Configurational entropy of polydisperse systems can never reach zero

Vasili Baranau and Ulrich Tallarek

Department of Chemistry, Philipps-Universität Marburg, Hans-Meerwein-Strasse 4, 35032 Marburg, Germany

(Dated: 10 September 2018)

We present examples of systems whose configurational entropy $S_{\text{conf}}$ can never reach zero and is instead limited from below by the entropy of mixing $S_{\text{mix}}$ of the corresponding ideal gas. We use $S_{\text{conf}}$ defined through the local minima of the potential energy landscape, $S_{\text{PEL}}$. We show that this happens in mean-field models, in collections of hard spheres with infinitesimal polydispersity, and for one-dimensional hard rods. We demonstrate that these results match recent advances in understanding the configurational entropy defined in the free energy landscape, $S_{\text{FEL}}$. We demonstrate that if $\min(S_{\text{FEL}}) = 0$, then for an arbitrary system $\min(S_{\text{PEL}}) = NA + S_{\text{mix}}$, where $N$ is the number of particles and $A$ is some constant determined by the interaction potential. We discuss which implications these results have on the Adam–Gibbs (AG) and RFOT relations and show that the latter retain a physically meaningful shape for both configurational entropies, $S_{\text{PEL}}^{\text{conf}}$ and $S_{\text{FEL}}^{\text{conf}}$.

I. INTRODUCTION

Recently, Ozawa and Berthier studied a problem of diverging and discontinuous configurational entropy per particle $S_{\text{conf}}/N$ in systems with continuous polydispersity. Divergence happens due to the diverging and discontinuous (with respect to small compositional changes) mixing entropy per particle $S_{\text{mix}}/N$. Specifically, the total entropy $S_{\text{tot}}$ contains the mixing entropy $S_{\text{mix}}$, while the vibrational entropy $S_{\text{vib}}$ does not. Thus, the configurational entropy $S_{\text{conf}}$ from the relation $S_{\text{tot}} = S_{\text{conf}} + S_{\text{vib}}$ shall contain $S_{\text{mix}}$. It is problematic because some observables are believed to depend on $S_{\text{conf}}$ but from physical considerations shall be continuous with slight updates of the system composition, as well as finite and non-zero for continuous polydispersity. Ozawa and Berthier suggested a redefinition of $S_{\text{vib}}$ (a “scheme” of merging the basins of attraction) so that $S_{\text{mix}}$ is moved into $S_{\text{vib}}$ and $S_{\text{conf}}$ thus remains finite. The authors refined their approach and provided a more robust and unambiguous procedure in a follow-up paper. Their approach essentially defines $S_{\text{conf}}$ through the free energy landscape (FEL) $^{14,15}$.

In an attempt to resolve this paradox in the potential energy landscape (PEL), we studied $S_{\text{PEL}}$ using a variant of thermodynamic integration $^{3,6,17,20}$ and suggested that it is in fact normal for $S_{\text{PEL}}$ to contain $S_{\text{mix}}$. We suggested that all the observables that depend on $S_{\text{PEL}}^{\text{conf}}$ and are believed to be well-behaving shall instead depend on $S_{\text{PEL}}^{\text{conf}} - S_{\text{mix}}$ or in general $S_{\text{PEL}}^{\text{conf}} - \min(S_{\text{PEL}}^{\text{conf}})$. For this, we implicitly assumed that $\min(S_{\text{PEL}}^{\text{conf}})$ can be non-zero, in particular $S_{\text{mix}}$, i.e., that $S_{\text{PEL}}^{\text{conf}}$ is bounded from below solely by the system composition.

In this paper, we investigate the lower bound on $S_{\text{PEL}}^{\text{conf}}$ in more detail and explicitly demonstrate that for some systems $S_{\text{PEL}}^{\text{conf}}$ is indeed bounded from below by $S_{\text{mix}}$. Additionally, we investigate connections between $S_{\text{PEL}}^{\text{conf}}$ and $S_{\text{conf}}$ defined through the free energy landscape, $S_{\text{FEL}}^{\text{conf}}$. We show that for our model systems $\min(S_{\text{FEL}}^{\text{conf}}) = 0$ and that the condition $\min(S_{\text{PEL}}^{\text{conf}}) = 0$ implies for an arbitrary system $\min(S_{\text{PEL}}^{\text{conf}}) = NA + S_{\text{mix}}$, where $A$ is some constant. We discuss which implications it has on the Adam–Gibbs (AG) and RFOT relations and show that they retain a physically meaningful shape for both configurational entropies, $S_{\text{PEL}}^{\text{conf}}$ and $S_{\text{FEL}}^{\text{conf}}$. We show that the two versions of the AG relation will differ by a well-behaving discrepancy term.

II. PRELIMINARIES

A. Differententropies

We study a canonical $NVT$ ensemble of classical systems and use a standard notation with $N$, $V$, $T$, $U$, $a$, and $A$ standing for the number of particles, volume, temperature, internal energy, dimensionality, and de Broglie wavelength, respectively. $S$, $F$, $Z$, and $U_N(\vec{r})$ stand for the entropy, Helmholtz free energy, partition function, and total potential energy in the configuration $\vec{r}$. We study polydisperse systems and denote with $N_m$ the number of particles of type $m$.

One can routinely derive from standard equations $S = (U - F)/T$, $F = -kBTr\ln Z$, and $Z = \frac{1}{N!} \sum_i e^{-U_N(\vec{r}_i)/kBT}$. For the total entropy of the system $^{12,21,22}$ It can be shown $^{16}$ that such an entropy will contain the mixing entropy $S_{\text{mix}} = -kB N \sum_i N_i \ln N_i / N$. It can also be shown that $S_{\text{mix}}/N$ diverges for continuous particle type distributions (in the simplest case, $N_i = 1$, $S_{\text{mix}} = kB N \ln N$) $^{16}$. $S_{\text{mix}}/N$ is also obviously discontinuous if the system composition is abruptly changed.

If we define the configurational entropy through the PEL, $S_{\text{PEL}}^{\text{conf}}$ counts (up to particle permutations) the density of potential energy minima $^{6,20,23,27}$ $N_{\min}(N, u_{\min})$ at a given energy per particle $u_{\min} = U_{\min}/N$. Specifically, $N_{\min}(N, u_{\min}) = e^{S_{\text{PEL}}^{\text{conf}}(N, u_{\min})}/w$, where $w$ is the...
characteristic interval that comes from the saddle point approximation. It is believed to be subexponential, i.e., \( \ln(w)/N \to 0 \) with \( N \to \infty \).

The vibrational partition function in the PEL is expressed as:

\[
Z_{\text{vib}}^{\text{PEL}} = \frac{\Pi_{i=1}^{M} N_{i}!}{(\Pi_{i=1}^{M} N_{i}) N^{M}} \int_{\text{basin}} e^{-U_{\text{vib}}(\vec{x})/k_{B}T} d\vec{x},
\]

where integration is performed over a certain basin of attraction in the PEL. The \( \Pi_{i=1}^{M} N_{i}! \) term in the denominator comes from particle indistinguishability as for the total partition function. Both versions of relaxation time do not change, i.e., indistinguishability of basins due to particle indistinguishability. Due to cancellation of these two terms, \( S_{\text{vib}}^{\text{PEL}} \) does not contain \( S_{\text{mix}} \). We showed on the basis of thermodynamic integration that \( S_{\text{mix}} \) is also hidden in the integral over a basin and that \( S_{\text{vib}}^{\text{PEL}} \) still contains the term \( \ln \left( \frac{\Pi_{i} N_{i}!}{\Pi_{i} N_{i}} N^{M} \right) \), which also enters \( S_{\text{tot}} \).

The three entropies are connected by the relation:

\[
S_{\text{tot}}(N, V, T) = S_{\text{conf}}^{\text{PEL}}(N, V, u_{\text{eq,min}}(T)) + S_{\text{vib}}^{\text{PEL}}(N, V, u_{\text{eq,min}}(T), T).
\]

Because \( S_{\text{tot}} \) contains \( S_{\text{mix}} \) and \( S_{\text{vib}}^{\text{PEL}} \) does not, \( S_{\text{mix}} \) shall be contained in \( S_{\text{conf}}^{\text{PEL}} \). If the configurational and vibrational entropies are defined through the FEL, the equation also holds.

The configurational entropy per particle \( S_{\text{conf}}^{\text{PEL}}/N \) (however it is defined) enters several relations for the relaxation time \( \tau \) of colloids and glassy systems at high volume fraction or low temperature. Both versions of \( S_{\text{conf}}^{\text{PEL}} \) are used by different authors: either \( S_{\text{conf}} \) or \( S_{\text{conf}}^{\text{PEL}} \). The well-known Adam–Gibbs relation reads as

\[
\tau = \tau_{0} \exp \left( \frac{C}{\nu_{\text{conf}} N} \right),
\]

where \( \tau_{0} \) and \( C \) are presumed to be approximately constant. The other relation stems from the Random First Order Theory (RFOT). If \( S_{\text{conf}}/N \) is divergent for continuous particle type distributions and discontinuous with a small system composition change, \( \nu \equiv 0 \) for systems with continuous particle type distributions and \( \nu \) will be discontinuous when the system composition is slightly changed. It is paradoxical because \( \tau \) shall be finite and continuous.

Even worse, particle type distribution can be induced “artificially”, by assigning arbitrary properties to particles without changing their interaction potential. For example, colloidal particles can be colored (dyed) arbitrarily. This will increase \( S_{\text{conf}}^{\text{PEL}} \) arbitrarily without changing \( \tau \).

a. Hard spheres A valid collection of \( N \) frictionless hard spheres with predefined radii \( R_{i} \) always has a zero potential energy, while an invalid collection has an infinite energy. Still, a pseudo-PEL can be introduced for hard spheres. At any system configuration \( \vec{x} \in \mathbb{R}^{3N} \) particle radii can be scaled proportionally to ensure that at least one pair of particles is in contact. The resulting solid volume fraction \( \varphi \) defines the pseudo-PEL \( U(\vec{x}) = -\varphi \) (or rather, \( U(\vec{x}) = -N \varphi \) for \( U(\vec{x}) \) to be extensive). Local minima in this PEL correspond to mechanically stable (jammed) configurations with some jamming densities \( \varphi_{J} \), while steepest descents correspond to proportionally scaling sphere radii and moving the spheres as little as possible in the configuration space to ensure the absence of intersections. Eq. (1) will then look like

\[
S_{\text{tot}}(N, \varphi, T) = S_{\text{conf}}(N, \varphi_{\text{eq},J}(\varphi)) + S_{\text{vib}}(N, \varphi_{\text{eq},J}(\varphi), T).
\]

B. Motivation

We argued that it is normal for \( S_{\text{conf}}^{\text{PEL}} \) to be divergent and discontinuous. Still, the relaxation time shall be finite for continuous particle type distributions and shall be continuous when slightly changing particle types or coloring the particles. We suggested that the equations for \( \tau \) and for any other “well-behaving” observables shall be changed instead. If such an observable depends on \( S_{\text{conf}}^{\text{PEL}} \), it shall always depend on \( S_{\text{conf}}^{\text{PEL}} - S_{\text{mix}} \) and can not depend on \( S_{\text{conf}}^{\text{PEL}} \) only. Thus, arbitrary changes in \( S_{\text{conf}}^{\text{PEL}} \) will be compensated.

Indeed, if \( S_{\text{mix}} \) is the lower bound for \( S_{\text{conf}}^{\text{PEL}} \), then only changes with respect to \( S_{\text{mix}} \) can matter for physical observables. A more detailed derivation for the updated Adam–Gibbs equation can be found in our previous paper. For this derivation, we implicitly assumed that \( S_{\text{conf}}^{\text{PEL}} \) can not decrease below \( S_{\text{mix}} \). In this paper, we provide a more detailed explanation and physical insight into this lower bound.

We do not discuss in this paper whether \( S_{\text{conf}}^{\text{PEL}} \) is a better candidate for such equations than \( S_{\text{conf}}^{\text{conf}} \). But we point out that there indeed is a body of work showing that \( S_{\text{conf}}^{\text{PEL}} \) can be a possible candidate for \( S_{\text{conf}} \) in the Adam–Gibbs and RFOT relations.

III. MAIN PART

In the worst case, the lowest equilibrium complexity \( S_{\text{conf}}^{\text{PEL}}(N, V, u_{\text{eq,min}}(T)) \) at some low temperature \( T_{0} \) will correspond to only one configuration of particles (up to particle permutations). This configuration will be the local minimum of a basin of attraction that is equilibrium at this \( T_{0} \) and dominates the phase space. If particles are considered distinguishable and there are \( N_{m} \) particles of each type \( m \), there are \( \Pi_{m} N_{m} \) such local minima. Still, there are \( N! \) particle permutations in total. Each of \( N! \) configurations (if particles are considered distinguish-

able) lies in a certain basin of attraction in the potential energy landscape and each of these basins has a corresponding energy minimum (inherent structure). The question is whether these basins will also be equilibrium at $T_0$ or not.

A. Mean-field limit

To determine if a certain configuration among these $N!$ is in equilibrium at $T_0$, we compare its chemical potential $\mu$ with the chemical potential from the original equilibrium configuration. To compute the chemical potential, we rely on the Widom particle insertion method.\textsuperscript{18,22,39–42} This method relates the chemical potential $\mu$ to the potential $\Psi_{N+1,i}(\vec{r})$ that is experienced by a $(N + 1)$th test particle of type $i$ if we try to insert this particle into the system at a position $\vec{r}$, sampled uniformly. Specifically,

$$-rac{\Delta\mu_i}{kT} = \ln \left[ \left\langle \exp \left( -\frac{\Psi_{N+1,i}}{kT} \right) \right\rangle \right], \quad (2)$$

where $\Delta\mu_i$ is the excess chemical potential for particles of type $i$ and averaging is performed with respect to $\vec{r}$ of particle insertion positions.\textsuperscript{18} If the original configuration is in equilibrium, then we estimate the chemical potential (the equilibrium one).

Thus, our main focus is how the field $\Psi_{N+1,i}$ changes when we perform any of the $N!$ particle permutations in the initial equilibrium configuration. We do not have an answer to this question in the general case, but this question can be resolved in the mean-field limit.

We will denote the potential $\Psi_{N+1,i}(\vec{r})$ perturbed by a permutation $\Sigma_p$ as $\Psi_{\Sigma_p,N+1,i}$. In the mean-field limit, the potential $\Psi_{\Sigma_p,N+1,i}$ does not depend on $\Sigma_p$,

$$\Psi_{\Sigma_p,N+1,i} \equiv \Psi_{N+1,i}. \quad (3)$$

Thus, all of the $N!$ configurations are equilibrium. The number of such configurations up to particle permutations is $\frac{N!}{\Pi_i N_i!}$ and the lowest possible equilibrium complexity is thus

$$\min(S_{\text{conf}}^{\text{PEL}}) = k_B \ln \left( \frac{N!}{\Pi_i N_i!} \right). \quad (4)$$

It can be easily shown with the help of the Stirling approximation $N! \sim N! \ln N - N$ that $\min(S_{\text{conf}}^{\text{PEL}})$ is

$$\min(S_{\text{conf}}^{\text{PEL}}) = -k_B N \sum_i \frac{N_i}{N} \ln \frac{N_i}{N} = S_{\text{mix}}. \quad (5)$$

B. Infinitesimally polydisperse systems

Let us assume that a system is monodisperse and the worst case is realized for it, i.e., there is only one equilibrium basin (up to particle permutations) at the lowest temperature $T_0$ where the system can still be equilibrated. Thus, there are $N!$ equilibrium basins and respective minima if particles are considered distinguishable. Let us now assume that particle types are slightly changed, e.g., particle charges that govern pair potentials or radii of colloidal particles are infinitesimally changed.

For sufficiently small particle type changes, the structure of the phase space and its basins will remain unchanged. Thus, all of the $N!$ basins will still be equilibrium at this $T_0$—but there are now $\Pi_i N_i!$ particle permutations that keep the system in the same state, instead of $N!$. Hence, the minimum configurational entropy becomes

$$\min(S_{\text{conf}}^{\text{PEL}}) = k_B \ln \left( \frac{N!}{\Pi_i N_i!} \right) = S_{\text{mix}}.$$}

C. 1D hard rods

Our last example is very brief and almost obvious. A collection of 1D hard rods has $N!$ jammed configurations (pseudo-PEL minima) if particles are considered distinguishable. Because there are $\Pi_i N_i!$ particle permutations if particles are considered indistinguishable, $S_{\text{conf}}^{\text{PEL}} = k_B \ln \left( \frac{N!}{\Pi_i N_i!} \right) = S_{\text{mix}}.$ Particle types can stem either from actual rod lengths or from artificial labeling assigned by the observer arbitrarily. This is actually the only value of $S_{\text{conf}}^{\text{PEL}}$ available for 1D hard rods.

D. Remark: colloids and hard spheres

The procedure outlined for the mean-field case looks as follows for hard spheres. Assume that the largest density at which the system can be equilibrated is denoted as $\varphi_K$. The corresponding jamming density can be denoted as $\varphi_{\text{GCP}}$, the Glass Close Packing density.\textsuperscript{29} Then, one has to take an equilibrium configuration at $\varphi = \varphi_K$ (maybe even the one with $\varphi = \varphi_{\text{GCP}}$ but with particle radii proportionally decreased to achieve $\varphi_K$) and performs particle permutations. Some pairs of particles may intersect after permutations. To avoid permutations, one decreases particle radii proportionally until the closest pair of particles just touches each other; the density is decreased in this process ($\varphi < \varphi_K$). Then, one increases particle radii proportionally and simultaneously moves particles to ensure minimal possible movement in the configuration space (moves particles along contact normals). This movement corresponds to the steepest descent in the pseudo-PEL. One performs this particle scaling until $\varphi = \varphi_K$. Then, one has to check if the resulting configuration is equilibrium. Numerically, this can be done by employing the Widom particle insertion method. If the system becomes jammed before reaching $\varphi_K$, then the new basin (after permutation) was definitely not in equilibrium.
IV. RELATIONSHIP WITH $S_{\text{conf}}$ DEFINED THROUGH THE FREE ENERGY LANDSCAPE

We would like to discuss how $S_{\text{conf}}^{\text{FEL}}$ relates to the configurational entropy defined in the free energy landscape, $S_{\text{conf}}^{\text{FEL}}$. The free energy landscape to compute $S_{\text{conf}}^{\text{FEL}}$ can stem, e.g., from the density functional theory. We will show that for our model systems the result $\min(S_{\text{conf}}^{\text{FEL}}) = S_{\text{conf}}$ complies with the requirement $\min(S_{\text{conf}}^{\text{FEL}}) = 0$ for a certain definition of $S_{\text{conf}}^{\text{FEL}}$.

A. $S_{\text{conf}}^{\text{FEL}}$ of Ozawa et al.

A recent advancement in understanding $S_{\text{conf}}^{\text{FEL}}$ can be found in a paper by Ozawa, Parisi, and Berthier. The free energy landscape to compute $S_{\text{conf}}^{\text{FEL}}$ can stem, e.g., from the density functional theory. We will show that for our model systems the result $\min(S_{\text{conf}}^{\text{FEL}}) = S_{\text{conf}}$ complies with the requirement $\min(S_{\text{conf}}^{\text{FEL}}) = 0$ for a certain definition of $S_{\text{conf}}^{\text{FEL}}$.

$$\min(S_{\text{conf}}^{\text{FEL}}) = S_{\text{conf}}$$

where $\Delta_{\alpha}^{T,S}$ is a mean-squared displacement defined by

$$\Delta_{\alpha}^{T,S} = \frac{1}{N} \left( \sum_{i=1}^{N} |r_i - r_{0i}|^2 \right)^{T,S},$$

and $S_{\text{mix}}(r_0^N, \beta)$ is a mixing entropy contribution defined by

$$S_{\text{mix}}(r_0^N, \beta) = -\ln \left( \frac{1}{N!} \sum_{\pi} e^{-\beta(U_0(N_0^x r_0^N) - U_0(r_0^N))} \right),$$

$S_{\text{conf}}^{\text{FEL}}$ is then given as usual by $S_{\text{tot}} - S_{\text{FEL}}$.

Compare Eq. (9) to a "usual" expression for $S_{\text{FEL}}$, when particle permutations are not included in the definition:

$$S_{\text{FEL}}^{\text{conf}} = \frac{Nd}{2} - N \ln \Lambda^{d} - \frac{Nd}{2} \ln \left( \frac{\alpha_{\text{max}}}{\pi} \right) + N \lim_{\alpha_{\text{min}} \to 0} \int_{\alpha_{\text{min}}}^{

The superscripts T and S represent the statistical average over positions (T) and permutations (S), respectively. Here, $U_0(\Sigma_\pi r_0^N, r_{0i}^N)$ is the potential energy at a configuration $r_0^N$ around a reference configuration $r_{0i}^N$ when particles are additionally permuted by a permutation $\pi$ (note that $\Sigma_\pi$, not $\Sigma_\pi^T$, represents a usual sum over permutations).

The glassy entropy (in our terms $S_{\text{FEL}}^{\text{conf}}$) is expressed according to their approach as

$$S_{\text{FEL}}^{\text{conf}} = S_{\text{glass}} + \frac{Nd}{2} - N \ln \Lambda^{d} - \frac{Nd}{2} \ln \left( \frac{\alpha_{\text{max}}}{\pi} \right) + N \lim_{\alpha_{\text{min}} \to 0} \int_{\alpha_{\text{min}}}^{

B. Model systems from our paper

For our examples (a mean-field system and an infinitely polydisperse system), particle permutations do not change the potential energy. Hence, $U_{\alpha}(\Sigma_\pi r_0^N, r_{0i}^N) = U_{\alpha}(r_0^N, r_{0i}^N)$. It then follows that $S_{\text{mix}}(r_0^N, \beta) = 0$ (cf. Eq. (11)) and $\Delta_{\alpha}^{T,S} = \Delta_{\alpha}^{T}$ (cf. Eqs. (9) and (11)). Hence, for these systems $S_{\text{FEL}}^{\text{conf}} = S_{\text{FEL}}^{\text{conf}} + S_{\text{mix}}$ (cf. Eqs. (4) and (12)) and finally $S_{\text{conf}}^{\text{FEL}} = S_{\text{conf}}^{\text{FEL}} - S_{\text{mix}}$. Thus, our bound $\min(S_{\text{conf}}^{\text{FEL}}) = S_{\text{mix}}$ is actually equivalent to the usual assumption $\min(S_{\text{conf}}^{\text{FEL}}) = 0$: $\min(S_{\text{conf}}^{\text{FEL}}) = 0 \iff \min(S_{\text{conf}}^{\text{FEL}}) = S_{\text{mix}}$. (14)

C. $\min(S_{\text{conf}}^{\text{FEL}})$ in the general case

By comparing Eqs. (9) and (12) and utilizing $S_{\text{tot}} = S_{\text{conf}} + S_{\text{FEL}}$, we get in the general case $S_{\text{conf}}^{\text{FEL}} = S_{\text{conf}}^{\text{FEL}} + $
\( S_{\text{conf}}^{\text{PEL}} - S_{\text{conf}}^{\text{FEL}} \) and finally

\[
S_{\text{conf}}^{\text{PEL}} = S_{\text{conf}}^{\text{FEL}} + N \lim_{\alpha_{\text{min}} \to 0} \int_{\alpha_{\text{min}}}^{\alpha_{\text{max}}} \text{d} \alpha \left( \Delta_{\alpha}^{T,S} - \Delta_{\alpha}^{T} \right) + S_{\text{mix}} - S_{\text{mix}}(r_0^N, \beta) .
\] (15)

One can presume that \( \lim_{\alpha_{\text{min}} \to 0} \int_{\alpha_{\text{min}}}^{\alpha_{\text{max}}} \text{d} \alpha \left( \Delta_{\alpha}^{T,S} - \Delta_{\alpha}^{T} \right) \) and \( S_{\text{mix}}(r_0^N, \beta) \) are decreasing functions of temperature. Indeed, the lower the temperature, the less statistical weight permuted configurations have and hence the closer \( S_{\text{conf}}^{\text{PEL}} \) reaches the minimum value when the phase space becomes non-ergodic (at \( T = T_K \)). It means that \( S_{\text{conf}}^{\text{PEL}} \) is defined in the same range of temperatures and is not defined for \( T < T_K \). Because Eq. (15) can be represented as a sum of terms that are either constant or decreasing with \( T \) and because \( S_{\text{conf}}^{\text{PEL}} \) is defined in the same range of temperatures as \( S_{\text{conf}}^{\text{FEL}} \), we conclude that \( \min(S_{\text{conf}}^{\text{PEL}}) \) happens at the same temperature as \( \min(S_{\text{conf}}^{\text{FEL}}) \). Hence, we write

\[
\min(S_{\text{conf}}^{\text{PEL}}) = \min(S_{\text{conf}}^{\text{FEL}}) + N \min( \lim_{\alpha_{\text{min}} \to 0} \int_{\alpha_{\text{min}}}^{\alpha_{\text{max}}} \text{d} \alpha \left( \Delta_{\alpha}^{T,S} - \Delta_{\alpha}^{T} \right) ) + S_{\text{mix}} - S_{\text{mix}}(r_0^N, \beta) \]
\[
= NA + S_{\text{mix}},
\] (16)

where \( A \) is some constant determined purely by particle interactions.

A crucial feature in Eq. (16) is that \( S_{\text{mix}} \) can be increased arbitrarily by infinitesimal changes in particle types or by artificial “coloring” of particles (assigning types that do not influence interaction potentials). If the distribution of “colors” is continuous, then \( S_{\text{mix}}/N \to \infty \). Thus, if we presume that \( \min(S_{\text{conf}}^{\text{PEL}}) = 0 \), then \( \min(S_{\text{conf}}^{\text{PEL}}) \) can be increased arbitrarily for a general system just by additional labeling of particles:

\[
\min(S_{\text{conf}}^{\text{PEL}}) = 0 \implies \min(S_{\text{conf}}^{\text{PEL}}) \text{ is arbitrary.} \] (17)

Additionally, \( \min(S_{\text{conf}}^{\text{PEL}})/N \) in this case is discontinuous with introducing a slight polydispersity to a monodisperse system and divergent for a continuous polydispersity.

D. Adam–Gibbs and RFOT relations

As we argued in our previous paper, an arbitrary value of \( \min(S_{\text{conf}}^{\text{PEL}}) \) and other problems with it are actually not problematic for observables that may depend on \( S_{\text{conf}}^{\text{PEL}} \), like the relaxation time \( \tau_R \) of glassy systems. If one re-derives the Adam–Gibbs and RFOT relations between \( \tau_R \) and \( S_{\text{conf}} \) assuming that \( \min(S_{\text{conf}}) \neq 0 \), one obtains

\[
\tau_R = f \left( \frac{S_{\text{conf}} - \min(S_{\text{conf}})}{N} \right) \] (18)

instead of the usual version \( \tau_R = f(S_{\text{conf}}/N) \). For example, the Adam–Gibbs relation shall be transformed from a standard version \( \tau_R^{\text{AG}} = \tau_0 \exp \left( \frac{C}{T[S_{\text{conf}} - \min(S_{\text{conf}})]/N} \right) \) into

\[
\tau_R^{\text{AG}} = \tau_0 \exp \left( \frac{C}{T[S_{\text{conf}} - \min(S_{\text{conf}})]/N} \right), \] (19)

where \( \tau_0 \) and \( C \) are (approximately) constants.

It is interesting to compare what will be the difference between \( \tau_R^{\text{PEL}} \) and \( \tau_R^{\text{FEL}} \), given that \( \tau_R^{\text{FEL}} = f(S_{\text{conf}}^{\text{FEL}}/N) \) and \( \tau_R^{\text{AG}} = \tau_0 \exp \left( \frac{C}{T[S_{\text{conf}} - \min(S_{\text{conf}})]/N} \right) \). By using Eqs. (15) and (16) and again presuming \( \min(S_{\text{conf}}) = 0 \), we get for the Adam–Gibbs equation

\[
\tau_R^{\text{PEL}} = \tau_0 \exp \left( \frac{C}{T[S_{\text{conf}}^{\text{PEL}}/N]} \right), \]
\[
\tau_R^{\text{PEL}} = \tau_0 \exp \left( \frac{C}{T[S_{\text{conf}}^{\text{PEL}}/N + \delta]} \right), \] (20)

where \( \delta \) is expressed as

\[
\delta = \lim_{\alpha_{\text{min}} \to 0} \int_{\alpha_{\text{min}}}^{\alpha_{\text{max}}} \text{d} \alpha \left( \Delta_{\alpha}^{T,S} - \Delta_{\alpha}^{T} \right) - \min( \lim_{\alpha_{\text{min}} \to 0} \int_{\alpha_{\text{min}}}^{\alpha_{\text{max}}} \text{d} \alpha \left( \Delta_{\alpha}^{T,S} - \Delta_{\alpha}^{T} \right) ) + S_{\text{mix}}(r_0^N, \beta) \]
\[
= \frac{S_{\text{mix}}(r_0^N, \beta) - \min(S_{\text{mix}}(r_0^N, \beta))}{N}. \] (21)

As can be seen from Eq. (21), \( \delta \) possesses nice properties: (i) it is a quantity per particle and (ii) the mixing entropy per particle \( S_{\text{mix}}/N \) is not present in \( \delta \) (it was canceled out). Thus, \( \delta \) will remain continuous with introduction of a small polydisperisty, finite for a continuous polydispersity, and independent of artificial particle labeling (defined only by interaction potentials). Thus, both forms of \( \tau_R^{\text{AG}} \) from Eq. (21) seem feasible. Which form better fits actual data can be tested through simulations. We plan to present in a follow-up paper results that demonstrate that \( \tau_R^{\text{PEL}} \) can fit relaxation times for polydisperse hard spheres well.

V. CONCLUSION

We presented several examples of systems where the lower bound of the configurational entropy \( S_{\text{conf}}^{\text{PEL}} \) is the mixing entropy \( S_{\text{mix}} \). Our examples are mean-field systems, infinitesimally polydisperse systems, and 1D hard rods. We believe these examples provide a deep physical insight into why \( S_{\text{conf}}^{\text{PEL}} \) shall in principle have a non-zero lower bound (which still does not preclude the existence of the ideal glass transition). Additionally, we demonstrated that this result is equivalent for our model systems to the condition \( \min(S_{\text{conf}}^{\text{PEL}}) = 0 \). Finally, we showed that the condition \( \min(S_{\text{conf}}^{\text{PEL}}) = 0 \) implies for an arbitrary system that \( \min(S_{\text{conf}}) = NA + S_{\text{mix}} \), where...
A is a constant determined by particle interaction potentials, while $S_{\text{mix}}$ can be increased arbitrarily by introducing “artificial” particle types (e.g., coloring colloidal particles). Thus, $\min(S_{\text{conf}}^{\text{PEL}})$ can be changed arbitrarily. If the distribution of “colors” is continuous, $\min(S_{\text{conf}}^{\text{PEL}})/N \to \infty$. Also, $\min(S_{\text{conf}}^{\text{PEL}})/N$ will be diverging by introducing slight polydispersity to particle types.

Nevertheless, we argued that the AG and RFOT relations will still retain a physically meaningful shape. We compared the AG relations derived through both versions of $S_{\text{conf}}$, $S_{\text{PEL}}^{\text{conf}}$ and $S_{\text{conf}}^{\text{PEL}}$ and demonstrated that they will be different, but the discrepancy term will be well-behaving. We suggested that one can check which version better describes relaxation times through simulations. We plan to present in a follow-up paper results that demonstrate that $\tau_{\text{PEL}}^{R}$ can fit relaxation times for polydisperse hard spheres well.

ACKNOWLEDGMENTS

We thank Misaki Ozawa and Ludovic Berthier for helpful correspondence about the present manuscript (though they do not necessarily agree with all the ideas presented here).

1. M. Ozawa and L. Berthier, J. Chem. Phys. 146, 014502 (2017)
2. R. J. Speedy, Mol. Phys. 95, 169 (1998)
3. F. H. Stillinger, P. G. Debenedetti, and T. M. Truskett, J. Phys. Chem. B 105, 11809 (2001)
4. S. Sastry, Nature 409, 164 (2001)
5. L. Angelani and G. Foffi, J. Phys.: Condens. Matter 19, 256207 (2007)
6. A. Donev, F. H. Stillinger, and S. Torquato, J. Chem. Phys. 127, 124509 (2007)
7. G. Foffi and L. Angelani, J. Phys.: Condens. Matter 20, 075108 (2008)
8. F. W. Starr, J. F. Douglas, and S. Sastry, J. Chem. Phys. 138, 12A541 (2013)
9. G. Adam and J. H. Gibbs, J. Chem. Phys. 43, 139 (1965)
10. A. Cavagna, Phys. Rep. 476, 61 (2009)
11. T. Kirkpatrick and D. Thirumalai, Rev. Mod. Phys. 87, 183 (2015)
12. P. Boulaud and G. Biroti, J. Chem. Phys. 121, 7347 (2004)
13. M. Ozawa, G. Parisi, and L. Berthier, arXiv:1805.06017 [cond-mat] (2018), arXiv: 1805.06017.
14. H. Reda, K. Miyazaki, and A. Ikeda, J. Chem. Phys. 145, 216101 (2016)
15. V. Baranau and U. Tallarek, J. Chem. Phys. 147, 224503 (2017)
16. D. Frenkel and A. J. C. Ladd, J. Phys. Chem. B, 81, 3188 (1984)
17. D. Frenkel and B. Smit, Understanding Molecular Simulation: From Algorithms to Applications, 2nd ed. (Academic Press, San Diego, 2002).
18. A. Donev, F. H. Stillinger, and S. Torquato, J. Comput. Phys. 225, 509 (2007)
19. D. Asenjo, F. Paillusson, and D. Frenkel, Phys. Rev. Lett. 112, 098002 (2014)
20. N. F. Carnahan and K. E. Starling, J. Chem. Phys. 53, 600 (1970)
21. D. J. Adams, Mol. Phys. 28, 1241 (1974)
22. S. S. Ashwin, J. Blawzdziewicz, C. S. O’Hern, and M. D. Shatuck, Phys. Rev. E 85, 061307 (2012)
23. S. Martiniani, K. J. Schrenk, J. D. Stevenson, D. J. Wales, and D. Frenkel, Phys. Rev. E 93, 022906 (2016)
24. F. H. Stillinger, E. A. DiMarzio, and R. L. Kornegay, J. Chem. Phys. 40, 1564 (1964)
25. F. H. Stillinger, Science 267, 1935 (1995)
26. S. Torquato and Y. Jiao, Phys. Rev. E 82, 061302 (2010)
27. G. Parisi and F. Zamponi, J. Chem. Phys. 123, 144501 (2005)
28. G. Parisi and F. Zamponi, Rev. Mod. Phys. 82, 789 (2010)
29. L. Berthier, H. Jacquin, and F. Zamponi, Phys. Rev. E 84, 051103 (2011)
30. F. H. Stillinger, Nature 410, 259 (2001)
31. D. Frenkel, Mol. Phys. 112, 2325 (2014)
32. G. Meng, N. Arkus, M. P. Brenner, and V. N. Manoharan, Science 327, 560 (2010)
33. D. Frenkel and Z. W. Salsburg, J. Stat. Phys. 1, 179 (1969)
34. R. J. Speedy, Mol. Phys. 80, 1105 (1993)
35. R. J. Speedy, J. Phys.: Condens. Matter 10, 4387 (1998)
36. V. Baranau and U. Tallarek, Soft Matter 10, 3826 (2014)
37. A. Zinchenko, J. Comput. Phys. 113, 298 (1994)
38. B. Widom, J. Chem. Phys. 39, 2908 (1963)
39. R. J. Speedy, J. Chem. Soc., Faraday Trans. 2 77, 329 (1981)
40. R. J. Speedy and H. Reiss, Mol. Phys. 72, 999 (1991)
41. V. Baranau and U. Tallarek, J. Chem. Phys. 144, 214503 (2016)