Decoupling phenomena and replica symmetry breaking of binary mixtures

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Size dispersity of constituent atoms, molecules, or colloids is ubiquitous in glassy systems. For most model glass formers employed in numerical studies, the size dispersion is deliberately introduced in order to avoid the crystallization. In experiments of colloidal or polymeric glasses, it is simply difficult to eliminate. When the size dispersion is small, it does not affect the nature of the glass transition qualitatively; it only shifts the transition point or changes the fragility slightly [1, 2]. However, if the size dispersion is large, the nature of the glass transition qualitatively and even dramatically changes. Due to the separation of the associated length and time scales, dynamics of constituent particles with different sizes decouple from each other [3]. A wide class of glassy systems exhibit such decoupling phenomena, which include ionic [4], metallic [5], and polymeric glasses [6, 7], as well as colloidal suspensions [8–10]. The simplest model which shows the decoupling is the binary mixture of large and small spherical particles with the disparate size ratio \( R \equiv \sigma_L / \sigma_S \gg 1 \), where \( \sigma_L \) and \( \sigma_S \) are the diameters of large and small spheres, respectively. In the limit of \( R = \infty \), small particles behave as a solvent and only large particles undergo the glass transition. When \( R \) is sufficiently large but finite, small particles still remain mobile, but induce a short-ranged depletion force between large particles and bring about the attractive glass transition, reentrant transition, and even gelation [11, 12]. As \( R \) is reduced to the order of unity, dynamics of small and large particles couple again and vitrify simultaneously. The question is when and how the dynamics of the two components decouple and the nature of the glass transition is altered as \( R \) is systematically changed.

Several experimental studies on binary colloidal mixtures [8–10] have reported such dynamical decoupling and the existence of multiple phases called the “single” glass where only large particles are frozen and “double” glass where both components vitrify simultaneously. But the properties of different glass phases remain elusive. Several simulation studies [13–15] hint the onset of the decoupling of the dynamics near the glass transition point. However, the size ratios and time scales which can be covered by simulations are limited. Currently, theoretical understanding of the decoupling phenomena largely relies on the mode-coupling theory (MCT) [16, 17]. Early studies have shown the decoupling of dynamics of small and large particles qualitatively [18, 19] and a recent detailed analysis predicted the emergence of rich multiple glass phases [20]. However, due to the series of uncontrollable approximations inherent in the MCT, it is difficult to assess the interplay of separate length scales and the validity of the theory. One resolution is to take the large dimension limit where mean field theories including the MCT are expected to become exact, but the validity of the current version of the MCT in this limit remains controversial [21, 22, 23].

In this Letter, we tackle this decoupling problem of the binary glasses using the thermodynamic counterpart of the mean-field theory of the glass transition. Our theory is based on the replica liquid theory (RLT) [24, 25], which was originally developed based on the classic mean-field spin-glass theory [21, 26, 27]. When the size dispersity is moderate, or the system is simply mono-disperse, the output of the RLT can be summarized as follows. The dynamic transition which the MCT prescribes corresponds to the “spinodal” point in the RLT [21]. Below the spinodal point, the RLT predicts the proliferation of exponentially large number of metastable states, or minima, in the free energy landscape. The logarithm of the num-

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FIG. 1. Schematic depiction of the free energy landscape in (a) the 1RSB and (b) the 2RSB formalisms.

... is the so-called configurational entropy \( \Sigma_c \). The RLT describes the thermodynamic, or ideal, glass transition at the point where \( \Sigma_c \) vanishes [26, 30]. This transition is accompanied by the one-step replica symmetry breaking (1RSB). This scenario becomes exact in the mean-field (or large \( d \)) limit [28, 32].

The RLT was extended to the binary mixtures but it fails to predict the decoupling phenomena even when the size ratio is large [33–36]. For the spin-glass models which have the well-separated length/energy scales, there arises the two-step replica symmetry breaking (2RSB) phase as the stable solution [37–40], which naturally captures the decoupling [37]. In this work, we develop the RLT of the binary mixtures taking fully both one and two step replica symmetry breakings into account. The new RLT predicts both single and double glass phases and the physical mechanism can be explained in the context of the energy landscape picture [41–42]. Interestingly, the new theory also predicts a new glass phase, called the 2RSB glass, which is characterized by the hierarchical structure of the free energy landscape.

We consider a binary mixture of large (L) and small (S) spheres interacting with a potential with a finite range, such as a harmonic potential, given by \( v_{\mu \nu}(r) = \phi(r/r_{\mu \nu})\theta(1 - r/r_{\mu \nu}) \), where \( \theta(x) \) is the Heaviside step function. \( \mu, \nu \in \{L, S\} \), \( \sigma_{LL} \) and \( \sigma_{SS} \) are the diameters of large and small particles, respectively. We also assume that the potential is additive, i.e., \( \sigma_{LS} = (\sigma_{LL} + \sigma_{SS})/2 \). The reason to consider a finite ranged potential is merely technical; as shown later, the functional form of \( \phi(r) \) and temperature become irrelevant parameters in the large dimension limit. The relevant parameters of the thermodynamic phase diagram are two only: the volume fractions of each component \( \varphi_{\mu} = N_\mu V_d(\sigma_{\mu \mu})/V \) \( (\mu \in \{L, S\}) \). Or equivalently, the total volume fraction \( \varphi = \varphi_S + \varphi_L \) and the concentration fraction (of small component), \( x = \varphi_S/(\varphi_L + \varphi_S) \). Here, \( V_d(\sigma) \) is the volume of a \( d \)-dimensional hypersphere with the diameter \( \sigma \), \( N_\mu \) denotes the particle number of the \( \mu \)-component, and \( V \) is a volume of the system. We represent the size ratio as \( \sigma_{LL}/\sigma_{SS} \equiv 1 + R/d \), so that the volume ratio, \( V_d(\sigma_{LL})/V_d(\sigma_{SS}) = (\sigma_{LL}/\sigma_{SS})^d \), remains finite in the limit of \( d \to \infty \).

First, we consider the conventional RLT with the 1RSB ansatz (1RSB-RLT). The main idea of the RLT is to introduce the \( m \) copies (replicas) of the original system to evaluate the free energy of the system. The overlap, or similarity, between the configurations of different replicas plays a role of the order parameter. The 1RSB ansatz claims that a replica symmetric (RS) liquid falls into a metastable glass state with a finite self-overlap but there is no overlap between different metastable glass states [26, 28, 35]. The landscape considered in the 1RSB formalism is schematically drawn in FIG. 1(a). The 1RSB-RLT for monodisperse systems is well developed [28, 35] and the extension to binary mixtures is straightforward [28, 35], aside from a subtlety related to the particle exchange in a glass state [33, 43, 45]. We first calculate the dynamical transition point of our model using the 1RSB-RLT. The dynamical transition is found to decouple when \( R \) is sufficiently large, i.e., the dynamics of large particles is frozen at a lower density than that of small particles (see Sec. I of Supplemental Material [46]). However, the 1RSB-RLT fails to predict the decoupling of the thermodynamic transition; the thermodynamic glass transitions for the two species take place simultaneously at a common \( \varphi_K \), irrespective of the value of \( R \) (see Sec. I of SM [46]). The phase diagram only shows the RS fluid phase and the 1RSB glass phase.

Next, we introduce the 2RSB ansatz into the RLT. Our 2RSB-RLT is inspired by the study of a binary spin glass model [37] and based on the following physical picture; the free energy landscape of the binary mixtures is divided into the multi-valleys due to the configurations of large particles, and each valley is further divided into smaller valleys due to small particles, as illustrated in FIG. 1(b). This implies the existence, at least, the two glass phases; (i) 1RSB phase, where the system is trapped in a large valley but a fraction of degree of freedoms still can travel between the lowest minima, which corresponds to the single glass. (ii) 2RSB glass state, where the system is trapped in the lowest minimum where all particles are frozen. The RLT with the 2RSB ansatz is formulated by dividing \( m \) replicas into \( m/m_1 \) sub-groups, each of which contains \( m_1 \) replicas. The \( m_1 \) replicas of small particles within a same sub-group are constrained around their center of mass, whereas the replicas of different sub-groups can move independently. For large particles, all \( m \) replicas are constrained around their center of mass. In other words, the replicated liquid is a \((m/m_1 + 1)\)-component “molecular” mixture which consists of \( m/m_1 \) types of molecules composed of \( m_1 \) small particles and one type of molecules composed of \( m \) large particles. There is no interaction between small molecules with different types. Note that the higher order RSB is a natural consequence of consecutive transitions of each component and this picture is distinct from the full RSB transition recently studied in the context of the “marginal” glass transition where each RSB state corresponds to one frozen state [47].
Based on the 2RSB ansatz, one can write down the free energy of the replica liquid using the virial expansion of the standard grand canonical partition function (see Sec. II of SM [46] for the derivation), which leads

\[
\frac{\log Z_m}{N} = \int d\rho_L(z)(1 - \log \rho_L(z)) + \sum_{k=1}^{m/m_1} \int d\rho_k \rho_k(z_k)(1 - \log \rho_k(z_k)) + \frac{1}{2} \int d\rho_L(z) \rho_L(z)^2 f_{LL}(z - z') + \sum_{k=1}^{m/m_1} \int d\rho_L(z) \rho_k(z_k) f_{LS}(z_k - z'k) + \sum_{k=1}^{m/m_1} \int d\rho_L(z) \rho_k(z_k) f_{SS}(z_k - z'k) + O(\rho_L^3, \rho_k^3),
\]

(1)

In this expression, \( \rho_\alpha (\alpha \in L, S_k) \) is the density field of large (L) and of small particles (S_k) of the k-th type, respectively. \( z_k = \{x^1, \ldots, x^m\} \) and \( z_k = \{x^1, \ldots, x^{m_1}\} \) represent their coordinates in the replica space. \( f_{\mu \nu}(z - z') (\mu, \nu \in L, S_k) \) is the Mayer function defined by

\[
f_{\mu \nu}(z - z') = \prod_a e^{-\beta \mu_\nu(r_a - r'_a)} - 1,
\]

where the product over \( a \) is made only for the replicas commonly included in the \( \mu \) and \( \nu \) molecules. The first and second terms of Eq. (1) are the ideal gas parts and the third to fifth terms represent the interaction contributions [28]. We assume that the profiles of \( \rho_L(z) \) and \( \rho_k(z_k) \) are Gaussian [28]. It should be emphasized that, in the large \( d \) limit, only the lowest order term in the Mayer expansions survives, which simplifies the analysis considerably. This implies that, in large \( d \) limit, the so-called “depletion force”, a short-ranged attraction between large particles induced by small ones, is absent [38], which is intrinsically the higher order effect.

The glass phases are determined by optimizing the free energy, Eq. (1), with respect to \( m \) and \( m_1 \). The glass transition density \( \varphi_K \) is the point at which the RS solution where \( m = m_1 = 1 \) becomes unstable. In the vicinity of \( \varphi_K \), the free energy can be simplified and written by an asymptotic expression [50],

\[
\frac{\log Z_m}{N} = g_1(m) + g_2(m_1) - d \log d,
\]

(3)

with the auxiliary functions defined by

\[
g_1(m) = \frac{1}{m} \left[ \frac{1 - x}{1 - x + xe^R} \right] d \log d - \frac{2d^2 \varphi}{2} \frac{(1 - x)^2}{1 - x + xe^R} I(m),
\]

\[
g_2(m_1) = \frac{1}{m_1} \left[ \frac{xe^R}{1 - x + xe^R} \right] d \log d - \frac{2d^2 \varphi x^2 e^R + 2x(1 - x)e^{R/2}}{1 - x + xe^R} I(m_1),
\]

(4)

where

\[
I(m) = \int_{-\infty}^{\infty} dy \ e^{y} \left[ 1 - e^{-m \hat{\varphi}(y)} \right]
\]

(5)

with \( \hat{\varphi}(y) = d^2 \varphi (1 + y/d) \). Inside the glass phases, \( \varphi > \varphi_K \), \( m \) and \( m_1 \) become smaller than unity. There are two possibilities, \( m < m_1 < 1 \) and \( m = m_1 < 1 \), which should be treated separately.

In the case of \( m < m_1 < 1 \), the glass phase is characterized by the 2RSB free energy as depicted in FIG. II (b). \( m \) and \( m_1 \) are determined by solving the saddle point equations, \( \partial_m g_1(m) = 0 \) and \( \partial_{m_1} g_2(m_1) = 0 \), or more explicitly,

\[
\frac{h(m)}{h(1)} = \frac{\varphi_K^{\text{mono}}}{\varphi(1 - x)}, \quad \frac{h(m_1)}{h(1)} = \varphi \left[ x + 2(1 - x)e^{-R/2} \right],
\]

(6)

where \( h(m) = -m^2 \partial_m (I(m)/m) \) and \( \varphi_K^{\text{mono}} = 2^{-d} d \log d / h(1) \) is the glass transition density of the one-component system. \( \varphi_K \) for large particles is obtained as the 1RSB solution by setting \( m = 1 \) in the first equation of Eq. (6) as

\[
\varphi_{K}^{\text{1RSB}}(x) = \frac{\varphi_K^{\text{mono}}}{1 - x}.
\]

(7)
Similarly, \( \varphi_K \) for small particles is obtained as the 2RSB solution by setting \( m_1 = 1 \) in the second equation of Eq. 1:

\[
\varphi_{2\text{RSB}}(x) = \frac{\varphi_{\text{mono}}}{x + 2(1 - x)e^{R/2}}.
\]  (8)

In the case of \( m = m_1 < 1 \), on the other hand, the glass phase is described by the 1RSB free energy (see Fig. 1 (a)). \( m (= m_1) \) is determined by \( \partial_m(g_1(m) + g_2(m)) = 0 \). The 1RSB and 2RSB free energies become identical when the fraction is \( x_c = \frac{1}{2}[1 - e^{-R/2}] \). This equation determines the phase boundary between the 1RSB and 2RSB glass phases. When \( x < x_c \), the 2RSB phase is more stable than 1RSB phase and vice versa for \( x > x_c \). For \( x_c \) to be positive, \( R \) must be larger than \( R_c = 2 \log 2 \), which is a necessary condition for the 2RSB phase, or, the decoupling of the two glass transitions, to exist. Note, all the arguments above are independent of the temperature and shape of the potential \( \phi \) if one use the rescaled density defined as \( \tilde{\phi} = \varphi / \varphi_{\text{mono}} \).

Combining all results discussed above, we draw the glass phase diagram. If \( R < R_c \), the phase diagram is determined by the 1RSB-RLT and only a single glass phase exists. If \( R > R_c \), four different phases emerge as shown in FIG. 2. At very low densities, the system is in the RS (fluid) phase where the solution with \( m = m_1 = 1 \) is the most stable. If \( \varphi \) is large and \( x \) close to 1, the solution with \( m = m_1 < 1 \) is the most stable and the system is in the 1RSB phase where all particles are frozen. We refer to this phase as the 1RSB(1) phase. In this phase, the majority is small particles and they drive the system into the glass phase and large particles are embedded in vitrified small particles. Indeed, \( \varphi_K(x) \) smoothly converges to \( \varphi_{\text{mono}} \) in the one-component limit, \( x \to 1 \). As \( x \) decreases and crosses \( x_c \), the system undergoes the transition from the 1RSB \((m = m_1 < 1)\) to 2RSB phase \((m < m_1 < 1)\). As \( x \) decreases further, \( m < m_1 = 1 \) becomes stable and small particles melt into a fluid phase whereas large particles remain frozen. We refer to this phase as the 1RSB(2) phase or the “single” glass. Although both the 1RSB(1) and 2RSB phases are “double” glass in that all particles are frozen, the difference of the two phases should be emphasized. In the 2RSB phase, small particles are vitrified inside a porous matrix formed by the pre-vitrified large particles. The matrix corresponds to one of the metabasins illustrated in FIG. 1(b). The dynamic phase diagram for \( \varphi_d \), on the other hand, is qualitatively very similar except that (i) \( \varphi_d \) scales as \( \varphi_d \sim d \) instead of \( d \log d \) and (ii) the 1RSB(2)-2RSB transition is absent (see Fig. 1 of SM 16).

If the density is increased for a fixed \( x \) below \( x_c \), the system undergoes the two step glass transitions: first from the fluid to the “single” glass and then to the 2RSB “double” glass phase. In order to clarify the nature of this multiple transitions, we calculate the configurational entropy, \( \Sigma_c \), from the 2RSB free energy given by Eq. 1. It can be written as a sum of the two contributions, \( \Sigma_c = \Sigma_1 + \Sigma_2 \).

\[
\Sigma_1 = -m^2 \frac{\partial}{\partial m} \left( \frac{\log Z_m}{mN} \right), \quad \Sigma_2 = -m_1^2 \frac{\partial^2}{\partial m_1 \partial m} \left( \frac{\log Z_m}{N} \right).
\]  (9)

We evaluate \( \Sigma_c \) using the asymptotic expression of the free energy, Eq. 1. FIG. 3 is the density dependence of \( \Sigma_c \) for \( R = 3 \) and \( x = 0.2 \). The result of the (metastable) 1RSB solution is also shown with the dashed line for a reference. One observes that \( \Sigma_1 \) bends twice; first at \( \tilde{\varphi}_{\text{2RSB}} \), where \( \Sigma_1 \) vanishes and the second at \( \tilde{\varphi}_{\text{2RSB}} \), where \( \Sigma_2 \) and, thus, the whole configurational entropy dies out.

In summary, we developed a new formalism of the RLT for binary mixtures of large and small spheres based on the 2RSB ansatz. We determined the glass phase diagram for a hard-sphere-like fluid in infinite dimension. The theory predicts that when the size ratio \( R \) is larger than a critical value, \( R_c \), the hierarchical energy landscape emerges and the decoupling of the glass transition of large and small particles takes place. As a consequence, three distinct glass phases, the 1RSB(1), 1RSB(2), and the 2RSB phases, arise. The 1RSB(2) is the “single” glass phase in which only large particles are frozen. The 1RSB(1) and 2RSB phases are “double” glass phases in which both large and small particles are frozen. It should be addressed that the 1RSB(1) and 2RSB are distinct phases with qualitative and topographical differences in their free energy landscapes. The energy landscape in the 2RSB phase has the two-step hierarchical structure where the two levels correspond to the configurations of large and small particles, respectively.
It is desirable to design experimental setup or simulation method which allows to delineate the difference of the two phases. We suspect a mechanical response or nonlinear rheology measurement to be one of ideal candidates [52–55]. For example, an anomalous two-step yielding in colloidal binary mixtures has been reported [56], which may be a reflection of complex an hierarchical energy landscape. Note that in a recent simulation study of hard-spheres near the jamming transition, two glass phases characterized by different status of the replica symmetry breaking are indeed separated well by rheological measurement [57]. The shape of the phase diagram predicted by our theory is qualitatively consistent with experiment and numerical results [8–10, 13, 14]; the “single” glass phase is located at high density and small x region while the “double” glass phase is at high density and large x region. For more quantitative comparison, it is necessary to extend our theory to finite dimensions. The relationship of our theory with the MCT, on the other hand, remains somewhat elusive. The MCT is the dynamic counterpart of the mean-field theory of the 1RSB glass transition. However our theory shows that the description of the single and double glass phases at smaller x requires the 2RSB ansatz. This means that the nature of the decoupling predicted by the MCT is essentially different from those of thermodynamic theory. It should be interesting to extend the MCT to include the 2RSB ansatz. We also believe that our higher order replica symmetric breaking picture is not restricted to binary mixtures of disparate size ratios, but can be adapted for other decoupling phenomena of the glass transitions, e.g., the decoupling of translational and rotational motions in anisotropic particles. These are left for the future work.

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Supplemental Materials

1. THE 1RSB-RLT

Here, we present the results with the conventional RLT based on the one-step replica symmetric breaking (1RSB) assumption [26, 28, 35]. Following the strategy of Ref. [28], we introduce the density distribution function in the replica space as

$$\rho_L(\mathbf{r}) = \sum_{i \in \text{Large}} \left\langle \prod_{a=1}^{m} \delta(r^a - r^a_i) \right\rangle, \quad \rho_S(\mathbf{r}) = \sum_{i \in \text{Small}} \left\langle \prod_{a=1}^{m} \delta(r^a - r^a_i) \right\rangle,$$

where $\mathbf{r} = \{r^1, \ldots, r^m\}$ represents the set of the particle positions in the replica space [28, 35]. Expanding the free energy of the replicated system by $\rho_L(\mathbf{r})$ and $\rho_S(\mathbf{r})$, we obtain

$$\log Z_m = S_{\text{id}} + S_{\text{int}},$$

$$S_{\text{id}} = \sum_{\mu \in \{L, S\}} \int d\mathbf{r} \rho_\mu(\mathbf{r})(1 - \log \rho_\mu(\mathbf{r})), $$

$$S_{\text{int}} = \sum_{\mu \nu \in \{L, S\}} \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \rho_\mu(\mathbf{r}) \rho_\nu(\mathbf{r}') f_{\mu\nu}(\mathbf{r} - \mathbf{r}') + O(\rho_L^3, \rho_S^3),$$

where the Mayer functions is defined by

$$f_{\mu\nu}(\mathbf{r} - \mathbf{r}') = \prod_{a=1}^{m} e^{-\beta v_{\mu\nu}(r^a - r'^a)} - 1.$$

We use the 1RSB Gaussian ansatz [28, 35]:

$$\rho_\mu(\mathbf{r}) = \rho_\mu \int d\mathbf{R} \prod_{a=1}^{m} \gamma_{A_\mu}(r^a - R),$$
can see that the free energy near the thermodynamic glass transition point, on the contrary, there arises the double glass phase only. The double glass phase in which all particles are frozen. Contrary, when transitions of large and small particles take place simultaneously (see the left panel of FIG. S1). One observes only further increases, small particles undergo the dynamical transition and enter to the double glass phase. For large $x$, the density for small particles undergo the dynamical transition at lower density than that of small particles (see the right panel of FIG. S1). If one increases the glass transition density scales as $\gamma$.

When the size ratio between large and small particles, $R$ defined by $\sigma_{LL}/\sigma_{SS} = 1 + R/d$, is small, the dynamical transitions of large and small particles take place simultaneously (see the left panel of FIG. S1). One observes only the double glass phase in which all particles are frozen. Contrary, when $R$ is sufficiently large, large particles undergo the dynamical transition at lower density than that of small particles (see the right panel of FIG. S1). If one increases the density for small $x$, there first arises the single glass phase in which only large particles are frozen. As the density further increases, small particles undergo the dynamical transition and enter to the double glass phase. For large $x$, on the contrary, there arises the double glass phase only.

Next we discuss the thermodynamic glass transition point, $\varphi_K$. In the large dimension limit, the thermodynamic glass transition density scales as $\varphi_K = O(2^{-d}d \log d)$ and the cage size scales as $A_\mu = O(1/d^2 \log d)$ [28]. Thus, one can see that $\gamma_{A_\mu}(x) \sim \delta(x)$ and $q_{\mu\nu}(r) \sim e^{-\beta_{\mu\nu}(r)}$. Substituting this into eq. (S8), we obtain the asymptotic form of the free energy near the thermodynamic glass transition point,

$$
\log Z_m = \frac{1}{m} \left[ \frac{d}{2} \log d - \frac{\varphi}{2} \frac{(1 - x + xe^{R/2})^2}{1 - x + xe^R} I(m) \right] - d \log d + O(d \log \log d),
$$

where $I(m)$ is defined by eq. (6) in the main text. The value of $m$ should be determined by the saddle point equation,

$$
\frac{\partial}{\partial m} \left( \frac{\log Z_m}{Nm} \right) = 0.
$$
FIG. S1. Dynamic phase diagram for $R = 0.5$ and $R = 3.0$: The circles and filled squares denote the dynamical transition points of large and small particles, respectively. The $y$-axis is scaled by the dynamical transition point of the monodisperse system, $\tilde{\phi}_{\text{mono}}$.

FIG. S2. 1RSB phase diagram for $R = 1$ and $R = 3$: The solid line denotes the normalized thermodynamic glass transition point, $\hat{\phi}_K$.

The thermodynamic glass transition point is calculated by the $m \to 1$ limit of above equation [28]. After some manipulations, we obtain

$$\hat{\phi}_K(x) = \frac{\varphi_K(x)}{\varphi_{\text{mono}}^K} = \frac{1 - x + xe^R}{(1 - x + xe^{R/2})^2},$$

(S12)

where $\varphi_{\text{mono}}^K$ denotes the glass transition point for the one-component system. Typical phase diagrams predicted by eq. (S12) are shown in FIG. S2. One can see that there are only the RS fluid phase in which all particles are mobile and the 1RSB glass phase in which all particles are frozen. In other words, the 1RSB RLT can not describe the decoupling of the thermodynamic glass transition points of large and small particles.
2. DERIVATION OF THE 2RSB FREE ENERGY

Here, we sketch the derivation of the 2RSB free energy (eq. (2) in the main text). The partition function of the 2RSB molecular system described in the main text is

$$Z_m = \left( \sum_{N_L=0}^{\infty} \frac{1}{N_L^m} \prod_{a=1}^{m} \prod_{i=1}^{a} \int dr_i^a \right)^{m/m_1} \prod_{k=1}^{m/m_1} \left( \sum_{N_{S_k}=1}^{\infty} \frac{1}{N_{S_k}!} \prod_{a \in B_k \in S_k} \prod_{i=1}^{a} \int dr_i^a \right) \times \exp \left[ -\beta \sum_{a=1}^{m} V_L^a \mu_{L_{a}} - \beta \Psi_L \right] \prod_{k=1}^{m/m_1} \exp \left[ -\beta \sum_{a \in B_k} (V_{S_k}^a + V_{L_{S_k}}^a) - \beta \Psi_{S_k} \right],$$

(S13)

where the subscripts $L$ and $S_k$ denote large particles and the small particles belonging into $k$-th sub-group, respectively. $B_k = \{(k-1) \times m_1 + 1, \cdots, k \times m_1\}$ is the set of the replicas belonging into $k$-th sub-group and $V_{L_{a}}^a$ is the interaction potential between particles of $\mu$ and $\nu$ species. The $\Psi_L$ and $\Psi_{S_k}$ are the intrinsic chemical potentials [58] for the molecules, which is defined by

$$\Psi_L = \sum_{i \in L} \psi_L(\vec{r}_i) = \sum_{i \in L} (\phi_L(\vec{r}_i) - \mu_L),$$

$$\Psi_{S_k} = \sum_{i \in S_k} \psi_{S_k}(\vec{r}_i) = \sum_{i \in S_k} (\phi_{S_k}(\vec{r}_i^k) - \mu_{S_k}),$$

(S14)

where $\vec{r}_i = \{r^1, \cdots, r^m\}$ and $\vec{r}_i^k = \{r^a | a \in B_k\}$ represent the sets of the configurations in the replica space, and $\mu_L$ and $\mu_{S_k}$ represent the chemical potentials. Here, we introduced the intra-molecular interaction potentials, $\phi_L(\vec{r}_i)$ and $\phi_{S_k}(\vec{r}_i^k)$. The intrinsic chemical potentials, eqs. (S14), allow us to calculate the one point density distribution functions for the molecules:

$$\rho_L(\vec{r}) = \sum_{i \in L} \left( \prod_{a=1}^{m} \delta(r^a - r_i^a) \right) = \frac{\delta \log Z_m}{\delta \psi_L(\vec{r})},$$

$$\rho_{S_k}(\vec{r}_i^k) = \sum_{i \in S_k} \left( \prod_{a \in B_k} \delta(r^a - r_i^a) \right) = \frac{\delta \log Z_m}{\delta \psi_{S_k}(\vec{r}_i^k)}.$$  

(S15)

One can see that the diagrams generated by this Mayer cluster expansion [58] are the same as those of the $1 + m/m_1$ component non-molecular system after the densities distributions, eqs. (S15), and the Mayer functions are replaced by those of the non-molecular system [58, 59]. Calculating second order for $\rho_L$ and $\rho_{S_k}$, we obtain eq. (2) in the main text.
The 2RSB-RLT predicts the same dynamical transition points as the 1RSB-RLT predicts because the dynamical transition takes place in the RS phase.

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