

## Possible origin of enhanced crystal growth in a glass

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Contrary to the common belief that a glassy state is stable against crystallization, Oguni and co-workers discovered unusual enhancement of the crystal growth rate of a few molecular liquids below the glass transition temperature  $T_g$ . We studied this phenomenon using *o*-terphenyl (OTP) and phenyl salicylate (salol), focusing on the roles of volume contraction  $\Delta V$  upon crystallization. We confirmed enhancement of crystal growth below  $T_g$  for OTP. For salol, which has two kinds of crystal, the crystal growth rate below  $T_g$  is faster for a crystal of larger  $\Delta V$  than for another crystal of smaller  $\Delta V$ . Our results suggest the following physical scenario for the phenomenon: for a material having large  $\Delta V$ , the volume contraction upon crystallization provides a crystal-glass interface with large excess free volume, which results in the mobility increase at the growth front and leads to enhancement of the crystal growth. This mechanism may be effective only below  $T_g$ , where density fluctuations cannot be quickly relaxed by hydrodynamic transport.

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Usually it is believed that the growth of a crystal in a glassy state is extremely slow because of its solid nature<sup>1,2</sup> and thus we can essentially assume that a glassy state is stable against crystallization. For example, this is the basis for storing materials in a glassy state for a long period of time while avoiding crystallization. However, this common sense does not always work. For example, crystallization often takes place in printing paper, where dye molecules are homogeneously dispersed in a glassy polymer matrix, even if it is stored on a shelf below the glass transition temperature  $T_g$  of the polymer matrix. Once crystallization takes place, the spatial distribution of dye molecules becomes inhomogeneous and thus the printing paper can no longer be used commercially. This problem has been recognized for a long time in industry; however, the physical mechanism has remained elusive.

Some time ago, Oguni and co-workers discovered a striking phenomenon relating to this issue. They observed the growth of a crystal from the surface of a crystal previously formed above  $T_g$ . They found discontinuous enhancement of crystal growth (DECG) behavior just below  $T_g$  for some molecular liquids.<sup>3</sup> The increase of the growth rate across  $T_g$  is far more than one order of magnitude. They explained this phenomenon by their homogeneous-nucleation-based crystallization scenario. They thought that the peculiar type of crystal nucleation occurring on a crystal surface helps the enhancement of crystal growth below  $T_g$ . According to their model, the kinetics of the crystal nucleation and crystal growth should obey the slow  $\beta$  (or Johari-Goldstein) process,<sup>1</sup> which is decoupled from the  $\alpha$  process at the so-called  $T_B \sim 1.2T_g$  and possesses the Arrhenius-type temperature dependence. Indeed, it was shown that the growth rate below  $T_g$  is similar to the rate of slow  $\beta$  relaxation. It was also argued that this phenomenon occurs only in molecules having phenyl rings.<sup>3</sup> However, why the growth rate is suddenly accelerated by many orders of magnitude across  $T_g$  and what the roles of phenyl rings are remain open questions.

First we review the classical theory of crystal growth in a metastable supercooled liquid.<sup>1</sup> The growth rate  $G$  of the crystal is described by the thermodynamic driving force for crystallization and material transport. The former is given by

the difference in the free energy between liquid and crystal,  $\Delta F$ , whereas the latter is given by the translational diffusion constant  $D$ . Thus, we have the following relation:

$$G \propto \Delta F D. \quad (1)$$

If we use the Stokes-Einstein relation  $D = k_B T / 6\pi\eta a$ , where  $k_B$  is Boltzmann's constant,  $T$  is temperature,  $\eta$  is viscosity, and  $a$  is molecular size,  $G$  is given by  $G \propto \Delta F T / \eta$ . The  $T$  dependence of  $\eta$  is described by  $\eta = \eta_0 \exp[d^* T_0 / (T - T_0)]$  where  $T_0$  is the so-called Vogel-Fulcher temperature,  $\eta_0$  is a prefactor, and  $d^*$  is the fragility index.<sup>1</sup> The fragility characterizes the super-Arrhenius nature of the dynamics, or cooperativity.<sup>1,2</sup> The smaller  $d^*$  the more fragile the liquid.  $\Delta F$  is given by

$$\Delta F \propto \exp[-CT_m / (T\Delta T)], \quad (2)$$

where  $T_m$  is the melting point,  $\Delta T = (T_m - T)$  is the degree of supercooling, and  $C$  is a constant.  $G$  becomes extremely small when  $T$  is near either  $T_m$  or  $T_g$ . This is the origin of the bell shape of the  $T$  dependence of  $G$ .

However, it was recently revealed that the translational diffusion is decoupled from the rotational diffusion, or the structural relaxation characterized by  $\tau_\alpha$  (or  $\eta$ ), below  $T_B$ .<sup>1,2,4-6</sup> In other words, the Stokes-Einstein relation assumed in the above argument breaks down in a supercooled state below  $T_B$ . The behavior of  $D$  is linked to that of  $\eta$  as  $D = \eta^{-\xi}$ , where the exponent  $\xi$  takes a value between 0 and 1.  $\xi$  decreases with an increase in the fragility, or with a decrease in  $d^*$ . Furthermore, the kinetics of the crystal growth below  $T_B$  was found to obey the translational diffusion constant and not the viscosity  $\eta$ .<sup>7-10</sup> This implies that the kinetics of the DECG behavior should also obey the translational diffusion rather than the slow  $\beta$  process. Thus, the conventional theory of crystallization cannot explain the DECG behavior.

To explain this counterintuitive phenomenon, Tanaka proposed the following scenario.<sup>10</sup> Crystal formation in a glassy material should induce extensional stress (negative pressure) around a nucleated crystal due to the volume contraction

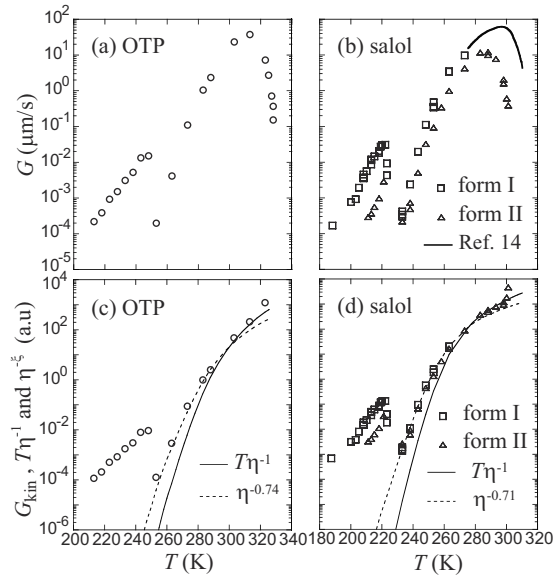


FIG. 1.  $T$  dependence of  $G$  [(a) OTP and (b) salol] and  $G_{kin}$  [(c) OTP and (d) salol]. In (b) and (d) squares are for form I of salol, and triangles for form II. The solid curve in (b) represents the data of Neumann and Micus (Ref. 16). The solid curves in (c) and (d) represent  $T/\eta$  calculated from the viscosity data, and the broken lines in (c) and (d) represent  $\eta^{-\xi}$  with  $\xi=0.74$  for OTP and  $\xi=0.71$  for salol (see text). The lines are vertically shifted to fit the data.

upon crystallization, which should provide free volume to molecules surrounding the crystal, increase their mobility, and help further crystallization.<sup>11</sup> This feature should become quite important especially below  $T_g$ , where the contraction cannot be compensated by material flow. Here we aim at experimentally checking the validity of this scenario concerning the stability of a metastable glassy state against crystallization, with the help of a free volume theory.

The samples used were *o*-terphenyl (OTP) and phenyl salicylate (salol), which were purchased from Sigma-Aldrich Chemical, Inc. and Nacalai Tesque, Inc., respectively.  $T_g$  and  $T_m$  of OTP are 244 and 329 K, respectively.<sup>12</sup> Salol has two forms of crystal, a stable (form I) and a metastable (form II) crystal.<sup>13</sup> The  $T_m$ 's of forms I and II are 315 and 302 K, respectively,<sup>13–16</sup> and  $T_g$  of salol is 218 K. We observed the process of crystal growth below and above  $T_g$  with optical microscopy (Keyence VH-7000C and VH-Z450) equipped with a temperature-controlled hot stage (Linkam LK-600PH) and a cooling unit (Linkam L-600A). We prepared a seed of crystal in a sample at a certain temperature between  $T_g$  and  $T_m$ , and measured the growth rate of the crystal  $G$  in a wide temperature range including below  $T_g$ , following Ref. 3.

The DECG behavior was confirmed for OTP and forms I and II of salol. Figures 1(a) and 1(b) show the  $T$  dependence of  $G$ , respectively, for OTP and salol (forms I and II).  $G$  discontinuously increases by a factor of  $10^2$ – $10^3$  across  $T_g$ , with a decrease in the crystallization temperature  $T_x$ . For salol the degree of the enhancement is smaller for form II than for form I. According to Eq. (1),  $G$  divided by  $\Delta F$ , which we express as  $G_{kin}$ , should be proportional to the translational diffusion  $D$ . Magill and Li<sup>17</sup> determined  $C$

$=36.4 \text{ K}^{-1}$  and  $T_m=331.65 \text{ K}$  from Eq. (2) for OTP. Combining our data, the data of Neumann and Micus,<sup>16</sup> and viscosity data,<sup>18</sup> we obtained  $C=43.0 \text{ K}^{-1}$  and  $T_m=318 \text{ K}$  from Eq. (2) for the form I crystal of salol.  $\Delta F$  of form II of salol itself was not available, but we estimated it from our data and viscosity data<sup>18</sup> as  $C=32.0 \text{ K}^{-1}$  and  $T_m=305.5 \text{ K}$  using Eq. (2). The  $T$  dependence of  $G_{kin}$  estimated in this way is shown for OTP and for forms I and II of salol, respectively, in Figs. 1(c) and 1(d).

For OTP the behavior of  $G_{kin}$  above  $T_B$  is well described by  $T\eta^{-1}$ ,<sup>19</sup> whereas the behavior below  $T_B$  is described by  $\eta^{-0.74}$ , where the exponent 0.74 is similar to that estimated by Ngai *et al.*<sup>7</sup> The degree of the discontinuous increase of the crystal growth across  $T_g$  is  $10^2$ – $3$ . For salol the behavior of  $G_{kin}$  above  $T_g$  is the same for forms I and II above  $T_g$ .  $G_{kin}$  above  $T_B$  is again well described by  $T\eta^{-1}$  (Ref. 18) for both forms I and II, as expected.  $G_{kin}$  below  $T_B$  is, on the other hand, well fitted by  $\eta^{-\xi}$  with  $\xi=0.71$ . The amount of discontinuous increase across  $T_g$  is larger by a factor of 10 for form I than for form II. We note that a scenario where the kinetics of the DECG is governed by the slow  $\beta$  process cannot explain this difference, because the slow  $\beta$  process is a unique process of a liquid and glass and not of a crystal: In this scenario, the crystallization behavior below  $T_g$  should be the same in that plot.

Now we explain the observed behavior, focusing on the difference in the specific volume  $\Delta V$  between a glass and a crystal ( $\Delta V=V_{glass}-V_{cryst}$ ), in terms of a free volume theory.<sup>20</sup> According to Doolittle,

$$D = D_0 \exp(-AV_{occ}/V_f), \quad (3)$$

where  $A$  and  $D_0$  are constants,  $V_{occ}$  is the occupied volume, and  $V_f$  is the free volume for molecules,  $V_f=V_0-V_{occ}$ . If we regard the volume at  $T_0$  as  $V_{occ}$  and assume the linear dependence of  $V_f$  on  $T$ , the Doolittle equation [Eq. (3)] reduces to the Vogel-Fulcher equation. We expect that for a material of large  $\Delta V$  the volume contraction upon crystallization provides the excess free volume  $V_{ef}$  to molecules in the crystal-glass interface, increases their mobility, and accelerates the crystal growth. Figures 2(a) and 2(b) show the  $T$  dependence of the specific volumes of crystal ( $V_{cryst}$ ), liquid ( $V_{liq}$ ), and glass ( $V_{glass}$ ), respectively, for OTP and salol. Here the  $T$  dependence of  $V_{cryst}$ ,  $V_{liq}$ , and  $V_{glass}$  for OTP were taken from data of Naoki and Koeda,<sup>12</sup> for salol, the  $T$  dependence of  $V_{cryst}$  and  $V_{liq}$  is estimated from experimental data of Comez *et al.*,<sup>21</sup> whereas the  $T$  dependence of  $V_{cryst}$  is estimated using density data as  $1.357 \text{ g/cm}^3$  at 213 K,<sup>14</sup> and  $1.35 \text{ g/cm}^3$  at 180 K,<sup>15</sup> respectively, for forms I and II. From Fig. 2,  $\Delta V$  is estimated as  $0.042 \text{ cm}^3/\text{g}$  for OTP,  $0.045 \text{ cm}^3/\text{g}$  for form I of salol, and  $0.037 \text{ cm}^3/\text{g}$  for form II. The values of  $\Delta V$  for OTP and form I of salol are similar, whereas the value of  $\Delta V$  for form II is smaller than that of form I. Our finding that  $G_{kin}$  of form I of salol below  $T_g$  is larger than that of form II is consistent with this difference in  $\Delta V$  according to our scenario, where the larger volume contraction (larger  $\Delta V$ ) should provide larger excess free volume  $V_{ef}$  and thus lead to a larger enhancement of mobility at the growth interface.

Now we use the free volume concept to understand the origin of the DECG behavior. Figures 3(a) and 3(b) show the

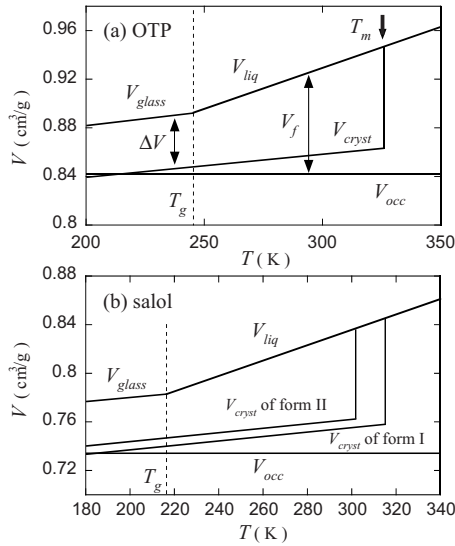


FIG. 2.  $T$  dependence of the specific volume for (a) OTP and (b) salol. The data for OTP are taken from Ref. 12 and those of salol are estimated from Refs. 14,15,21. Each  $V_{occ}$  is estimated from  $V_{liq}$  at  $T_0$ .

dependence of  $G_{kin}$  on  $V_{liq}$  and  $V_{glass}$ , respectively, for OTP and salol. The  $V$  dependence of  $G_{kin}$  below  $T_g$  is parallel to that above  $T_g$  for all the samples. We assume that the excess free volume  $V_{ef}$  provided by the volume contraction upon crystallization is proportional to  $\Delta V$  as  $V_{ef} = \alpha\Delta V$ . According to the free volume theory [Eq. (3)], the translational diffusion is a function of only the free volume. Thus, the translational diffusion responsible for the DECG behavior below  $T_g$  should be equivalent to that for  $(V_{glass} + \alpha\Delta V)$ . For  $\alpha=0.3$ , the data for  $G_{kin}$  of the DECG for OTP and salol can be superimposed on the data for  $G_{kin}$  above  $T_g$ , as shown in Fig. 3. The slopes of  $G_{kin}$  for crystallization above and below  $T_g$ , which are different in Fig. 1, become the same in Fig. 3.

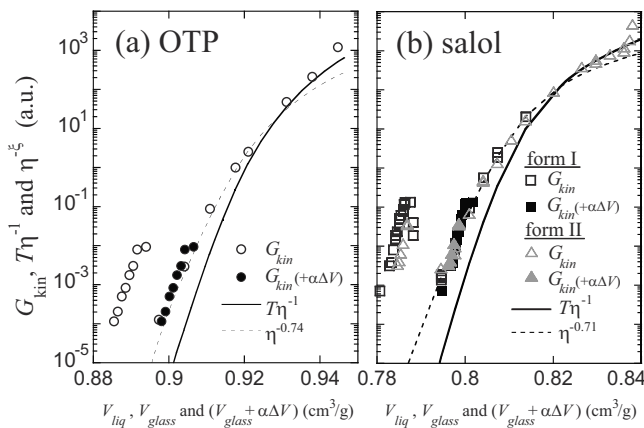


FIG. 3. Volume dependence of  $G_{kin}$  of (a) OTP (circles) and (b) form I (squares) and form II (triangles) of salol. Open symbols are  $G_{kin}$  as a function of  $V_{liq}$  and  $V_{glass}$ , and filled symbols are  $G_{kin}$  as a function of  $(V_{glass} + \alpha\Delta V)$ . Here  $\alpha\Delta V$  amounts to the excess free volume given to the crystal-glass interface. All the filled symbols are superimposed on the open symbols with  $\alpha=0.3$  for all materials.

TABLE I. Values of  $\Delta V$  and  $\Delta H$  for several materials (Ref. 22). These values were calculated from the data in the references listed.

Materials	$\Delta V$ (cm <sup>3</sup> /g)	$\Delta H$ (kJ/mol)
Toluene	0.052 (Refs. 28 and 29)	6.64 (Ref. 30)
OTP	0.042 (Ref. 12)	17.2 (Ref. 31)
Salol (form I)	0.045 (Refs. 14, 15, and 21)	18.6 (Ref. 32)
Salol (form II)	0.037 (Refs. 14, 15, and 21)	16.5 (Ref. 32)
Indomethacin ( $\gamma$ )	0.021 (Ref. 23)	39.4 (Ref. 23)

Furthermore, the shift by  $\alpha\Delta V$  in  $V$  axis leads to the superposition. This strongly supports our scenario that the DECG behavior is the consequence of the excess free volume provided by the volume contraction upon crystallization.

Next we consider the role of  $\Delta V$  in the DECG behavior. The data for  $\Delta V$  are listed for several materials in Table I. We note that the DECG behavior was reported for toluene.<sup>3,22</sup> For indomethacin, it was also reported that the growth of  $\gamma$ -form crystals occurs very slowly below  $T_g$  (Refs. 23 and 24) but faster than expected.<sup>25</sup> The increase of  $G$  across  $T_g$  is at most about one order of magnitude. Combining these facts and Table I, we speculate that the larger the value of  $\Delta V$  is, the more the DECG behavior is enhanced. The presence of phenyl rings in a molecular structure may be positively correlated with  $\Delta V$ , which is consistent with the proposition of Oguni and co-workers.<sup>3</sup> We note that the latent heat  $\Delta H$  is not correlated with the strength of the DECG behavior since  $\Delta H$  is actually smaller for materials with weaker DECG behavior (see Table I). However, further studies on materials with various  $\Delta V$ 's are necessary to confirm our prediction.

Finally we consider a remaining important question, i.e., why the growth rate “discontinuously” increases at  $T_g$ . Usually, the glass transition is believed to be a continuous transition of kinetic origin. Thus, the origin of such a strong discontinuity is not very obvious. We propose the following scenario. The volume contraction upon crystallization, or density change, can be relaxed only by material transport: diffusion and hydrodynamic flow. In the liquid state, the density can be transported by a pressure gradient produced by volume contraction, following the Navier-Stokes equation. This transport process is much faster than the diffusion process. So the density can be quickly relaxed above  $T_g$ . In the glassy state, where shear elasticity appears associated with the broken ergodicity, this transport by flow is prohibited. Accordingly, the only transport process becomes diffusion. Then the density cannot be relaxed before crystal growth, and thus the excess free volume becomes available for crystal growth. We speculate that this switching off of hydrodynamic transport due to an ergodic-nonergodic transition may be the origin of the discontinuity. The dynamic balance between the volume contraction rate determined by  $G$  and  $\Delta V$  and the volume relaxation rate determined by  $\Delta V$  and  $D$  determines the growth rate below  $T_g$ . We note that, without the latter process, the steady growth could not be realized and the growth rate would keep increasing. We also note that the negative pressure is created only locally near the growth front since it can be relaxed by the volume relaxation of the

surrounding matrix phase. This local nature is essentially different from macroscopic negative pressure which may make a system mechanically unstable<sup>26</sup> (cavitations) or boundary-condition dependent.<sup>27</sup>

In sum, we experimentally demonstrate that the DECG behavior below  $T_g$  is well described by the excess free volume provided by volume contraction upon crystallization. We found that about 30% of the volume contraction is used as the free volume for crystal growth, although further stud-

ies are necessary for revealing the physical meaning of this value. Our model suggests that a material of small  $\Delta V$  may be more stable against crystallization in the glassy state and thus more suitable for a long-term storage. This proposition should be checked carefully in the future.

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<sup>1</sup>P. G. Debenedetti, *Metastable Liquids* (Princeton University Press, Princeton, NJ, 1997).

<sup>2</sup>C. A. Angell, K. L. Ngai, G. B. McKenna, P. F. McMillan, and S. W. Martin, *J. Appl. Phys.* **88**, 3113 (2000).

<sup>3</sup>T. Hikima, M. Hanaya, and M. Oguni, *J. Mol. Struct.* **479**, 245 (1999); M. Hatase, M. Hanaya, and M. Oguni, *J. Non-Cryst. Solids* **333**, 129 (2004), and references therein.

<sup>4</sup>E. Rössler, *Phys. Rev. Lett.* **65**, 1595 (1990).

<sup>5</sup>H. Sillescu, *J. Non-Cryst. Solids* **243**, 81 (1999).

<sup>6</sup>M. D. Ediger, *Annu. Rev. Phys. Chem.* **51**, 99 (2000).

<sup>7</sup>K. L. Ngai, J. H. Magill, and D. J. Plazek, *J. Chem. Phys.* **112**, 1887 (2000).

<sup>8</sup>M. K. Mapes, S. F. Swallen, and M. D. Ediger, *J. Phys. Chem. B* **110**, 507 (2006).

<sup>9</sup>A. Masuhr, T. A. Waniuk, R. Busch, and W. L. Johnson, *Phys. Rev. Lett.* **82**, 2290 (1999).

<sup>10</sup>H. Tanaka, *Phys. Rev. E* **68**, 011505 (2003).

<sup>11</sup>The effects of stress on the crystal (rather than the surrounding liquid) were considered previously [J. W. P. Schmelzer *et al.*, *J. Non-Cryst. Solids* **352**, 434 (2006)].

<sup>12</sup>M. Naoki and S. Koeda, *J. Phys. Chem.* **93**, 948 (1989).

<sup>13</sup>L. Deffet, *Bull. Soc. Chim. Belg.* **44**, 97 (1935).

<sup>14</sup>J. H. Bilgram, U. Doring, M. Wachter, and P. Seiler, *J. Cryst. Growth* **57**, 1 (1982).

<sup>15</sup>R. B. Hammond, M. J. Jones, K. J. Roberts, H. Kutzke, and H. Klapper, *Z. Kristallogr.* **217**, 484 (2002).

<sup>16</sup>K. Neumann and G. Micus, *Z. Phys. Chem. (Munich)* **2**, 25 (1954).

<sup>17</sup>J. H. Magill and H. M. Li, *J. Cryst. Growth* **20**, 135 (1973).

<sup>18</sup>W. T. Laughlin and D. R. Uhlmann, *J. Chem. Phys.* **76**, 2317 (1972).

<sup>19</sup>D. J. Plazek, C. A. Bero, and I. C. Chay, *J. Non-Cryst. Solids* **172-174**, 181 (1994).

<sup>20</sup>G. D. Grest and M. H. Cohen, *Adv. Chem. Phys.* **48**, 455 (1981).

<sup>21</sup>L. Comez, S. Corezzi, D. Fioretto, H. Kriegs, A. Best, and W. Steffen, *Phys. Rev. E* **70**, 011504 (2004).

<sup>22</sup>Crystallization of toluene is known to occur in the form of the *b*-type crystal near  $T_g$  (Ref. 29), whose  $\Delta V=0.023$  cm<sup>3</sup>/g. Thus, we need to take special care with the results of toluene.

<sup>23</sup>M. Yoshioka, B. C. Hancock, and G. Zografi, *J. Pharm. Sci.* **83**, 1700 (1994).

<sup>24</sup>See, e. g., V. Andronis and G. Zografi, *J. Non-Cryst. Solids* **271**, 236 (2000).

<sup>25</sup>T. Wu and L. Yu, *J. Phys. Chem. B* **110**, 15694 (2006).

<sup>26</sup>C. A. Angell and Zheng Qing, *Phys. Rev. B* **39**, 8784 (1989).

<sup>27</sup>R. J. Greet and D. Turnbull, *J. Chem. Phys.* **46**, 1243 (1967).

<sup>28</sup>D. Morineau, Y. Xi, and C. Alba-Simionesco, *J. Chem. Phys.* **117**, 8966 (2002).

<sup>29</sup>A. V. A. Kummar, S. Yashonath, and S. L. Chaplot, *J. Chem. Phys.* **113**, 8070 (2000).

<sup>30</sup>D. W. Scott, G. B. Guthrie, J. F. Messerly, S. S. Todd, W. T. Berg, I. A. Hossenlopp, and McCullough, *J. Phys. Chem.* **66**, 911 (1962).

<sup>31</sup>S. S. Chang and A. B. Bestul, *J. Chem. Phys.* **56**, 503 (1972).

<sup>32</sup>J. J. Ramos, N. T. Correia, and H. P. Diogo, *Phys. Chem. Chem. Phys.* **6**, 793 (2004).