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Size-dispersity effects in two-dimensional melting

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In order to investigate the effect of size dispersity on two-dimensional melting transitions, hard-disk systems with equimolar bidispersity are studied by means of particle dynamics simulations. From the nonequilibrium relaxation behaviors of bond-orientational order parameters, we find that (i) there is a critical dispersity at which the melting transition of the hexagonal solid vanishes and (ii) the quadratic structure is metastable in a certain region of the dispersity-density parameter space. These results suggest that the dispersity not only destroys order but produces new structures under certain specific conditions.

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Recently, there has been considerable interest in the melting behavior of systems with size dispersity, i.e., these systems in which the radii of constituent particles are not all identical. The randomness involved in the size dispersity of particles has been found to play an essential role in the behaviors of complex systems such as colloidal systems and granular media; for example, highly inhomogeneous force networks are involved because of size dispersity in granular media [1] and in segregation behavior in a rotating drum [2]. Therefore, investigations of the influence of size dispersity will be fruitful for understanding such complex systems. The effect of the size dispersity was first treated by Dickinson and Parker [3]. They investigated the phase diagram of a model colloidal dispersion. Vermölen and Ito studied the melting behavior of elastic-disk systems [4]. By observing a plateau in the pressure-density diagram, they found that there are no quantitative differences between the behaviors of binary and Gaussian distributed dispersion systems. They also found that the intermediate phase between the solid and the fluid phase vanishes above a critical dispersity. Sadr-Lahijany *et al.* studied the density-dispersity phase diagram of Lennard-Jones particle systems [5]. They observed that there is a critical value of dispersity above which the phase transition between the solid and fluid phases become of first order. They concluded that there is a multicritical point in the density-dispersity phase diagram.

In spite of these studies, two issues remain; the reason why the melting transition disappears, and the possibility of other regular structures in the system with dispersity aside from the hexagonal structure. In order to answer these questions, the hard-disk system with size dispersity is studied in this work by observing the nonequilibrium behavior of bond-orientational order parameters. A method to study critical phenomena using the nonequilibrium relaxation process of systems is called the nonequilibrium relaxation (NER) method. This method provides critical points and critical exponents accurately [6,7]. It has also been applied to investigate the Kosterlitz-Thouless (KT) transition [8] and random systems [9]. Recently, the melting behavior of the hard-disk system was studied by the NER method. The critical point ρ_i between the hexatic and solid phases was determined by a dynamic scaling analysis [10] and the critical exponent was also determined by observing the fluctuation of the order parameter [11]. This scaling technique for determining the melting point can be applied directly to the system with dispersity.

In this work, hard-disk systems with equimolar bidispersity (two kinds of particles of the same number) are treated. The density of the system is defined to be $\rho=4\Sigma_i^N r_i^2/A$, with the number of particles N, radius r_i, and area of the system A. With this definition, the density is normalized to be 1 when the system is in the quadratic dense packing configuration. The dispersity σ is defined by the ratio of the standard deviation to the average radius. For the equimolar bidisperse system, $\sigma=(r_a-r_b)/(r_a+r_b)$ with two radii r_a and $r_b (r_a > r_b)$.

The closest density of the system depends on its dispersity. In the infinite monodisperse system, the closest packing configuration is the hexagonal one and its density is $2/\sqrt{3}$. Here, the closest density of the hexagonal packing ρ_h is considered in order to investigate the effect of dispersity. The closest hexagonal packing with the dispersity is achieved when the larger particles are just in contact [see Fig. 1(a)]. The closest density is expected to be

$$\rho_{\mathrm{h}} = \frac{r_a^2 + r_b^2}{\sqrt{3} r_a^2}. \tag{1}$$

Equation (1) is also expressed to be

$$\rho_{\mathrm{h}}(\sigma) = \frac{2}{\sqrt{3}} \frac{\sigma^2+1}{(\sigma+1)^2}. \tag{2}$$

Clearly, $\rho_{\mathrm{h}}(0)=2/\sqrt{3}$ when $r_a=r_b$. While Eq. (2) is a simply decreasing function of dispersity σ, the melting point will

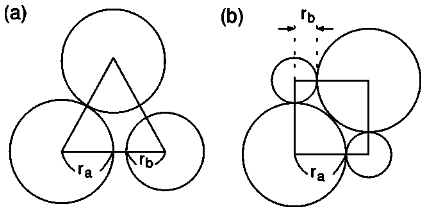

FIG. 1. Structures of the bidisperse system. (a) Hexagonal structure. (b) Quadratic structure.

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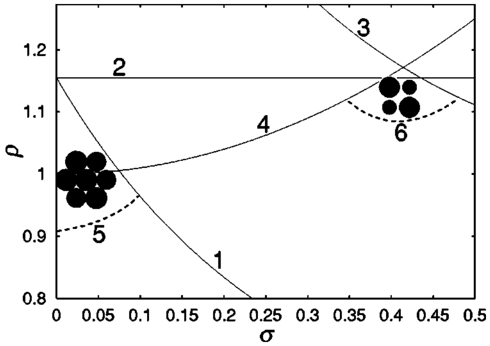

FIG. 2. Predicted phase boundaries of the equimolar bidisperse systems. Units of all plots in this paper are dimensionless. Solid lines: 1. Upper density limit of the hexagonal structure $\rho_{\mathrm{h}}(\sigma)$ in Eq. (2). 2. The highest density of the hexagonal packing $\rho=2/\sqrt{3}$. 3. A condition for highest density of the quadratic packing in Eq. (3). 4. Another condition for the quadratic packing in Eq. (4). Dashed lines are expected lower boundaries of the hexatic 5 and of the quadratic solid 6. Other possible structures are not shown here.

shift to a higher density with a larger dispersity since it becomes more difficult to maintain a regular structure with dispersity. Therefore, the melting point will disappear in the dispersity-density parameter space when the melting density becomes higher than the highest density of the hexagonal structure.

For the case of the bidisperse system, the regular quadratic structure can be considered as shown in Fig. 1(b). There are two conditions in the relation between density and dispersity; one is that overlapping does not occur between two larger particles and the other is that overlapping does not occur between larger and smaller particles. These conditions can be expressed with σ as

$$\rho_{\mathrm{q}} < \frac{2(\sigma^2+1)}{(\sigma+1)^2} \text{ and} \tag{3}$$

$$\rho_{\mathrm{q}} < \sigma^2 + 1. \tag{4}$$

While the closest packing density of the hexagonal structure is a simply decreasing function, the closest density of the quadratic packing becomes larger with a larger dispersity, and will reach the maximum value of $\rho_{\mathrm{q}}=4-2\sqrt{2}(\simeq 1.17)$ when $\sigma=\sqrt{2}-1(\simeq 0.414)$ (see Fig. 2). Note that the maximum density is larger than $2/\sqrt{3}(\simeq 1.15)$ which is the closest density of the monodisperse system. Therefore, it is possible that the quadratic solid structure is stable around $(\sigma,\rho)=(\sqrt{2}-1,4-2\sqrt{2})$ in the dispersity-density parameter space.

These two structures, hexagonal and quadratic, can be characterized by bond-orientational order (BOO) parameters [12]. The sixfold BOO parameter ϕ_6 is defined to be

$$\phi_6 = \frac{1}{N}\sum_{k}^{N}\sum_{l}^{n_k}\frac{\exp(6i\theta_{kl})}{n_k}, \tag{5}$$

where n_k denotes the number of neighbors of particle k, and θ_{kl} denotes the angle between a fixed axis and the bond connecting particles k and l. The sixfold parameter ϕ_6 becomes 1 when the structure of the system is the perfect hexagonal, and becomes 0 when the structure is completely disordered. Therefore, ϕ_6 describes how close the system is to the perfect hexagonal structure. The fourfold parameter ϕ_4 is similarly defined as $\phi_4=\langle\exp(4i\theta)\rangle$. This parameter ϕ_4 describes how close the system is to the perfect quadratic structure.

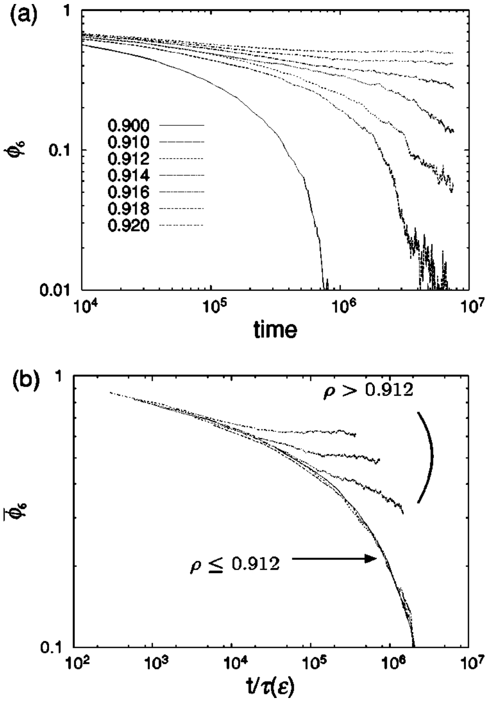

FIG. 3. The system of $\sigma=0.06$. The decimal logarithm is taken for both axes. (a) Relaxation behavior of ϕ_6. (b) Scaled data. While the data of $\rho\leqslant 0.912$ are collapsed to the single curve, the data of $\rho\geqslant 0.914$ are not.

We perform particle simulations and observe the nonequilibrium relaxation behavior of the BOO parameters. The starting configuration is set to be the perfect packing configuration, i.e., $\phi_6(t=0)=1$ or $\phi_4(t=0)=1$. Radii of particles are chosen randomly from two sizes. Periodic boundary conditions are taken for both directions of the simulation box. The particle number N is fixed at 23 288 for the hexagonal and 10 000 for the quadratic configurations, throughout the simulations [13]. The time evolution of the system is performed by a event-driven molecular dynamics simulation. About 10^9 collisions are performed for each run and up to 512 independent samples are averaged for each density.

For the hexagonal packing configuration, the systems of $\sigma=0$, 0.02, 0.04, 0.06, and 0.08 are studied. The time evolution of $\phi_6(\sigma=0.06)$ is shown in Fig. 3(a). To determine the critical density on the basis of this data, the dynamic scaling analysis is performed. The melting transition of the monodisperse hard-disk system is predicted to be the KT transition [12] (see the review by Strandburg [14]) and a number of studies have supported this prediction [10,15]. Therefore, systems with small dispersity are also expected to have a KT transition. Accordingly, the dynamic KT scaling [8] is performed in order to determine melting points from the results. Near the critical point, a natural scaling form of the BOO parameter is expected to be

TABLE I. The dispersity effect on the melting points. The critical points and exponents between the isotropic and hexatic phases are shown for several dispersities.

σ	0	0.02	0.04	0.06	0.08
ρ_i	0.893(2)	0.898(2)	0.901(1)	0.913(15)	0.935(2)
λ	0.02(2)	0.08(2)	0.10(15)	0.08(1)	0.11(1)

$$\phi_6(t,\varepsilon) = \tau(\varepsilon)^{-\lambda}\overline{\phi_6}(t/\tau(\varepsilon)) \qquad \left(\varepsilon = \frac{\rho_i - \rho}{\rho_i}\right), \tag{6}$$

with a correlation time τ, an exponent λ, and a critical point ρ_i. While the correlation time depends on the density, the dynamic exponent λ is independent of the density (it is only a function of dispersity). Based on Eq. (6), the relaxation curves of $\tau^{\lambda}\phi_6$ plotted as a function of t/τ will collapse to a single curve with appropriately chosen λ and $\tau(\varepsilon)$.

In the KT transition, the correlation length diverges exponentially as $\xi \sim \exp(a'/\sqrt{\varepsilon})$ [16]. On the basis of the dynamical scaling hypothesis [17], the relation between ξ and τ is expected to be $\tau = \xi^z$ with a dynamic exponent z and the divergence behavior of the relaxation time τ is expected to be

$$\tau(\varepsilon) = b\exp(a/\sqrt{\varepsilon}). \tag{7}$$

The critical point can be determined by fitting the divergence behavior (7) to $\tau(\varepsilon)$ obtained above. One can only scale the results in the disordered phase ($\rho < \rho_i$) since the correlation time of the system involving the KT transition always diverges in the ordered phase ($\rho > \rho_i$).

The scaled result is shown in Fig. 3(b). While the data of $\rho \leqslant 0.912$ collapse onto a single curve, the data of $\rho \geqslant 0.914$ do not. The determined critical points for each dispersity are listed in Table I and plotted in Fig. 4. The melting points are found to be almost proportional to the square of the dispersity. The hexagonal solid phase cannot exist in the region $\sigma > 0.1$ since the density of the melting transition will be higher than the highest density limit of the hexagonal packing configuration.

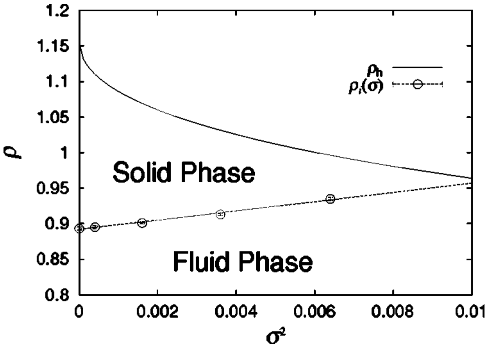

FIG. 4. The shift of melting points between the isotropic and hexatic phases. The range of the hexatic phase is not shown since it is too narrow at the scale of this figure. The melting points are found to be almost linear to σ^2. The hexagonal solid phase can exist only in the region $\sigma < 0.1$.

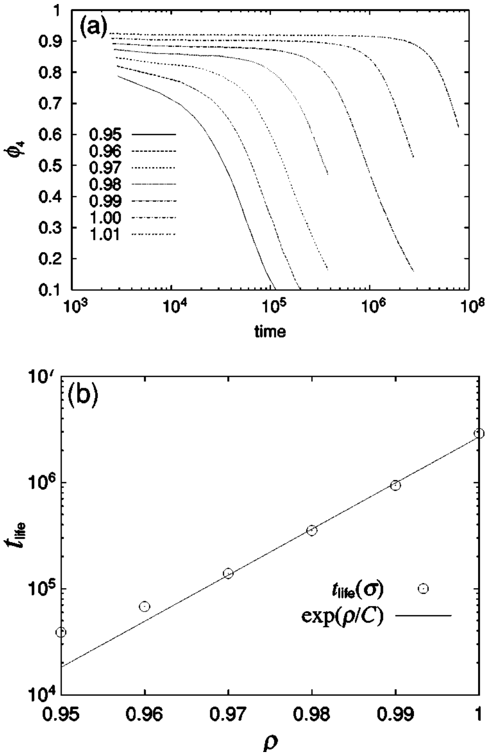

FIG. 5. (a) Relaxation behavior of ϕ_4 of the system with $\sigma = 0.4$. The decimal logarithm is taken for the horizontal axis. (b) Lifetime of the quadratic structure. The decimal logarithm is taken for the vertical axis. The lifetime is found to increase exponentially. The solid line is drawn for visual reference ($C = 0.01$).

For the quadratic packing configuration, systems whose dispersities are $\sigma = 0.3$–0.5 are studied. For the cases of $\sigma = 0.3$ and 0.5, the quadratic structure was destroyed quickly even at the highest density. Therefore, if a quadratic solid exists, it is expected to be in the region of $0.3 < \sigma < 0.5$. The relaxation behavior of ϕ_4 at $\sigma = 0.4$ is shown in Fig. 5(a). The figure shows that the quadratic structure is stable for a certain period, and it is destroyed after that. The lifetime t_{life} is defined by $\phi_4(t = t_{\mathrm{life}}) = 0.5$. The density dependence of the lifetime is shown in Fig. 5(b). Although the transition behavior of the quadratic solid is not observed, the lifetime diverges exponentially. Note that the lifetime should be infinite at $(\sigma, \rho) = (\sqrt{2} - 1, 4 - 2\sqrt{2})$ since all particles are in contact with the four neighbor particles and therefore cannot move.

To summarize, the size dispersity effects on two types of order, hexatic and quadratic, are studied in hard-disk systems with equimolar bidispersity. By considering the relation between the closest packing density and the dispersity, we have predicted (i) the phase boundary of the hexagonal solid and (ii) the existence of the quadratic solid. Particle simulations have been performed in order to investigate the stability of the hexagonal and quadratic structures. From the dynamic KT scaling analysis of the bond-orientational order parameters, the melting points of the hexagonal structure have been determined to be a function of dispersity. The critical densities become higher at higher dispersities, and the shift in density is proportional to the square of the dispersity. This result is consistent with past research [4]. The hexagonal solid phase cannot exist in the region $\sigma > 0.1$ since the melting density becomes higher than the density limit of the hexagonal structure. Sadr-Lahijany *et al.* studied Lennard-Jones systems with dispersity and reported that the intermediate hexatic phase vanished at $\sigma \simeq 0.097$, which is close to our result [5]. While they concluded that the vanishing point is the multicritical point and the line of first order transitions separates the liquid and solid phases, we have not obtained similar results yet since it is more difficult to study the higher density of hard-disk systems than Lennard-Jones systems. The stability of the quadratic structure is examined, and found to be metastable around $(\sigma, \rho) = (\sqrt{2}-1, 4-2\sqrt{2})$. It is not yet clear whether the quadratic structure is a thermodynamic phase, since no transition behavior is observed. In this work, only equimolar bidisperse systems have been studied. The discussion of the relation between the closest density and the dispersity is difficult to apply to polydisperse systems in general. Possible other structures are not considered here. These problems should be addressed in future studies.

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[1] D. M. Mueth, H. M. Jaeger, and S. R. Nagel, Phys. Rev. E **57**, 3164 (1998).
[2] L. Prigozhin and H. Kalman, Phys. Rev. E **57**, 2073 (1998).
[3] E. Dickinson and R. Parker, Chem. Phys. Lett. **79**, 578 (1981).
[4] W. Vermöhlen and N. Ito, Phys. Rev. E **51**, 4325 (1995); see also **54**, 3055(E) (1996).
[5] M. R. Sadr-Lahijany, P. Ray, and H. E. Stanley, Phys. Rev. Lett. **79**, 3206 (1997).
[6] N. Ito, Physica A **192**, 604 (1993).
[7] N. Ito, K. Hukushima, K. Ogawa, and Y. Ozeki, J. Phys. Soc. Jpn. **69**, 1931 (2000).
[8] Y. Ozeki, K. Ogawa, and N. Ito, Phys. Rev. E **67**, 026702 (2003).
[9] N. Ito, T. Matsuhisa, and H. Kitatani, J. Phys. Soc. Jpn. **67**, 1188 (1998).
[10] H. Watanabe, S. Yukawa, Y. Ozeki, and N. Ito, Phys. Rev. E **66**, 041110 (2002). Note that the definition of the bond-orientational order was not correct. Therefore the critical point ρ_i without dispersity was different from that in this study. We are preparing an erratum.
[11] H. Watanabe, S. Yukawa, Y. Ozeki, and N. Ito, Phys. Rev. E **69**, 045103(R) (2004).
[12] B. I. Halperin and D. R. Nelson, Phys. Rev. Lett. **41**, 121 (1978); A. P. Young, Phys. Rev. B **19**, 1855 (1979).
[13] The number of particles of the quadratic packing is smaller than that of the hexagonal one, since higher density and dispersity require greater computational power.
[14] K. J. Strandburg, Rev. Mod. Phys. **60**, 161 (1988).
[15] A. Jaster, Phys. Rev. E **59**, 2594 (1999).
[16] J. M. Kosterlitz and D. J. Thouless, J. Phys. C **6**, 1181 (1973); J. M. Kosterlitz, *ibid.* **7**, 1046 (1974).
[17] B. I. Halperin and P. C. Hohenberg, Phys. Rev. **177**, 952 (1969).