Positional order and diffusion processes in particle systems

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The relaxation of a nonequilibrium solid to a fluid is determined by observing the positional order parameter in Monte Carlo simulations, and discussed based on diffusion processes in the hard-particle systems. From the cumulant expansion up to the second order, the relation between the positional order parameter Ψ and the mean square displacement $\langle u_i^2 \rangle$ is obtained to be $\Psi \sim \exp(-\mathbf{K}^2 \langle u_i^2 \rangle / 2d)$ with a reciprocal vector $\mathbf{K}$ and the dimension of the system d. On the basis of this relation, the positional order should decay exponentially as $\Psi \sim \exp(-\mathbf{K}^2 Dt)$ when the system involves normal diffusion with a diffusion constant D. A diffusion process with swapping positions of particles is also discussed. The swapping of particles contributes to the higher orders of the cumulants, and swapping positions allows particles to diffuse without destroying the positional order while the normal diffusion destroys it.

The melting behavior of the hard-disk system was first reported by Alder *et al.* [1], where they showed that particles can undergo a melting transition even when the interactions are purely repulsive. This melting transition is also confirmed in the three-dimensional system and is now often referred to as the Alder transition. However, Mermin ruled out the positional long range order in two-dimensional particle systems [2]. Therefore, the melting processes of two-dimensional systems are different from that of three-dimensional systems. Halperin, Nelson, and Young proposed the two-dimensional melting theory [3] based on Kosterlitz–Thouless transition [4], and Chui proposed another theory predicting the first order transition based on the grain boundaries excitation [5]. While many researchers have been studying this problem [6–11], the nature of two-dimensional melting has been still a matter of debate [12]. So far, most numerical works have focused on the equilibrium state of the system mainly using Monte Carlo methods. Recently, the nonequilibrium behavior of the bond-orientational order parameters has been studied to obtain the equilibrium properties of the hard-disk system [13]. These studies are based on a strategy for the simulation, called the nonequilibrium relaxation (NER) method [14]. Zahn and Maret studied time-dependent parameters in two-dimensional colloidal particle systems [15]. They pointed out that static properties are not appropriate measures to distinguish between the solid and the fluid, since the mean square displacement diverges very slowly. Therefore, it is necessary to study the dynamic behaviors of order parameters in the particle systems. In the present paper, we study the relaxation of the positional order parameter based on diffusion processes. We also treat two- and three-dimensional systems at the same time, since many studies have focused only on the two-dimensional melting, and to our knowledge, there are fewer studies about the three-dimensional positional order.

Consider a d-dimensional system with N particles. A positional order parameter Ψ is defined to be

$$\Psi = \frac{1}{N} \sum_{j}^{N} \exp(-i\mathbf{K} \cdot \mathbf{r}_j), \qquad (1)$$

with the position of the particles $\mathbf{r}_i$ and one of the reciprocal vectors $\mathbf{K}$ of the system. Let $\mathbf{R}_i$ be the equilibrium positions of the particles and $\mathbf{u}_i$ be the deviations from it, namely, $\mathbf{r}_i = \mathbf{R}_i + \mathbf{u}_i$. The positional parameter is reduced to be

$$\Psi = \langle \exp[-i\mathbf{K} \cdot (\mathbf{R}_j + \mathbf{u}_j)] \rangle = \langle \exp(-i\mathbf{K} \cdot \mathbf{u}_j) \rangle, \qquad (2)$$

since $\mathbf{K} \cdot \mathbf{R}_j = 0$. The average for all particles is denoted by $\langle \cdots \rangle$. Assuming that $\mathbf{u}_i$ is a linear combination of Gaussian distribution [17], Eq. (2) is reduced to be

$$\Psi = \exp[-1/2 \langle (\mathbf{K} \cdot \mathbf{u}_i)^2 \rangle]. \qquad (3)$$

Assuming that $\mathbf{u}_i$ is isotropic, we have

$$\langle (\mathbf{K} \cdot \mathbf{u}_i)^2 \rangle = K^2 \langle \mathbf{u}_i^2 \rangle / d \quad (K \equiv |\mathbf{K}|). \qquad (4)$$

From Eqs. (3) and (4), we obtain the relation between the positional order and the diffusion to be

$$\Psi = \exp\left(-\frac{K^2 \langle \mathbf{u}_i^2 \rangle}{2d}\right), \qquad (5)$$

or equivalently,

$$\langle \mathbf{u}_i^2 \rangle = -\frac{2d}{K^2} \ln \Psi. \qquad (6)$$

When a system involves the normal diffusion, the asymptotic behavior of the mean square displacement is expected to be

$$\langle \mathbf{u}_i^2 \rangle \sim 2dDt, \qquad (7)$$

with a diffusion constant D. From Eqs. (5) and (7), the asymptotic behavior of the positional order is obtained to be

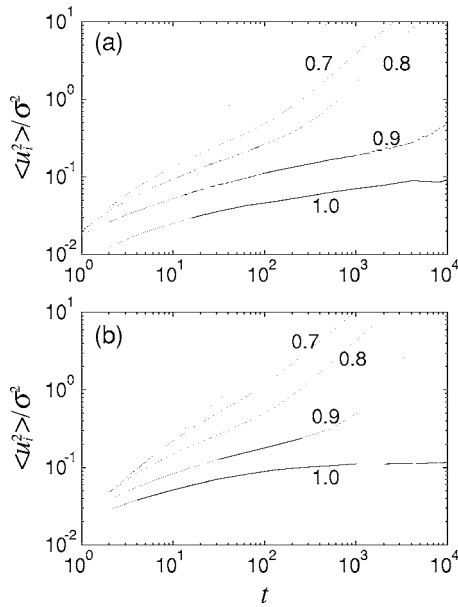*Electronic address: hwatanabe@is.nagoya-u.ac.jp

FIG. 1. Time evolution of the mean square displacement $\langle u_i^2 \rangle$ in (a) two- and (b) three-dimensional systems. The values are normalized by the radius σ and therefore the unit is dimensionless. The decimal logarithm are taken for both axes. The dashed lines denote the diffusion in the low density limit [16]. Number of particles $N = 23\,288$ for two- and $N = 36\,000$ for three-dimensional system with the periodic boundary condition.

$$\Psi(t) \sim \exp(-K^2 Dt), \tag{8}$$

regardless of the dimension. It implies that when the system involves the normal diffusion, the positional order should decay exponentially with the decay time D^{-1}. This limits the diffusion behavior in solid phases. In the solid phase of the system with $d \geq 3$, the system can have a finite value of Ψ in the equilibrium state. Therefore, the mean displacement cannot become larger than some constant value. The behavior in a two-dimensional solid is different from those in $d \geq 3$. On the basis of the Halperin-Nelson-Young theory [3], the positional order parameter in a two-dimensional solid behaves as

$$\Psi(t) \sim t^{-\lambda}. \tag{9}$$

Therefore, the two-dimensional solid cannot involve the normal diffusion in the usual sense, since the mean square displacement in this system behaves logarithmically as

$$\langle \mathbf{u}_i^2 \rangle = \frac{4\lambda}{K^2} \ln t. \tag{10}$$

The above arguments are based on the cumulant expansion up to the second order. The positional order parameter Ψ is the characteristic function of displacements. Assuming the distribution of the displacement to be the Gaussian distribution, we can express the positional order parameter only with the second order cumulant, which is diffusion.

In order to check our arguments, we perform Monte Carlo simulations. For simplicity, we treat the hard-particle systems. One Monte Carlo procedure on the hard-particle system is (1) choose one particle randomly, (2) choose a new position for the center of this chosen particle. The new position is chosen uniformly in the circle of radius σ_s, called a
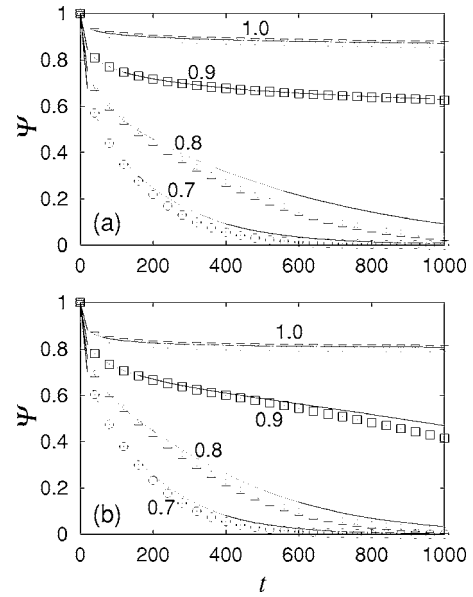

FIG. 2. Time evolution of the positional order parameter and calculated values from the diffusion for (a) two- and (b) three-dimensional systems. The solid lines are the positional order parameters and the symbols are the calculated values using Eq. (5). The densities $\rho = 0.7$, 0.8, 0.9, and 1.0 are studied, and the numbers on the graphs denote each density. It shows good agreement in the region where Ψ is not so small.

step length, (3) this trial move is accepted when the new position has no overlap with any other particles. Each particle does not have velocity, therefore, temperature is not defined in the hard-particle systems. The time in MC simulations is defined to be the number of MC moves. Each system contains N particles with the radius σ. The density is normalized to be $\rho \equiv 1$ when the system is in the perfect square/cubic lattice, that is, $\rho = N(2\sigma/L)^d$ with the dimension of the system d and the linear size of the system L. The lattice constant a is fixed to be 2, and the density is controlled by changing the radius σ. Therefore, the value of the reciprocal vector K is π since $K = 2\pi/a$. Throughout this study, the number of particles $N = 23\,288$ for two- and $N = 32\,000$ for three-dimensional systems and up to 512 independent samples are averaged for each density. The step length is set to be $\sigma_s = 0.2\sigma$ with the radius σ. We have also performed simulations with other values of step length $\sigma_s = 0.01$, 0.05, and 0.1, and confirmed that the parameter only changes the time scale of the system and the results are not changed qualitatively. At the beginning of each run, the particles are set up in the perfect ordered configuration (the hexagonal lattice in two- and the FCC lattice in the three-dimensional system). The periodic boundary conditions are taken along all the axes. The densities from $\rho = 0.7$ to 1.0 are studied.

The time evolutions of the mean square displacements are shown in Fig. 1 and that of the positional order parameters are shown in Fig. 2. Note that, all the quantities plotted in all figures are dimensionless. One can find that the normal diffusion starts after the positional order is almost destroyed. While the positional order is well approximated by Eq. (5) when Ψ is not so small, there are differences especially in the low densities.
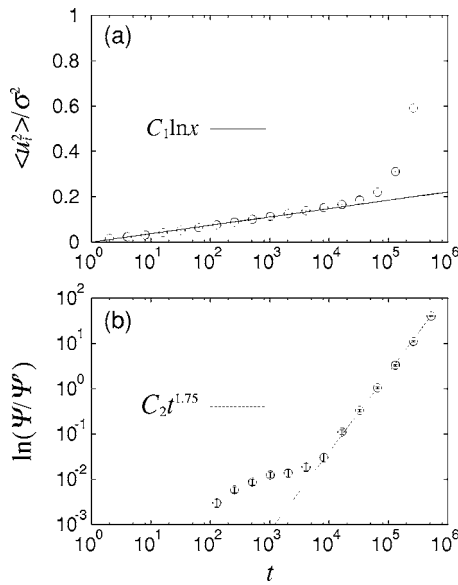
FIG. 3. (a) Mean square displacement of the two-dimensional solid. The number of particles $N=23\,288$ and the density $\rho=0.92$. The solid line is $C_1 \ln t$ with $C_1=1.6\times10^{-2}$. It varies from the logarithmic behavior at around $t=10^4$. (b) The time evolution of the value $\ln(\Psi/\Psi')$ in Eq. (13). The decimal logarithms are taken for both axes. The solid line $C_2 t^{1.75}$ is drawn as a guide to the eyes with $C_2=2.2\times10^{-6}$. It shows that the exchanging rate increases as $E_r \sim t^{0.75}$.

These differences come from the higher order cumulants, which are ignored in Eq. (3). The contribution from the higher order cumulants can be explained by a swapping diffusion process, which is the hopping of the caged particle from cage to cage. While the normal diffusion destroys the positional order as described in Eq. (5), the swapping does not. The diffusion behavior in a two-dimensional solid is shown in Fig. 3(a). The density is $\rho=0.92$, which is high enough for the melting points [6,8,13]. While the diffusion shows logarithmic behavior up to $t \sim 10^4$, it varies from the logarithmic behavior in $t > 10^4$. The distribution of the displacement $\mathbf{u}_i$ at $t=10^5$ is shown in Fig. 4. The points around the center correspond to the results of the normal diffusion
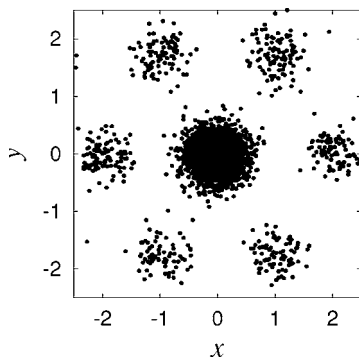

FIG. 4. Distribution of displacements $\mathbf{u}_i$ at $t=5\times10^5$ of the two-dimensional system with $N=2900$ and $\rho=0.92$. The lattice constant is $a=2$ and the radius of particles is $\sigma=0.89$ in this scale. The points around at the center correspond to the normal diffusion, and the six small groups around the center group correspond to the swapping diffusion.

and the six groups around the center group correspond to that of the swapping diffusion.

In order to treat the effect of the swapping, we consider the system with two types of diffusion, the continuous diffusion and the swapping diffusion with a swapping rate E_r on the lattice with a lattice constant a. The rate E_r denotes the probability to jump to the nearest position at equilibrium per unit time. The diffusion with swapping $\langle \mathbf{u}_i^2 \rangle'$ is expressed to be

$$\langle \mathbf{u}_i^2 \rangle' = \langle \mathbf{u}_i^2 \rangle + da^2 E_r t, \qquad (11)$$

with the diffusion without swapping $\langle \mathbf{u}_i^2 \rangle$ [18]. In the following, the positional order parameter calculated from Eq. (5) is denoted by Ψ' in order to distinguish from the original definition in Eq. (1). From Eq. (11), we can have the relation between Ψ and Ψ' as

$$\Psi' = \exp\left(-\frac{K^2 \langle \mathbf{u}_i^2 \rangle'}{2d}\right) = \Psi \exp(-2\pi^2 E_r t). \qquad (12)$$

Note that Ψ' is always smaller than Ψ, since $E_r > 0$. The contribution from the higher order cumulants is expressed to be

$$\ln(\Psi/\Psi') = 2\pi^2 E_r t. \qquad (13)$$

The time evolution of the value $\ln(\Psi/\Psi')$ is shown in Fig. 3(b). It increases as $\sim t^{1.75}$, which is faster than linear increase. Therefore, the exchanging rate E_r is not constant, but increases as $\sim t^{0.75}$. It implies that the destruction of the positional order enhances the swapping of the particles. We also study other values of the density $\rho=0.89$, 0.90, and 0.91, and find that $E_r \sim t^{0.75}$ for all cases.

To summarize, we study the dynamics of the positional order in the particle systems based on the diffusion processes. We discuss the relation between the positional order parameter and the mean square displacement with the cumulant expansion. We find that the normal diffusion contributes to the second order cumulant, and the swapping diffusion contributes to the higher orders. We also find that the behavior of exchanging rate E_r increases as $t^{0.75}$, regardless of density. It implies that the swapping diffusion is independent of the melting transition. Therefore, we need other strategies to discuss the melting from Ψ. The presented arguments are general and applicable to other systems with general pair potentials. We presented the results of hard-particle systems, which do not have any temperature dependence. If one uses the particle with a soft potential, like Lennard-Jones, there can be some temperature dependences. Therefore, it should be one of further issues to investigate whether the behavior $E_r \sim t^{0.75}$ is unique in the hard-disk system.

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[18] Consider a diffusion process on the grid with the lattice constant a. If particles jump randomly to the next site every τ, the system involves diffusion with a diffusion constant $D = a^2/2\tau$ and the exchanging rate E_r is denoted by $E_r = \tau^{-1}$.