PHYSICAL REVIEW E **95**, 042804 (2017)

Critical nucleus size for crystallization of supercooled liquids in two dimensions

Tomoko Mizuguchi[*]
Institute for the Promotion of University Strategy, Kyoto Institute of Technology, Kyoto 606-8585, Japan

Yuki Higeta and Takashi Odagaki[†]
Division of Science, School of Science and Engineering, Tokyo Denki University, Hatoyama, Saitama 350-0394, Japan

(Received 22 December 2016; revised manuscript received 4 April 2017; published 24 April 2017)

Using molecular dynamics simulations, we study the crystallization of supercooled liquids in two dimensions in which particles interact with other particles via the Lennard-Jones-Gauss potential. We first prepare supercooled liquids at various temperatures by rapid quenching from the melt. The simulations are performed with a crystalline seed inserted at the center of the initial system. We investigate the time evolution of the inserted nucleus and its surroundings and determine the critical nucleus size n_c defined as the smallest nucleus which survives. The results show that n_c scales as $\sim(T_m - T)^{-2}$ with the melting temperature T_m, as expected in the classical nucleation theory. We also obtain the crystallization time at various temperatures as a function of nucleus size and show that the presence of a crystalline seed significantly affects the crystallization time when the temperature is higher than the characteristic temperature T^* at which the crystallization time becomes the shortest. This indicates that the crystallization is controlled by thermodynamics in this temperature range. When the temperature is lower than T^*, the effect of the inserted nucleus on crystallization is less significant, which indicates that crystallization is controlled by emergence and merging of small crystalline nuclei.

DOI: 10.1103/PhysRevE.95.042804

I. INTRODUCTION

Crystallization of supercooled liquids plays important roles in various phenomena. To list a few, prion diseases are believed to be caused by partial crystallization of normal prion [1,2], and the taste of chocolate depends strongly on the partial crystallization of its constituents [3–6]. It is thus important to understand the mechanism of crystallization of supercooled liquids in both basic and applied research. In this context, classical nucleation theory (CNT) predicts that the size of a critical nucleus depends on the decrease in free energy of a bulk molecule $\Delta\psi$ during the phase change as

$$n_c \propto \Delta\psi^{-d}, \tag{1}$$

where n_c is the number of particles in a critical nucleus, and d is the dimension of space [7,8]. According to the Landau theory of phase transitions, $\Delta\psi$ is proportional to $T_m - T$, so n_c is expected to behave as

$$n_c \propto (T_m - T)^{-d}, \tag{2}$$

where T_m is the melting temperature.

Conversely, the crystallization time of supercooled liquids shows a characteristic shape, called the nose shape, when it is plotted as the temperature on the vertical axis and the logarithm of the crystallization time on the horizontal axis. This plot is commonly known as a time-temperature-tranformation (TTT) diagram [9,10]. When we denote by T^* the characteristic temperature at which the crystallization time becomes the shortest, the crystallization time increases with temperature for $T > T^*$, and it decreases with temperature for $T < T^*$. The shape of TTT diagram can be understood from the viewpoint of two-step process in crystallization, that is, nucleation and growth. It is believed that macroscopic crystallization is dominated by nucleation process in $T > T^*$ and by growth process in $T < T^*$. To confirm the difference in the mechanism of crystallization at various temperatures, we examine the effect of nucleus on the TTT diagram.

In this paper, we investigate the effects of a nucleus on the crystallization of supercooled liquids in two dimensions by using molecular dynamics (MD) simulations and determine the critical nucleus size as a function of temperatures. We insert a crystalline disk at the center of the supercooled liquid and observe whether the disk grows or shrinks with time at a fixed temperature. A similar seeding approach has been applied to the analysis of crystallization in several water models [11,12] and in other systems such as NaCl, Lennard-Jones, and Hard Spheres [13,14] and successfully described the nucleation rate in a wide range of supercooling in these systems. In this work, we model the interaction of particles by using the Lennard-Jones-Gauss (LJG) potential. With this potential, the TTT diagram has been reported in two dimensions [15], in which no crystalline seed was inserted. We also investigate how the TTT diagram depends on the size of the inserted disk.

We organize this paper as follows. In Sec. II we explain our model system and the method of the MD simulations. In Sec. III we analyze the time evolution of the inserted disk and determine the critical nucleus size. We also determine the dependence of the TTT diagram on the size of the inserted disk. In Sec. IV we discuss the results.

II. METHODS

A. Model potential

We consider a system of atoms that interact isotropically through the LJG potential:

$$V(r) = \epsilon_0\left[\left(\frac{r_0}{r}\right)^{12} - 2\left(\frac{r_0}{r}\right)^{6}\right] - \epsilon \exp\left[-\frac{(r-r_G)^2}{2\sigma^2}\right]. \tag{3}$$

---

[*] mizuguti@kit.ac.jp

[†] Present address: Research Institute for Science Education, Kitaku, Kyoto 603-8346, Japan.

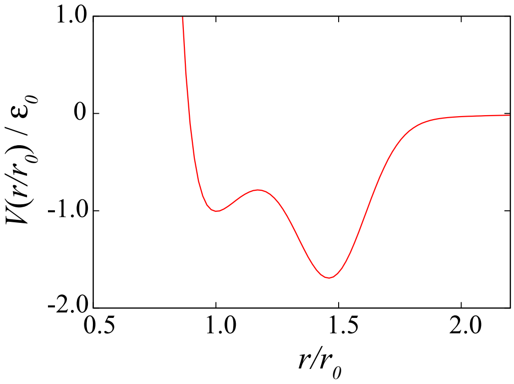

FIG. 1. The LJG potential for the parameters $r_G = 1.47r_0$, $\epsilon = 1.5\epsilon_0$, $\sigma^2 = 0.02r_0^2$.

The LJG potential consists of the LJ potential and a pocket represented by the Gaussian function. It forms a double-well potential for most values of the parameters, with the second well at position r_G, of depth ϵ, and with width σ. This potential has been used to represent the self-assembly of two-dimensional monatomic complex crystals and quasicrystals [16]. It has also been used to stabilize some types of simple lattices [17,18] and to represent water-like anomalies [19,20].

In this work, we set parameters to the following values: $r_G = 1.47r_0, \epsilon = 1.5\epsilon_0$, and $\sigma^2 = 0.02r_0^2$. Figure 1 shows the LJG potential with these parameters. With these parameters, the potential has two minima, with the second minimum being deeper than the first. The melting temperature T_m is $0.44\epsilon_0/k_B$, which was determined from heating simulations of the crystal in a bulk system [15]. The system with these parameters is known to crystallize in equilibrium [15,21], and its crystalline state in two dimensions is the pentagon-triangle phase in the ground state [21].

Previous works have also found that these parameters prompt a glassy state in both two [15] and three dimensions [22]. The system has strong geometric frustration because the pentagonal structure is stabilized by the potential form, and thus quenching of the system can produce a glassy state.

B. Simulation details

We performed two-dimensional MD simulations in the isothermal-isochoric (NVT) ensemble under free boundary conditions. The free boundary condition was realized by placing an assembly of particles in the center of a large box. The box was made sufficiently large so that the particles felt zero pressure. We did not use periodic boundary conditions because the shape of a simulation box has an influence on crystallization [23], although the choice of boundary conditions does not have a significant effect on determining whether the inserted nucleus shrinks or not. The temperature was controlled by a generalized Nosé-Hoover thermostat [24]. The units of length, energy, and time in the present simulations are r_0, ϵ_0, and $(mr_0^2/\epsilon_0)^{1/2}$, respectively. In this paper, all results are given in reduced units. In all the simulations, the interaction potential is cut off at $r_c = 2.5$ and a time step of 0.01 is used.

First, we prepared 10 liquid samples, each consisting of 4096 particles, and disk-shaped crystal nuclei of various sizes.

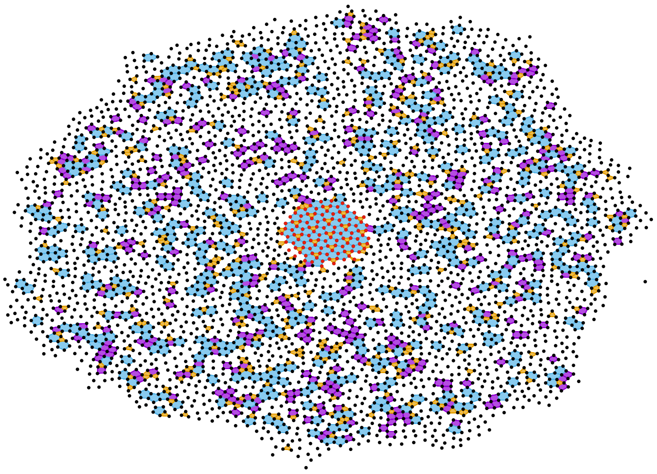

FIG. 2. The initial configuration, before quenching, of a liquid sample with a crystal nucleus at the center. The local structure can be classified by a few basic tiles which are drawn by lines between the first neighbor particles. Pentagon, triangle, and square tiles are shown in blue, orange, and purple, respectively.

In each liquid sample, the disk of particles at the center is replaced by the crystal disk with the same radius. The number of particles was kept constant by removing a few liquid atoms from the outermost region of the liquid sample. Figure 2 shows the initial state of a liquid sample with a crystal nucleus at the center. Next, we quenched the system instantaneously to a target temperature T_{set} that was below the melting temperature, that is, the velocity of each particle was reassigned so that the velocity distribution of the system satisfied the Maxwell-Boltzmann distribution for $T = T_{set}$. Instantaneous cooling was employed to avoid any nucleation during cooling, because nucleation may hinder proper comparison of the crystallization process.

C. Method for measuring the extent of crystallization

The crystal structure of the system is composed of pentagonal and triangular tiles (see Fig. 2). It has been shown in a previous work [15] that there exist three basic tiles in this system: pentagon (P), triangle (T), and square (S) tiles, and the number of combined structures of them is a good index for measuring the crystallization time. Figure 3(a) shows three combined tiling structures: PPPT, PPP, and PPTS. Figure 3(b) shows the time evolution of the number of particles whose surroundings can be identified as those three combined tiling structures and a sum of them. When crystallization proceeds, the number of PPTS decreases a bit, while the numbers of PPPT and PPP increase and finally reach constant values. The sum of the numbers of three combined tiling structures also reaches a constant value; thus, it may be possible to use it for determining the crystallization time. This concept is appropriate for higher temperatures, but for lower temperatures the definition is incomplete, because the system is often trapped in the local minimum of the potential energy. In this case, the sum of the numbers of tiling structures become constant, but the system has not reached a crystalline state at the moment. Thus, we defined the crystallization time as the

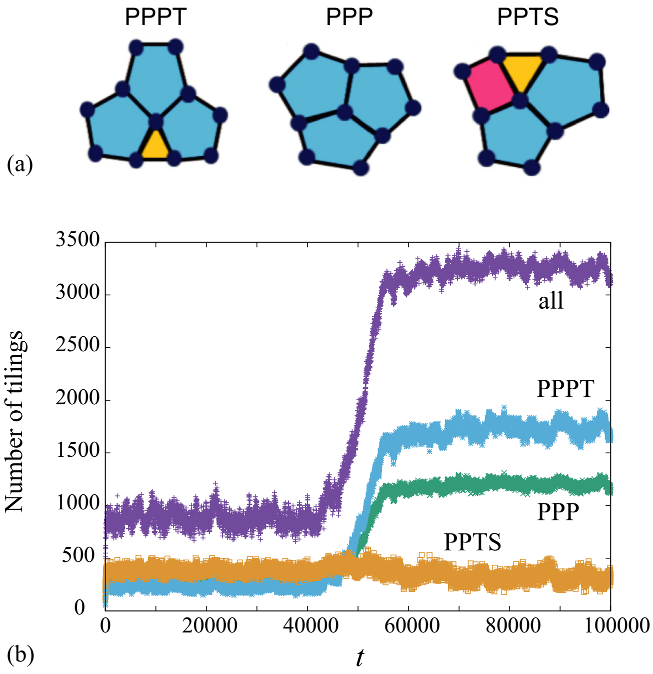

FIG. 3. (a) Three characteristic tiling structures: PPPT, PPP, and PPTS, adapted from Ref. [15]. (b) The time evolution of the number of characteristic tiling structures at $T = 0.34$. The curves (PPPT), (PPP), and (PPTS) correspond to the structures shown in (a). The curve (all) represents the sum of the numbers of those three tiling structures.

time at which the sum of the numbers of such tilings reaches a threshold value, 3000. This value corresponds to about 73% of the total number of particles. Since there are boundaries and edges, most part of the system has a crystalline structure at the threshold. The TTT diagram thus determined is shown in Sec. III B.

To evaluate the critical nucleus size, we examined the time evolution of the total number of such three combined tiling structures n_x in three regions defined by the radius of the initially inserted nucleus R: (i) $r \leqslant R$, (ii) $R < r < R + 5$, and (iii) $R + 5 \leqslant r \leqslant R + 10$, where r is measured from the center of mass of the seed [25]. We normalized n_x for comparison with the initial density of crystal tilings in the seed $\rho_0 = n_x(t = 0)/\pi R^2$ by multiplying the area of the region of interest A_j, where j is a number of the region ($j = 1,2,3$). We can judge whether the seed shrinks or not by n_x in region (i). From the time evolution of n_x in regions (ii) and (iii), we can confirm that the crystal structure grows.

III. RESULTS

A. Time evolution of the crystalline seed

The time evolution of n_x with a crystalline seed of $R = 6$ and 12 is shown in Fig. 4. With the nucleus of $R = 6$, the crystal structure of the nucleus breaks after a very short time at $T = 0.34$. Particles around the nucleus, in regions (ii) and (iii), form crystal structures at first, but they do not grow. An initial nucleus also breaks at $T = 0.30$, whereas the number of crystal tilings in outer areas grows as time passes. This

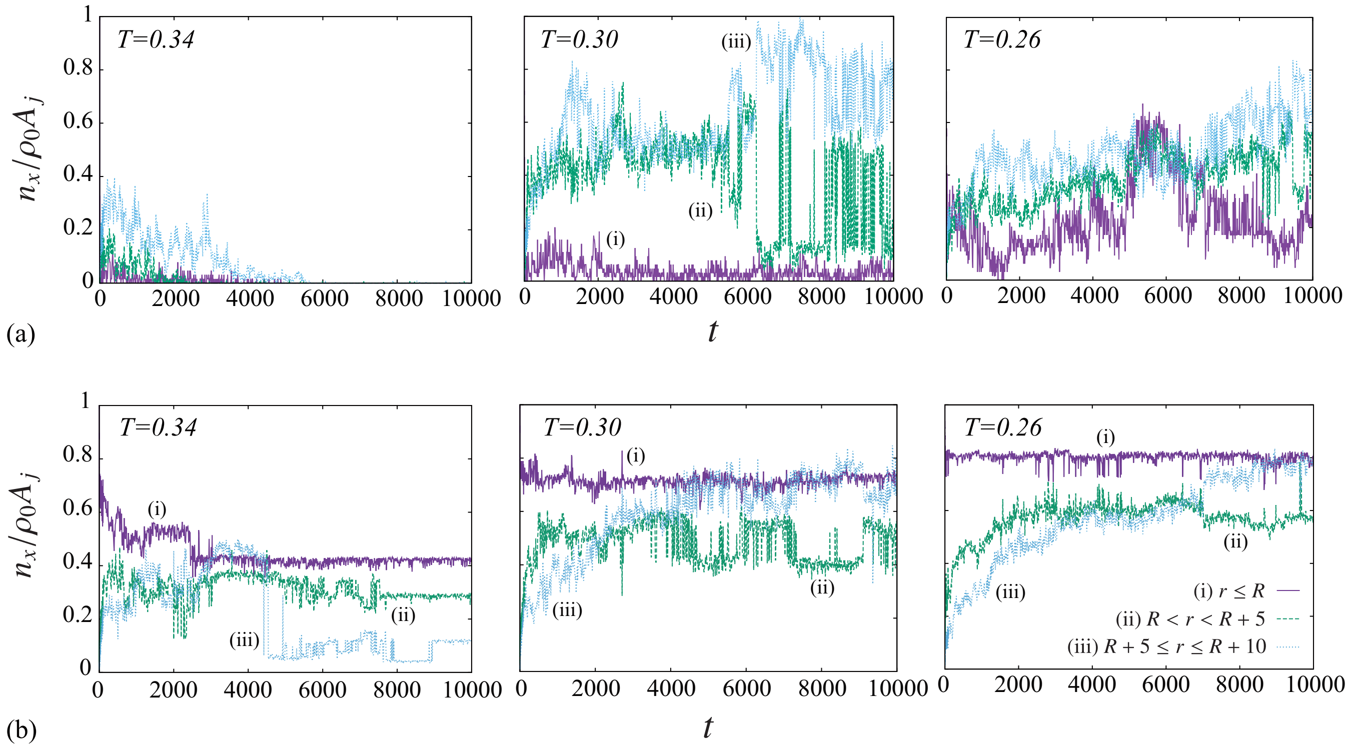

FIG. 4. The time evolution of the number of crystal tilings n_x for $T = 0.34$, 0.30, and 0.26 in three regions: (i) $r \leqslant R$ (purple solid line), (ii) $R < r < R + 5$ (green dashed line), and (iii) $R + 5 \leqslant r \leqslant R + 10$ (blue dotted line), where R is the radius of the initially inserted nucleus. The abscissa represents time in reduced units. The sizes of the inserted nuclei are (a) $R = 6$ and (b) 12. n_x is normalized by the initial density of crystal tilings in the seed ρ_0 by multiplying the area of the region of interest $A_j (j = 1,2,3)$.

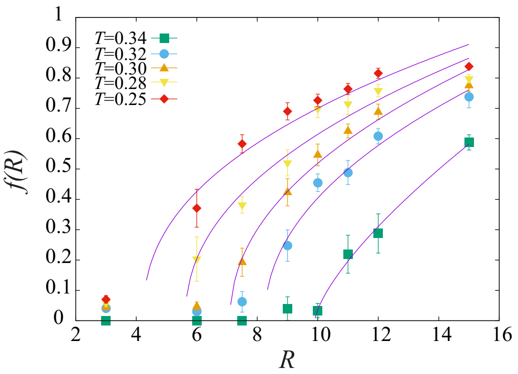

FIG. 5. The average fraction $f(R)$ of crystal tilings in region (i) $r \leqslant R$, where R is the radius of the initially inserted nucleus. The calculations were performed over the period from $t = 9000$ to 10 000. Solid lines are fitting functions of $f(x) = a(x - b)^c$, where a, b, and c are fitting parameters.

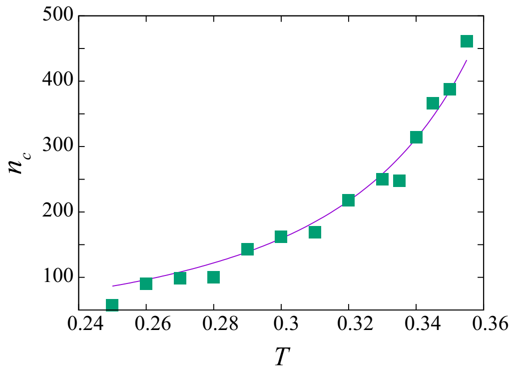

FIG. 6. Temperature dependence of the critical nucleus size. The solid line is a fitting function of Eq. (4).

result means that spontaneous nucleation occurs in outer areas but does not mean that the inserted nucleus moves to outer areas and grows there. The seed breaks after a very short time (see Supplemental Material [26]). The fraction of crystal tilings of initial nucleus also goes to ~0 at $T = 0.26$; thus, this nucleus size ($R = 6$) is not sufficiently large to induce crystal growth at these temperatures. In contrast, for the nucleus of size $R = 12$, the fraction of crystal tilings in region (i) stays constant at 0.4. It is difficult to determine whether this nucleus is or is not sufficiently large to induce crystal growth. The time evolutions of the number of crystal tilings, however, are different from those with the nucleus of size $R = 6$. At $T = 0.30$ and 0.26, the fractions of crystal tilings in region (i) are ~0.7 and ~0.8, respectively. These values indicate that the initial nuclei almost keep their crystalline structures, although their values decrease from 1 due to the configurational arrangement mainly at the boundary. In addition, n_x in regions (ii) and (iii) increase; it grows first in region (ii) followed by region (iii). Note that n_x in region (iii) surpasses that in region (ii) at long t since spontaneous nucleation occurs outside the region (iii). Thus, we conclude the nucleus size of $R = 12$ is sufficiently large to induce crystallization of the whole system at $T = 0.30$ and 0.26.

As shown in Fig. 4, $t = 10\,000$ is sufficiently long to judge whether an initial nucleus shrinks or not. We thus calculated the average fraction $f(R)$ of crystal tilings in the region (i) from $t = 9000$ to 10 000 at a variety of temperatures, as shown in Fig. 5, to determine the critical nucleus size. Fitting functions of $f(x) = a(x - b)^c$ are also shown as solid lines, where a, b, and c are fitting parameters. We defined the critical nucleus radius as the radius at which $f(R)$ vanishes, namely, from $R = b$. The radius defined here is a lower limit of radius of the nucleus which survives in the system.

We define the critical nucleus size n_c as the number of particles in the smallest nucleus which survives in the system and show it as a function of temperature in Fig. 6. We fitted the temperature dependence in the form of Eq. (2) with the melting temperature T_m as

$$n_c = \frac{\alpha}{(T_m - T)^2}, \tag{4}$$

where α is a fitting parameter. We found that α is 3.1 by least-squares fitting. It well obeys CNT, although it slightly deviates at low temperatures. This result is discussed in Sec. IV. The relationship between critical nucleus size and supercooling temperature has been reported in the LJ system, and it also agrees with CNT [27,28].

B. TTT diagram

Extending the MD simulations, we obtained the TTT diagram, which is shown in Fig. 7. Here we plotted the crystallization time t' as a function of temperature, where t' is scaled as

$$t' = \frac{N}{N - n} t, \tag{5}$$

where N is the total number of particles, n is the number of particles in the inserted nucleus, and t is the crystallization time, which is directly determined in the simulation using the method described in Sec. II C, namely, $N - n$ is the number of (remaining) liquid particles excluding the seed nucleus, and t' represents the crystallization time in the system with N liquid particles. As shown in Fig. 7, when the number of particles in a crystal nucleus n is more than 464, which corresponds to $R = 12$, the crystallization time becomes evidently shorter.

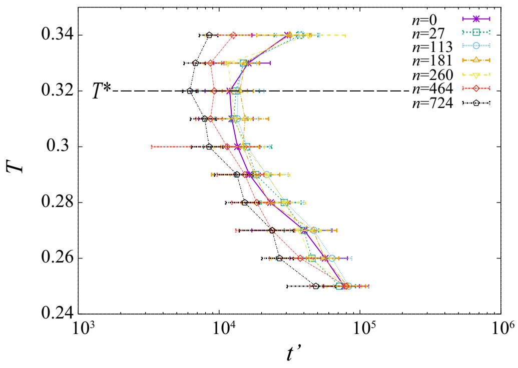

FIG. 7. The time-temperature-transformation diagram for various sizes of crystal nuclei. The crystallization time t' is defined by Eq. (5). T^* is the temperature at which the crystallization time becomes the shortest without an inserted nucleus. The melting temperature of bulk system is 0.44.

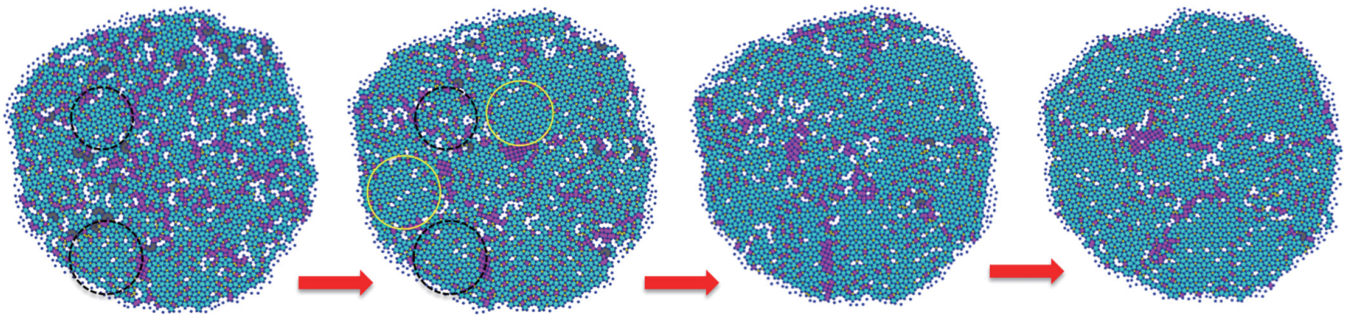

FIG. 8. Crystallization process at $T = 0.26$. The local structures are classified by a few basic tiles: blue is pentagon, orange is triangle, and purple is square. The circles are drawn for eye guide.

This behavior is noticeable especially near the melting temperature. At low temperatures, the TTT diagram does not change when the inserted nucleus size exceeds the critical size, but it changes for much larger nucleus. This result is discussed in Sec. IV.

IV. DISCUSSION

We have investigated effects of a crystalline nucleus on the crystallization of supercooled LJG liquid in two dimensions by controlled MD simulations, where a nucleus is inserted in the system at the initial state of simulations. We first observed if the nucleus survives or not, and we obtained the critical nucleus size as the smallest size of the nucleus which survives in the system. We found that the temperature dependence of the critical nucleus size well obeys CNT, as shown in Fig. 6. We then examined the effect of the inserted nucleus on the crystallization time, and obtained the TTT diagram for each size of the inserted nucleus. As shown in Fig. 7, the effect of the inserted nucleus on the crystallization is much stronger above the temperature T^* at which the crystallization time becomes the shortest. In the temperature range $T^* < T < T_m$, diffusion of atoms is sufficiently fast to survey a large area in the phase space, and the crystallization is controlled by thermodynamics, i.e., by the difference in free energy between liquid and crystalline phases, $\Delta G = G_{\text{liquid}} - G_{\text{crystal}}$. Since $\Delta G(T_m) < \Delta G(T^*)$ and ΔG is a driving force of crystallization, it is easier to crystallize at T^* than just below T_m. The crystallization time is an increasing function of temperature and so is the critical nucleus size.

For temperatures below T^*, diffusion of atoms is slow and so is the growth of the nucleus. Therefore, it is harder to crystallize at lower temperatures below T^* despite the fact that $\Delta G(T^*) < \Delta G(T < T^*)$. In fact, we clarified in our previous work [29] for spontaneous nucleation that the crystallization at low temperatures is the merging process of small nuclei which emerge in many different areas. The crystallization process at $T = 0.26 < T^*$ is shown in Fig. 8. The circles show nuclei that appear at some places. They cannot grow easily because of the slow diffusion of particles, and other nuclei appear with time in other parts of the system. They gradually grow and merge each other, and finally the system reaches a polycrystalline state. It may transform into a perfect crystal after much long time, but in a practical sense, it is quite difficult to occur. Due to this mechanism, the effect of the nucleus on the crystallization time is less significant in $T < T^*$ as one can see in Fig. 7, although we found in the present work that a much bigger nucleus stimulate the system to crystallize. Because of the slow diffusion, it takes a long time for atoms to rearrange themselves into the ordered structure. Therefore, the crystallization time becomes a decreasing function of temperature since the diffusion becomes slower as the temperature is decreased. The slow dynamics is related to the glass transition which is observed when the system is heated from a temperature below T^* [29,30].

In the free energy landscape picture of nonequilibrium systems [31], the crystallization is a first passage process of a representation point from the supercooled liquid (SC) basin through the gate (G) basin with crystalline nucleus to the crystalline (X) basin. The higher temperature regime of the TTT diagram is related to the transition rate from the G basin to the X basin and the lower temperature regime of the TTT diagram is related to the rate from the SC basin to the G basin. Therefore from the detailed analysis of the TTT diagram one can deduce information on the transition rates which will help better understanding of the crystallization process of supercooled liquids.

ACKNOWLEDGMENTS

The work at Tokyo Denki University was supported in part by JSPS KAKENHI Grants No. JP22540400 and No. JP25400429. We thank Michael Engel for the visualization software on which some figures were made.

---

[1] J. T. Jarrett and J. P. T. Lansbury, Cell **73**, 1055 (1993).

[2] K. J. Knaus, M. Morillas, W. Swietnicki, M. Malone, W. K. Surewicz, and V. C. Yee, Nat. Struct. Biol. **8**, 770 (2001).

[3] K. Sato, Chem. Eng. Sci. **56**, 2255 (2001).

[4] I. Rothkopf and W. Danzl, Eur. J. Lipid Sci. Technol. **117**, 1714 (2015).

[5] A. Rigolle, L. Gheysen, F. Depypere, A. Landuyt, K. V. D. Abeele, and I. Foubert, Eur. J. Lipid Sci. Technol. **117**, 1722 (2015).

[6] S. B. Gregersen, R. L. Miller, M. D. Andersen, and M. Hammershøj, Eur. J. Lipid Sci. Technol. **117**, 1782 (2015).

[7] E. R. Buckle, Proc. Roy. Soc. A **261**, 189 (1961).

[8] P. G. Debenedetti, *Metastable Liquids: Concepts and Principles* (Princeton University Press, Princeton, 1996).

[9] R. Busch, JOM **52**, 39 (2000).

[10] E. B. Moore and V. Molinero, Nature (London) **479**, 506 (2011).

[11] E. Sanz, C. Vega, J. R. Espinosa, R. Caballero-Bernal, J. L. F. Abascal, and C. Valeriani, J. Am. Chem. Soc. **135**, 15008 (2013).

[12] J. R. Espinosa, E. Sanz, C. Valeriani, and C. Vega, J. Chem. Phys. **141**, 134709 (2014).

[13] J. R. Espinosa, C. Vega, C. Valeriani, and E. Sanz, J. Chem. Phys. **142**, 194709 (2015).

[14] J. R. Espinosa, C. Vega, C. Valeriani, and E. Sanz, J. Chem. Phys. **144**, 034501 (2016).

[15] T. Mizuguchi and T. Odagaki, Phys. Rev. E **79**, 051501 (2009).

[16] M. Engel and H.-R. Trebin, Phys. Rev. Lett. **98**, 225505 (2007).

[17] M. C. Rechtsman, F. H. Stillinger, and S. Torquato, Phys. Rev. E **73**, 011406 (2006); **75**, 019902(E) (2007).

[18] M. C. Rechtsman, F. H. Stillinger, and S. Torquato, Phys. Rev. E **74**, 021404 (2006).

[19] A. B. de Oliveira, P. A. Netz, T. Colla, and M. C. Barbosa, J. Chem. Phys. **124**, 084505 (2006).

[20] S. A. Egorov, J. Chem. Phys. **128**, 174503 (2008).

[21] M. Engel and H.-R. Trebin, Z. Kristallogr. **223**, 721 (2008).

[22] V. V. Hoang and T. Odagaki, Physica B **403**, 3910 (2008).

[23] The unit cell of crystal structure in our system is not simple, unlike fcc or bcc, and so is the shape of a simulation box.

[24] G. J. Martyna, D. J. Tobias, and M. L. Klein, J. Chem. Phys. **101**, 4177 (1994).

[25] The center of the circular regions is fixed in space when time evolves. We observe whether the seed grows or shrinks, which can be determined in a relatively short time. A big seed hardly moves in such a short time range. A small seed also hardly moves if the temperature is sufficiently low. It can move at higher temperatures, but the seed shrinks and disappears in a very short time at such higher temperatures. Thus, we think that fixing the center does not bring a serious effect on evaluating the critical nucleus size. Supplemental Material would partly support this statement.

[26] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevE.95.042804 for a movie in which an inserted nucleus shrinks quickly with time ($R = 6$, $T = 0.30$, time period is 200 steps).

[27] X.-M. Bai and M. Li, J. Chem. Phys. **122**, 224510 (2005).

[28] X.-M. Bai and M. Li, J. Chem. Phys. **124**, 124707 (2006).

[29] T. Mizuguchi and T. Odagaki, J. Phys. Soc. Jpn. **81**, 024601 (2012).

[30] K. Trachenko and V. V. Brazhkin, Phys. Rev. B **83**, 014201 (2011).

[31] T. Odagaki and A. Okada, in 4th International Workshop on Dynamics in Viscous Liquids (Montpellier, France, May 2015); APS March Meeting (San Antonio, TX, March 2015).