model,[24] in any liquid there always exist two competing orderings, i.e. density ordering and bond ordering. The density order maximizes the globe density or packing and leads to the crystallization representing the long-range ordering. The bond order maximizes the quality of local bonds and leads to the formation of the locally favoured structures representing the short-range order, which can be viewed as a consequence of specific many-body interactions. Thus, there exists a competition between a local preference of local structure (such as, tetrahedral configuration and icosahedral structure) and the global requirement of filling space. Our recent work[23] has shown that Q_6 can be used as a bond order parameter of the two-order-parameter model due to the existence of a great number of icosahedral units in liquid Al. The temperature dependences of Q_6 in liquid Al under five different pressures can be well fitted by functional expression $Q_6/(1-Q_6) = Q_{60}\exp(E_f/k_BT)$, where E_f is defined as the favourable energy, representing the energy gain originating from the formation of a locally favoured structure, and depends linearly on pressure. $E_f = \Delta E - P\Delta V$, which produces energy gain ΔE and volume change ΔV upon the formation of a locally favoured structure: $\Delta E = 0.025$ eV and $\Delta V = -0.27$ Å ^{3} (1 Å = 0.1 nm). On the one hand, the entropy of a liquid can be expressed as $S = S^{id} + S^{ex}$, where the first term S^{id} on the right-hand side is the entropy of an ideal gas with the temperature and the density the same as those of the liquid, so it is an upper limit to the entropy. On the other hand, the entropy of a liquid can also be written as $S(T,P) = S_B(T,P) - \Delta S\overline{\phi}/(1-\overline{\phi})$ in the light of the two-order-parameter model of liquids (see Eq. (3)),[39] where the first term $S_B(T,P)$ on the right-hand side represents the entropy of normal liquid structure. The background part, $S^{id} - S_B$, is assumed to have linear-temperature dependence: $a(P)+b(P)T$, similar to the density in liquid Al,[23] the thermodynamic quantities in liquid water[39] and liquid Si.[40] Consequently, the temperature and pressure dependence of the excess entropy can be expressed as

$$-S^{ex}(T,P)/k_B = a(P) + b(P)T + c(P)\exp(E_f/k_BT), \quad (4)$$

where a, b and c are the fitting parameters. Using the above-obtained values of ΔE and ΔV, we make the fits of Eq. (4) to all data as shown in Fig. 4. These fits shown by solid lines in Fig. 4 are quite satisfactory, indicating that with the obtained ΔE and ΔV the two-order-parameter model can soundly describe the temperature and pressure dependence of the excess entropy in liquid Al. For making the discussion more quantitative and testing the validity of the assumption on the background part, the fitting parameters a, b and c are presented in Fig. 5 each as a function of pressure. The value of a ranges from -15.14 to -10.73 and the value of b ranges between 9.8×10^{-4} K^{-1} and -1.0×10^{-5} K^{-1}. If we take the temperature to be 1200 K (the middle temperature of liquid Al investigated), then the background part $a+bT$ ranges from -13.9 to -10.7, in good agreement with $-11(k_B)$, the average entropy changes per particle of liquid metals from gas to liquid.[36] Parameter c is a key parameter and its values range from 13.2 to 10.8 for various pressures, which are in agreement with the positive values in entropy expression of two-order-parameter model. The ratio of E_f/k_BT is about $0.2 \sim 0.3$, so we can expand approximately $\exp(E_f/k_BT)$ as $1 + E_f/k_BT$. Then the excess entropy can be rewritten as $-S^{ex} \simeq a(P)k_B + b(P)Tk_B + c(P)k_B + c(P)E_f/T$. The above results in Fig. 5 show that $a(P) + b(P)T + c(P) \simeq 0$. That is to say, the excess entropy can be rewritten as extremely simple form $S^{ex} \simeq -c(P)E_f/T$. Therefore, based on the two-order-parameter model we can

also obtain a similar relationship between excess entropy and temperature. It turns out to be that there exists a simple relation between $E_{a(S^{ex})}$ and E_f, i.e. $E_{a(S^{ex})} \simeq c(P)E_f$, which together with the linear pressure dependence of E_f helps us understand the linear dependence of $E_{a(S^{ex})}$ displayed in Fig. 3(b). Here c is about 12 and decreases slightly with pressure increasing, suggesting that the pressure dependence of E_f is mainly responsible for a similar pressure dependence of $E_{a(S^{ex})}$. This is in agreement with the fact that both E_f and $E_{a(S^{ex})}$ depend linearly on pressure . In a dense liquid each atom lies in a potential well. And for a movement of an atom from one site to another it is necessary first for a vacancy to be formed and then for an atom to jump over a potential barrier into the vacant site. To generate the vacancy and stabilize the jump to a new site, a number of neighbouring atoms are required to co-operate with each other.[41] Thus, in our studied liquid Al the value of c (~ 12) may be related to the number of nearest-neighbouring atoms.

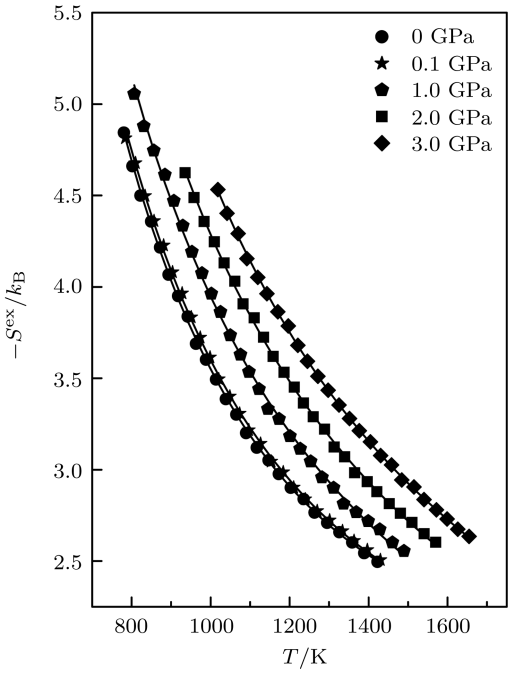


Fig. 4. The temperature dependence of the excess entropies under five different pressures. The solid lines are fits obtained assuming $-S^{ex}/k_B = a(P) + b(P)T + c(P)\exp[(\Delta E - P\Delta V)/k_BT]$, a, b and c are fitting parameters.

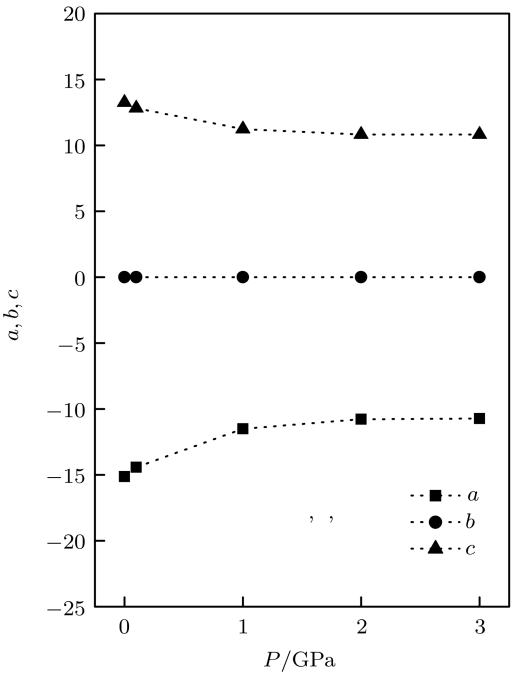


Fig. 5. Fitting parameters a, b and c each as a function of pressure. Both a and c are dimensionless constants and b is in units of K^{-1}. The dot lines are guides to the eyes.

4. Conclusion

In the present work, we find that both $E_{a(D)}$ and $E_{a(S^{ex})}$, with the same slope (0.022±0.001 eV/GPa), increase linearly with pressure increasing. The temperature and pressure dependence of the excess entropy can be well fitted by functional expression $-S^{ex}(T,P)/k_B = a(P) + b(P)T + c(P)\exp(E_f/k_BT)$, which can be rewritten as $S^{ex} \simeq -cE_f/T$ due to the small ratio of E_f/k_BT. Our presently obtained relationship of excess entropy to temperature and pressure based on the two-order-parameter model is in good accordance with the previously obtained relation $S^{ex} = -E_{a(S^{ex})}/T$. Thus, there exists a simple relation between $E_{a(S^{ex})}$ and E_f, i.e. $E_{a(S^{ex})} \simeq cE_f$, where c is about 12 and E_f is linearly dependent on pressure, being responsible for the linear pressure dependence of diffusion activation energy.

References

[1] Rosenfeld Y 1977 *Phys. Rev.* A **15** 2545
[2] Rosenfeld Y 1999 *J. Phys.: Condens. Matter* **11** 5415
[3] Rosenfeld Y 2000 *Phys. Rev.* E **62** 7524
[4] Dzugutov M 1996 *Nature* **137** 381
[5] Mittal J, Errington J R and Truskett T M 2006 *Phys. Rev. Lett.* **96** 177804
[6] Mittal J, Errington J R and Truskett T M 2006 *J. Chem. Phys.* **125** 076102
[7] Errington J R, Truskett T M and Mittal J 2006 *J. Chem.*

Phys. **125** 244502
[8] Nettleton R E and Green M S 1958 *J. Chem. Phys.* **29** 1365
[9] Mountain R D and Raveche H 1971 *J. Chem. Phys.* **35** 2250
[10] Baranyai A and Evans D J 1989 *Phys. Rev.* A **40** 3817
[11] Hoyt J J, Asta M and Sadigh B 2000 *Phys. Rev. Lett.* **85** 594
[12] Samanta A, Ali S M and Ghosh S K 2001 *Phys. Rev. Lett.* **87** 245901
[13] Samanta A, Ali S M and Ghosh S K 2004 *Phys. Rev. Lett.* **92** 145901
[14] Samanta A, Ali S M and Ghosh S K 2005 *J. Chem. Phys.* **123** 084505
[15] Li G X, Liu C S and Zhu Z G 2005 *Phys. Rev.* B **71** 094209
[16] Young T and Andersen H C 2005 *J. Phys. Chem.* B **109** 2985
[17] Sharma R, Chakraborty S N and Chakravarty C 2006 *J. Chem. Phys.* **125** 204501
[18] Sharma M and Yashonath S 2008 *J. Chem. Phys.* **129** 144103
[19] Hoover W G 1986 *Molecular Dynamics: Lecture Notes in Physics* (Berlin: Springer-Verlag)
[20] Bisquert J, Henn F and Giuntini J C 2005 *J. Chem. Phys.* **122** 094507
[21] Grabowski C A and Mukhopadhyay A 2007 *J. Chem. Phys.* **127** 171101
[22] Egelstaff P A 1992 *An Introduction to The Liquid State* (Oxford: Clarendon Press)
[23] Li Y D, Hao Q H, Cao Q L and Liu C S 2008 *Phys. Rev.* B **78** 174202
[24] Tanaka H 1998 *Phys. Rev. Lett.* **80** 5750
[25] Hou Z Y, Liu L X, Liu R S and Tian Z A 2009 *Acta Phys. Sin.* **50** 4817 (in Chinese)
[26] Hou Z Y, Lin Y, Liu Q H, Liu R S, Tian Z A and Zhou L L 2008 *Acta Phys. Sin.* **57** 3653 (in Chinese)
[27] Bian X F, Li H, Song X G, Zhang J and Zhang J X 2009 *Chin. Phys.* B **18** 4949
[28] Ercolessi F and Adams J B 1994 *Europhys. Lett.* **26** 592
[29] Sun D Y and Gong X G 1998 *Phys. Rev.* B **57** 4730
[30] Fang Q F and Wang R 2000 *Phys. Rev.* B **62** 9317
[31] Liu C S, Zhu Z G, Xia J and Sun D Y 2001 *J. Phys.*: *Condens. Matter* **13** 1873
[32] Li G X, Liang Y F, Zhu Z G and Liu C S 2003 *J. Phys.*: *Condens. Matter* **15** 2259
[33] Forsblom M, Sandberg N and Grimvall G 2004 *Phys. Rev.* B **69** 165106
[34] Forsblom M and Grimvall G 2005 *Phys. Rev.* B **72** 132204
[35] Abaraham F F 1980 *J. Chem. Phys.* **72** 359
[36] Iida T and Guthrie R I L 1988 *The Physical Properties of Liquid Metals* (Oxford: Clarendon Press)
[37] Steinhardt P J, Nelson D R and Ronchetti M 1983 *Phys. Rev.* B **28** 784
[38] Honeycutt J D and Andersen H C 1987 *J. Phys. Chem.* **91** 4950
[39] Tanaka H 2000 *J. Chem. Phys.* **112** 799
[40] Tanaka H 2002 *Phys. Rev.* B **66** 064202
[41] Qin J, Gu T and Yang L 2009 *J. Non-cryst. Solids* **355** 2333