Formation of double glass in binary mixtures of anisotropic particles

Kyohei Takae and Akira Onuki
Department of Physics, Kyoto University, Kyoto 606-8502, Japan
(Dated: May 21, 2013)

We study glass transitions in mixtures of elliptic and circular particles in two dimensions using an orientation-dependent Lennard-Jones potential. Changing anisotropic parameters of the potential, the size ratio, and the concentration, we realize double glass, where both the particle positions and orientations are disordered but still hold mesoscopic order. The ellipses are anchored around the circular impurities in the homeotropic or planar directions. We examine slowing-down of rotational and translational time-correlation functions. Turnover motions of the ellipses are activated more frequently than the configuration changes, where the latter cause the structural relaxation.

PACS numbers: 64.70.Q-, 64.70.P-, 61.20.Lc, 61.43.Fs

Much attention has been paid to various types of glass transitions, where the structural relaxations become extremely slow with lowering the temperature \( T \). In experiments, colloidal particles can be spherical, but real molecules are mostly nonspherical. The translational and rotational diffusion constants have thus been measured in molecular systems near the glass transition \[3\]. Using generalized mode-coupling theories, some authors \[4\] have studied the coupled translation-rotation dynamics to predict translational glass and orientational glass. Molecular dynamics simulations have also been performed on glass-forming binary mixtures composed of anisotropic particles \[7\]–\[12\].

For mild differences in sizes and shapes, mixtures of anisotropic particles such as \((\text{KCN})_x(\text{KBr})_{1-x}\) form a cubic crystal without orientational order (plastic solid) at relatively high \( T \). With further lowering \( T \), they undergo a structural phase transition in dilute cases and become orientational glass in nondilute cases \[13\]–\[14\]. On the other hand, if the two species have significantly different sizes or shapes, translational glass emerges from liquid at low \( T \). Here, the molecular rotations sensitively depend on the molecular shapes and, for not large aspect ratios, flip motions can occur without large positional displacements. In the previous simulations \[4\]–\[11\], the translational and rotational degrees of freedom were strongly coupled. Theoretically, for double glass \[6\], they can be simultaneously arrested at the same temperature.

In the literature, the physical picture of double glass remains quite unclear. In this Letter, we visualize the particle configurations below a double glass transition. We shall see marked orientational and positional heterogeneities on mesoscopic scales, where the latter have been detected for circular or spherical particles \[15\]–\[17\]. As a related experiment, Zheng et al. \[18\] visualized twodimensional motions of colloidal ellipsoids in monolayers at glass transition.

**Model and numerical method-** In two dimensions, we consider mixtures of anisotropic and circular particles with numbers \( N_1 \) and \( N_2 \), where \( N = N_1 + N_2 = 4096 \). The concentration of the circular species is \( c = N_2/N \). The particle positions are written as \( r_i \) (\( i = 1, \cdots, N \)). The orientation vectors of the anisotropic particles are expressed as \( n_i = (\cos \theta_i, \sin \theta_i) \) in terms of angles \( \theta_i \) (\( i = 1, \cdots, N_1 \)). The pair potential \( U_{ij} \) between particles \( i \in a \) and \( j \in b \) (\( \alpha = 1, 2; \beta = 1, 2 \)) is a truncated modified Lennard-Jones potential. If the particle distance \( r_{ij} \) is shorter than a cut-off \( r_c \), it is written as

\[
U_{ij} = 4\epsilon \left[ (1 + A_{ij}) \frac{\sigma_{ij}^{12}}{r_{ij}^6} - (1 + B_{ij}) \frac{\sigma_{ij}^6}{r_{ij}^2} \right] - C_{ij},
\]

where \( \epsilon \) is the interaction energy. We introduce characteristic lengths \( \sigma_1 \) and \( \sigma_2 \) by setting \( \sigma_{\alpha\beta} = (\sigma_\alpha + \sigma_\beta)/2 \). We set \( U_{ij} = 0 \) for \( r_{ij} > r_c \), where \( r_c/\sigma_1 = 3 \) for \( \sigma_2/\sigma_1 < 1 \) and is 4.5 for \( \sigma_2/\sigma_1 > 1 \). The \( C_{ij} \) ensures the continuity of \( U_{ij} \) at \( r_{ij} = r_c \). The particle anisotropy is accounted for by the factors \( A_{ij} \) and \( B_{ij} \) depending on the angles between \( \mathbf{n}_i, \mathbf{n}_j \), and the relative direction \( \mathbf{r}_{ij} = r_{ij}^{-1}(\mathbf{r}_i - \mathbf{r}_j) \). We set

\[
A_{ij} = \chi [\delta_{a_1}(\mathbf{n}_i \cdot \mathbf{r}_{ij})^2 + \delta_{b_1}(\mathbf{n}_j \cdot \mathbf{r}_{ij})^2],
\]

\[
B_{ij} = \zeta [\delta_{a_2}(\mathbf{n}_i \cdot \mathbf{r}_{ij})^2 + \delta_{b_2}(\mathbf{n}_j \cdot \mathbf{r}_{ij})^2],
\]

where \( \delta_{a_2} \) is the Kronecker delta, \( \chi \) is the anisotropy strength of repulsion, and \( \zeta \) is that of attraction between the two species. The Newton equations of motion are

\[
md^2 \mathbf{r}_i/dt^2 = -\partial U/\partial \mathbf{r}_i, \quad \text{and} \quad d^2 \theta_i/dt^2 = -\partial U/\partial \theta_i,
\]

where \( U = \sum_{i<j} U_{ij} \) is the total potential, \( m \) is the mass common to the two species, and \( I \) is the moment of inertia of the first species. We note that similar angle-dependent potentials were used for liquid crystals \[12\]–\[13\], water \[20\], glass-forming liquids \[16\], and lipids \[21\].

We treat the anisotropic particles as ellipses. For fixed orientations of two ellipses \( i \) and \( j \), \( U_{ij} \) is minimized at \( r_{ij} = 2^{1/6}/(1 + A_{ij})^{1/6} \sigma_1 \). Then varying \( \mathbf{n}_1 \) and \( \mathbf{n}_2 \) yields the shortest and longest diameters, \( a_s = 2^{1/6}/\sigma_1 \) and \( a_t = (1+2\chi)^{1/6}2^{1/6}/\sigma_1 \). The aspect ratio is \( a_t/a_s = (1+2\chi)^{1/6} \), which is 1.23 for \( \chi = 1.2 \). The ellipses have the molecular area \( \mathcal{S}_1 = \pi a_s a_t/4 \) and the momentum of inertia \( I = (a_s^2 + a_t^2)m_1/16 \). We fix the average packing fraction \( (\mathcal{S}_1 N_1 + \mathcal{S}_2 N_2)/L^2 \) at 0.95, where \( \mathcal{S}_2 = \pi 2^{1/3} \sigma_2^2/4 \). The system length \( L \) is about \( 70\sigma_1 \).
FIG. 1. Orientational angles $\theta_j$ (left) and sixfold bond orientation angles $\alpha_j$ (right) in Eq.(3) for small impurities with $\zeta = 0.5$ (top) and 1 (bottom) in double glass, where $c = 0.2$, $\chi = 1.2$, $\sigma_2/\sigma_1 = 0.6$, and $T = 0.05$. Heterogeneities become finer with increasing $\zeta$.

We integrated the Newton equations under the periodic boundary condition. We assumed a Nosé-Hoover thermostat [22] to prepare the initial particle configurations, but it was switched off during calculating the time-correlation functions. We measure time in units of $\tau_0 = \sigma_1 \sqrt{m/\epsilon}$ and temperature in units of $\epsilon/k_B$, where $k_B$ is the Boltzmann constant. We lowered $T$ from 1 to 0.1 at a cooling rate of $dT/dt = 0.9 \times 10^{-5}$. We then changed $T$ to a final temperature and waited for $2 \times 10^5 \tau_0$.

At low $T (\lesssim 0.1)$, we observed only thermal vibrations in the particle orientations and positions for each $\chi$, $\zeta$, $\sigma_2/\sigma_1$, and $c$. For not large $\chi$ and $\zeta$, we may study orientational glass with increasing $c$ [14]. In this Letter, we assume relatively small or large $\sigma_2/\sigma_1$ to induce disorder both in the orientations and the positions. The second species is treated as impurities for $c \lesssim 0.2$.

Small impurities- First, we consider small impurities with $\sigma_2/\sigma_1 = 0.6$ setting $\chi = 1.2$, and $c = 0.2$. We are interested in the effect of the anisotropic attraction arising from $\zeta > 0$. At $T = 0.05$, Fig.1 displays the angles $\theta_j$ of the ellipses and the sixfold bond-orientation angles $\alpha_j$ for all the particles. In the range $0 \leq \alpha_j < \pi/3$, we define $\alpha_j$ by [15 23]

$$\sum_{k \in \text{bonded}} \exp[6i\theta_{jk}] \propto \exp[6i\alpha_j],$$

where $\theta_{jk}$ is the angle between $r_k - r_j$ and the $x$ axis, the bonded particles $k$ are within the range $|r_{jk}| < 1.5\sigma_{\alpha\beta}$, and $6\alpha_j$ is the phase angle of the left hand side.

In Fig.1, orientationally ordered regions are finely divided by the impurities. For $\zeta = 0.5$ we can see small orientationally ordered domains and small polycrystal grains, while for $\zeta = 1$ orientational and positional disorders are both enhanced, resulting in double glass. Namely, with increasing $\zeta$, the orientation domains and the grain sizes become smaller. Similar positional patterns have been observed in glass [15–17]. Note that the crossover between polycrystal and glass is gradual and mesoscopic order still remains in glass.

The left panels of Fig.2 display expanded snapshots of $\theta_j$ around impurities, where anchoring is homeotropic [12]. With increasing $\zeta$, the ellipses tend to attach to each impurity and the impurity clustering is gradually suppressed, where the clustering took place during solidification. Similar homeotropic anchoring occurs in water around small ions as hydration, which breaks tetrahedral order resulting in vitrification at low $T$ [25].

FIG. 2. Left: Expanded snapshots of orientational angles $\theta_i$ around small impurities in the box regions in the left panels in Fig.1. Anchoring is homeotropic and impurity clustering is suppressed with increasing $\zeta$. Right: Delaunay triangulations, where small impurities have four or five surrounding triangles and host ellipses have seven or eight triangles.
functions \( G_1(t) \) and \( G_2(t) \) defined by

\[
G_i(t) = \frac{1}{N_i} \sum_{1 \leq j \leq N_i} \langle \cos[\ell \theta_j(t + t_0) - \ell \theta_j(t_0)] \rangle, \tag{5}
\]

where \( \ell = 1, 2 \). We took the average \( \langle \cdots \rangle \) over the initial time \( t_0 \) and over five runs. Here, \( G_1(t) \) decays due to turnover motions \( \theta_j \to \theta_j \pm \pi \), while \( G_2(t) \) is unchanged by them. Such flips have been observed in some simulations \([7, 9]\). While \( G_2(t) \) exhibits a considerable initial decay, it decays more slowly for \( t \gtrsim 1 \). In Fig.3(c)-(d), we divide the ellipses \( j \in 1 \) into those near the impurities \( (r_{jk} < 1.8 \sigma_1) \) for some \( k \in 2 \) and those far from the impurities \( (r_{jk} > 1.8 \sigma_1) \) for any \( k \in 2 \). Their numbers are given by \( N_n \sim 2400 \) and \( N_\ell \sim 900 \) and their rotational time-correlation functions are written as \( G_{n\ell}(t) \) and \( G_{\ell\ell}(t) \), respectively.

In our case, the impurities strongly anchor the nearby ellipses, so the decay of \( G_{n\ell}(t) \) is much slower than that of \( G_{\ell\ell}(t) \). On the other hand, Fig.3(e) gives the self part of the density time-correlation functions \( F_s(q, t) \) at \( q = 2\pi/\sigma_1 \) for the first species. Notice close resemblance between \( G_{2\ell}(t) \) and \( F_s(q, t) \). In Fig.3(f), we plot the corresponding relaxation times \( \tau_1, \tau_2, \) and \( \tau_{\alpha} \), where \( \tau_{\alpha} \equiv \tau_2 \gg \tau_1 \). They are determined by \( G_1(\tau_1) = 1/e, G_2(t) \propto \exp[-(t/\tau_2)\beta] \) for \( t > 1 \), and \( F_s(q, t) \propto \exp[-(t/\tau_{\alpha})\gamma] \) for \( t > 1 \), where the exponents \( \beta \) and \( \gamma \) are about 0.4 for \( T \sim 0.2 \). Here, \( \tau_1 \) exhibits the Arrhenius behavior \( \ln \tau_1 \propto 1/T \). The turnover motions are thermally activated and are decoupled from the translational motions. However, the slow decay of \( G_2(t) \) and the positional relaxation are strongly coupled, as a characteristic feature of double glass \([3, 6, 11]\).

For \( T \gtrsim 0.2 \), we could realize steady states. However, for \( T \lesssim 0.15, \tau_\alpha(\sim \tau_2) \) exceeds \( 10^5 \) and the waiting time was too short and the aging process continued in the whole simulation time \( \sim 10^6 \). At \( T = 0.05 \) in Figs.1 and 4, there was no appreciable configuration changes in the orientations and positions in our simulation time."

**Large impurities** - Next, we consider large impurities with \( \sigma_2/\sigma_1 = 1.5 \) setting \( \chi = 1.2, \zeta = 0 \), and \( T = 0.05 \). In the upper plates in Fig.4, the orientations are highly frustrated, while the particles still form polycrystal with very small sizes. In the lower plates, we show that the anchoring is planar at the impurity surfaces \([12]\) (left). In this case, impurity clustering is conspicuous, because association of impurities lowers the total potential energy by a few \( \epsilon \) per impurity particle \([14]\). We also show point defects in the Delaunay triangulation (right). Here, we have \( n_t = 6 \) (67%) or 7 (33%) for large impurities and \( n_t = 6 \) (89%) or 5 (10%) for small host particles. In liquid, host small particles form appreciable liquidlike defects (2% at \( T = 0.4 \)).

In Fig.5, we show the rotational time correlation functions \( G_1(t) \) and \( G_2(t) \) in (a) and (b), the self part of the density time-correlation function \( F_s(q, t) \) at \( q = 2\pi \) in (c), and relaxation times \( \tau_1, \tau_2, \) and \( \tau_{\alpha} \) vs \( 1/T \) in (d).
These quantities are defined in Fig.3. Their behaviors, including those of $G_{i\alpha}(t)$ and $G_{i\beta}(t)$, are also very similar to those in Fig.3, though the types of impurities are very different in the two cases. We again find $\tau_{a}^{'} \sim \tau_{2} \gg \tau_{1}$ and the Arrhenius behavior of $\tau_{1}$.

Summary and remarks- With an angle-dependent Lennard-Jones potential, we have performed simulation of mixtures of elliptic and circular particles. For mild anisotropy, the ellipses tend to form a lattice of isosceles triangles far from the impurities but are anchored around them in homeotropic or planar alignment at low $T$. The positional disorder is produced if the size ratio $\sigma_{2}/\sigma_{1}$ considerably deviates from unity. In such cases, the orientational order and the positional order decrease with increasing the impurity concentration $c$. For small impurities, their clustering is suppressed with increasing the impurity-ellipse interaction ($\propto \zeta$) in Fig.2. For large impurities, it can also be suppressed with increasing repulsion among them, for example, by adding a term proportional to $\delta_{ij}\delta_{k\beta}$ in $A_{ij}$ in Eq.(2).

We have also studied the rotational dynamics of the ellipses, whose turnover motions occur more frequently than the configuration changes in agreement with the previous papers. In addition, the ellipses near the impurities rotate more slowly than those far from them.

Our potential energy is invariant with respect to the turnover motions. However, if it has no such flip symmetry, a flip-translation coupling arises. For example, $\tau_{1}$ increases with introduction of the dipolar interaction, which will be reported shortly.

The spatial scales of the structural heterogeneities depend on various parameters as in Figs.1 and 4. If the oriented domains are not too small, there arises a large orientation-strain coupling, leading to soft elasticity and a shape-memory effect [14]. Such effects were found for Ti-Ni alloys [26] (where atomic displacements within unit cells cause structural changes). When anisotropic particles have electric dipoles[13], we will report appearance of mesoscopic polar domains yielding large response to electric field, as in ferroelectric relaxors [27].

This work was supported by Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan. K. T. was supported by the Japan Society for Promotion of Science.

[1] C. A. Angell, K. L. Ngai, G. B. McKenna, P. F. McMullan, and S. W. Martin, J. Appl. Phys. 88, 3113 (2000).
[2] K. Binder and W. Kob, Glassy Materials and Disordered Systems.
Solids (World Scientific, Singapore, 2005).

[3] F. Fujara, B. Geil, H. Sillescu, and G. Fleischer, Z. Phys. B 88, 195 (1992); M. T. Cicerone and M. D. Ediger, J. Chem. Phys. 104, 7210 (1996).

[4] A. Winkler, A. Latz, R. Schilling, and C. Theis, Phys. Rev. E 62, 8004 (2000).

[5] S.-H. Chong and W. Götze, Phys. Rev. E 65, 041503 (2002).

[6] R. Zhang and K. S. Schweizer, J. Chem. Phys. 133, 104902 (2010); ibid. 136, 154902 (2012).

[7] P. Sindzingre and M. L. Klein, J. Chem. Phys. 96, 4681 (1992).

[8] S. Kämmerer, W. Kob, and R. Schilling, Phys. Rev. E 56, 5450 (1997).

[9] C. De Michele and D. Leporini, Phys. Rev. E 63, 036701 (2001); ibid. 63, 036702 (2001).

[10] T. G. Lombardo, P. G. Debenedetti, and F. H. Stillinger, J. Chem. Phys. 125, 174507 (2006).

[11] S.-H. Chong, A. J. Moreno, F. Sciortino, and W. Kob, Phys. Rev. Lett. 94, 215701 (2005); S.-H. Chong and W. Kob, ibid. 102, 025702 (2009).

[12] D. Antypov and D. J. Cleaver, J. Chem. Phys. 120, 10307 (2004).

[13] U. T. Höchli, K. Knorr, and A. Loidl, Adv. Phys. 39, 405 (1990).

[14] K. Takae and A. Onuki, EPL 100, 16006 (2012).

[15] T. Hamanaka and A. Onuki, Phys. Rev. E 74, 011506 (2006); ibid. 75, 041503 (2007).

[16] H. Shintani and H. Tanaka, Nat. Phys. 2, 200 (2006).

[17] T. Kawasaki, T. Araki, and H. Tanaka, Phys. Rev. Lett. 99, 215701 (2007).

[18] Z. Zheng, F. Wang, and Y. Han, Phys. Rev. Lett. 107, 065702 (2011).

[19] J. G. Gay and B. J. Berne, J. Chem. Phys. 74, 3316 (1981); J. T. Brown et al., Phys. Rev. E 57, 6685 (1998).

[20] A. Ben-Naim, J. Chem. Phys. 54, 3682 (1971); K. A. T. Silverstein, A. D. J. Haymet, and K. A. Dill, J. Am. Chem. Soc. 120, 3166 (1998).

[21] J. M. Drouffe, A. C. Maggs and S. Leibler, Science 254, 1353 (1991); H. Noguchi, J. Chem. Phys. 134, 055101 (2011).

[22] S. Nosé, Mol. Phys. 52, 255 (1984).

[23] D. R. Nelson and B. I. Halperin, Phys. Rev. B 19, 2457 (1979).

[24] H. G. E. Hentschel, V. Ilyin, N. Makedonska, I. Procaccia, and N. Schupper, Phys. Rev. E 75, 050404(R) (2007).

[25] C. A. Angell and E. J. Sare, J. Chem. Phys. 49, 4713 (1968); M. Kobayashi and H. Tanaka, J. Phys. Chem. B, 115, 14077 (2011).

[26] S. Sarkar, X. Ren, and K. Otsuka, Phys. Rev. Lett. 95, 205702 (2005); Y. Wang, X. Ren, and K. Otsuka, Phys. Rev. Lett. 97, 225703 (2006).

[27] R. A. Cowley, S.N. Gvasaliya, S.G. Lushnikov, B. Roessli, and G.M. Rotaru, Adv. Phys. 60, 229 (2011).