Effective structure of a system with continuous polydispersity

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In a system of N particles, with continuous size polydispersity there exists N(N-1) number of partial structure factors making it analytically less tractable. A common practice is to treat the system as an effective one component system which is known to exhibit an artificial softening of the structure. The aim of this study is to describe the system in terms of M pseudo species such that we can avoid this artificial softening but at the same time have a value of M ≪ N. We use potential energy and pair excess entropy to estimate an optimum number of species, M0. We find that systems with polydispersity width, ∆σ, can be treated as a monodisperse system. We show that M0 depends on the degree and type of polydispersity and also on the nature of the interaction potential, whereas, ∆σ0 weakly depends on the type of polydispersity, but shows a stronger dependence on the type of interaction potential. Systems with softer interaction potential have a higher tolerance with respect to polydispersity. Interestingly, M0 is independent of system size, making this study more relevant for bigger systems. Our study reveals that even 1% polydispersity cannot be treated as an effective monodisperse system. Thus while studying the role of polydispersity by using the structure of an effective one component system care must be taken in decoupling the role of polydispersity from that of the artificial softening of the structure.

I. INTRODUCTION

Most natural systems are inherently polydisperse. Polydispersity can be of different kinds like in size, in mass, and also in the shape of the particles. Also, the type of polydispersity and the degree of it varies with systems. Polydispersity brings variation in the properties of the material and there are specially designed controlled experiments to create monodisperse particles. However, in some cases polydispersity is a desirable property. The size polydispersity is one of the most common types and it has been found that systems beyond terminal polydispersity are good glass formers. It was shown that in a polydisperse system due to an increase in surface free energy, the crystal nucleation is suppressed promoting glass formation. Thus in study of supercooled liquids, polydisperse systems play an important role.

In recent time, it has been shown that structure plays an important role in the dynamics of glass forming supercooled liquids. Since polydisperse systems are good glass former describing the structure of these systems becomes important. For a continuous polydisperse system, the number of species is the number of particles in the system. In this case, describing the system’s partial structure in terms of independent species becomes an impossible task. Thus it is common practice to treat a polydisperse system in terms of an effective one component system. However, it has been shown that we not only lose a large deal of information of the system by pre averaging the structure, the properties of the liquid thus predicted can also give spurious results. Truskett and coworkers have shown that for moderate polydispersity the thermodynamic quantities like the pair excess entropy obtained from the effective one component radial distribution function (rdf) predicts that with an increase in interaction the static correlation becomes weaker thus predicting structural anomaly. The study showed that when the system is expressed in terms of 60 pseudo neighbors and the excess entropy is calculated in terms of the partial structure factors (radial distribution functions), this structural anomaly disappears. Weysser et. al. while working with Mode coupling theory have shown that for a polydisperse system, we need to provide information about the partial structure factors to obtain the correct dynamics. These studies thus emphasize the importance of describing the structure of a polydisperse system in terms of the partial structure factors of the pseudo species.

The present study attempts to develop a general framework to describe the structure of a system having continuous polydispersity. As discussed before, for a system with continuous polydispersity the number of species is the same as the number of particles which makes its difficult to describe the structure. We also know that describing all the particles in terms of a single species does not work. So the aim of the study is to describe the system in terms of M pseudo species such that the properties of this system are the same as the original system. The questions that we ask are i) Can we determine the minimum number of pseudo species M0 required to describe the structure of the system? ii) Is this dependent on the property that we study? iii) Does it depend on the degree and nature of polydispersity? iv) Does it depend on the interaction potential?

To answer these questions we use the route of calculating thermodynamic quantities which can be obtained from the structure of the liquid. Namely the potential energy of the system and the pair excess entropy. Note that

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the former is a linear function of the structure whereas the latter is a nonlinear function of the structure and thus can have different sensitivities to the effective structure. We find that by studying the thermodynamical quantities we can determine a value of $M_0$. It depends on the type of polydispersity, the degree of polydispersity, and the interaction potential. We also provide an estimate of the width of polydispersity that can be treated like a one component system. This width appears to depend primarily on the interaction potential of the system. Systems with longer range and softer interaction potential have a better tolerance towards polydispersity. In these cases, systems with a wider spread of size can be addressed in terms of one component system.

The organization of the rest of the paper is the following. Section II contains the simulation details. In Section, III we discuss the methods used for evaluating the various quantities of interest. Section IV contains results with discussions and the paper ends with a brief conclusion in Section V.

### II. SIMULATION DETAILS

In this study, we perform molecular dynamics simulations for three-dimensional polydisperse system with continuous size polydispersity in the canonical ensemble. The system contains $N=1000$ number of particles in a cubic box of volume $V$. The number density for all the systems is $\rho = N/V = 1$.0. In our simulations, we have used periodic boundary conditions and Nosé-Hoover thermostat with integration timestep 0.001 $\tau$. The time constants for the Nosé-Hoover thermostat are taken to be 100 timesteps. We have carried out the molecular dynamics simulations using the LAMMPS package. For all state points, three to five independent samples with run lengths $> 100\tau$ ($\tau_a$ is the $\alpha$-relaxation time) are analyzed. The study involves two different kinds of systems with respect to size polydispersity, constant volume fraction (CVF) and Gaussian (as shown in Fig. I) and three different kinds of interaction potentials. The distributions of the particle size are continuous. The form of the constant volume fraction distribution is given by

$$P_l(\sigma) = \frac{A}{\sigma^3}, \quad \sigma \in [\sigma_{max}, \sigma_{min}]$$

where $A$ is the normalization constant and $\sigma_{max}$ and $\sigma_{min}$ are the maximum and minimum values of particle diameter. $\sigma_{max}$ and $\sigma_{min}$ values are given in Table I. The degree of polydispersity is quantified by $\delta$, the normalized root mean square deviation

$$PDI = \frac{\sqrt{\sigma^2 - \langle \sigma^2 \rangle}}{\langle \sigma \rangle}$$

Where $\langle .. \rangle$ defines the average of the particle size distribution.

The Gaussian distribution is given by

$$P_2(\sigma) = \frac{1}{\sqrt{2\pi}\delta^2} \exp\left(-\frac{(\sigma - \langle \sigma \rangle)^2}{2\delta^2}\right)$$

![Table I: Details of the size distributions, constant volume fraction and Gaussian, for different degrees of polydispersity PDI = $\delta/\sigma$](chart)

| Distribution | PDI % | $\sigma_{max}$ | $\sigma_{min}$ | $\Delta\sigma$ | $\eta$ |
|-------------|------|----------------|----------------|---------------|------|
| $P_l(\sigma)$ | 5%   | 1.1            | 0.92           | 0.18          | 0.53 |
|              | 10%  | 1.21           | 0.83           | 0.30          | 0.54 |
|              | 15%  | 1.34           | 0.78           | 0.54          | 0.56 |
| $P_2(\sigma)$ | 5%   | 1.13           | 0.75           | 0.46          | 0.54 |
|              | 10%  | 1.3            | 0.75           | 0.66          | 0.56 |
|              | 15%  | 1.43           | 0.75           | 0.96          | 0.56 |

Where $\delta$ is the standard deviation. In this distribution we consider $\sigma_{max/min} = \langle \sigma \rangle \pm \delta$. The degree of polydispersity is quantified by,

$$PDI = \frac{\sqrt{\sigma^2 - \langle \sigma^2 \rangle}}{\langle \sigma \rangle} = \delta/\sigma$$

For all the polydisperse systems the particle sizes are such chosen that $\langle \sigma \rangle = \int P(\sigma)\sigma d\sigma = 1$ and is kept as the unit of length for all the systems studied here.

The three different interaction potentials studied here are inverse power law (IPL) potential, Lennard-Jones (LJ) potential and its repulsive counterpart the Weeks-Chandler-Andersen (WCA) potential. The inverse power law potential (IPL) between two particles i and j is given by

$$U_{ij} = \begin{cases} \epsilon_{ij} \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} + \sum_{l=1}^{2} c_{2l} \left(\frac{r_{ij}}{\sigma_{ij}}\right)^{2l}, & \frac{r_{ij}}{\sigma_{ij}} \leq x_c \\ 0, & \frac{r_{ij}}{\sigma_{ij}} > x_c \end{cases}$$

The constants $c_0, c_2$ and $c_4$ are selected such that the potential becomes continuous up to its second derivative at the cutoff $x_c = 1.25\sigma_{ij}$.

The LJ potential between the two particles i and j is described using truncated and shifted LJ potential;

$$U_{ij} = \begin{cases} U^{(LJ)}(r_{ij}; \sigma_{ij}, \epsilon_{ij}) = U^{(LJ)}(r_{ij}^{(c)}; \sigma_{ij}, \epsilon_{ij}), & r_{ij} \leq r_{ij}^{(c)} \\ 0, & r_{ij} > r_{ij}^{(c)} \end{cases}$$

where $U^{(LJ)}(r_{ij}; \sigma_{ij}, \epsilon_{ij}) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]$. The cutoff for the LJ system is $r_{ij}^{(c)} = 2.5\sigma_{ij}$ and for the WCA system is $r_{ij}^{(c)} = 2.5\sigma_{ij}$. The interaction strength between two particles i and j is $\epsilon_{ij} = 1.0, \sigma_{ij} = (\sigma_{i} + \sigma_{j})/2$, where, $\sigma_{i}$ is a diameter of particle i and it varies according to the system. Length, temperature and times are given in units of $\langle \sigma \rangle$, $\epsilon_{ij}$ and $\frac{m \langle \sigma^2 \rangle}{\epsilon_{ij}}$ respectively.
written in terms of the partial radial distribution function, $E_x$.

$$E_x = \frac{\rho}{2} \sum_{\alpha \beta} M_{\alpha \beta} \int_0^\infty 4\pi r^2 U_{\alpha \beta}(r) g_{\alpha \beta}(r) dr$$  \hspace{1cm} (7)$$

In the effective one component treatment the energy can be written as $E^{eff}_2$,

$$E^{eff}_2 = \frac{\rho}{2} \int_0^\infty 4\pi r^2 U(r) g(r) dr$$  \hspace{1cm} (8)$$

C. Excess entropy

Excess entropy $S_{ex}$ is a loss of entropy due to the interaction between the particle or in other words excess entropy is a difference between $S_{total}$ and $S_{ideal}$ at same temperature $T$ and density $\rho$. The value of $S_{ex}$ is always a negative. $S_{ex}$ can be evaluated by thermodynamic integration (temperature density landscape). Entropy at high temperature and low density is an ideal gas entropy ($S_{ideal}$). This $S_{ideal}$ is a relative reference for any other state points entropy calculation. Other state point entropy can be calculated using a combination of isotherms and isochoric paths, making sure that no phase transitions occur along the selected path.

Isotherms path integration -

$$S(T, V') - S(T, V) = \frac{U(T, V') - U(T, V)}{T} + \int_V^{V'} \frac{P(V)}{T} dV$$  \hspace{1cm} (9)$$

Isochoric path integration -

$$S(T', V) - S(T, V) = \int_T^{T'} \frac{1}{T} \frac{\delta U}{\delta T} dT$$  \hspace{1cm} (10)$$

Addition of Eq. (9) and Eq. (10) give the total excess entropy.

D. Pair Entropy

Using Kirkwood factorization, the excess entropy can also be expressed in terms of an infinite series,

$$S_{ex} = S_2 + S_3 + S_4 + \ldots$$  \hspace{1cm} (11)$$

Where $S_n$ is an entropy contribution due to $n$ particle spatial correlation. The pair excess entropy, $S_2$ includes 80% of the total excess entropy. We can calculate $S_2$ from the partial rdf of $M$ species.

$$S_2 = -2\pi \rho \sum_{\alpha, \beta = 1}^M x_{\alpha} x_{\beta} \int_0^\infty r^2 dr \{ g_{\alpha \beta}(r) \ln g_{\alpha \beta}(r) - (g_{\alpha \beta}(r) - 1) \}$$  \hspace{1cm} (12)$$

where $g_{\alpha \beta}$ is a pair correlation between $\alpha$ and $\beta$ atom type, $k_B$ is a Boltzmann constant, $x_\alpha$ is a mole fraction of the $\alpha$ species and $\rho$ is a density of a system.

If we do not consider the different species then the entropy for an effective one component system can be written as $S^{eff}_2$,

$$S^{eff}_2 = -2\pi \rho \int_0^\infty r^2 dr \{ g(r) \ln g(r) - (g(r) - 1) \}$$  \hspace{1cm} (13)$$
E. Onset temperature calculation from Inherent structure energy

The inherent structure energy is the potential energy evaluated at the local minimum of the energy reached from the configuration via the steepest descent procedure. As suggested earlier, the onset temperature is connected to the inherent structure energy. At high temperatures as the system is not influenced by the landscape properties, the average inherent structure energy is almost temperature independent. However, below a certain temperature, where the landscape properties influence the system, the inherent structure energy starts to decrease rapidly. Usually, the two different regimes are fitted to two straight lines and the point where these lines cross is identified as the onset temperature, \( T_{\text{onset}} \).

F. Overlap function

To characterize the dynamics we consider the self part of the overlap function \( Q(t) \):

\[
Q(t) = \frac{1}{N} \sum_{i=1}^{N} \left( \omega(|\mathbf{r}_i(t) - \mathbf{r}_i(0)|) \right),
\]

where the function \( \omega(x) \) is 1 if \( 0 \leq x \leq a \) and \( \omega(x) = 0 \) otherwise. The parameter \( a \) is chosen to be 0.3, a value that is slightly larger than the size of the cage.

IV. RESULT

A. Effective one-component description

In this work, we will intermittently use the word radial distribution function and structure both referring to the rdf. As discussed before it is a common practice to describe the structure of a polydisperse system in terms of an effective one component system.

In Fig. 2 we plot the average per particle potential energy as obtained from the simulation, \( E_{\text{sim}} \) and the species agnostic \( E_{\text{eff}} \) for systems with different PDI values (5%, 10%, and 15%). In the simulation study, the particle sizes are obtained from \( P_1(\sigma) \) distribution and they interact via IPL potential. In Fig. 3 we also plot the \( S_{\text{ex}} \) and the species agnostic \( S_{\text{eff}} \) for the above mentioned systems. Note that if the structure is described properly then \( E_{\text{sim}} = E_2 \) and \( S_2 \) is not exactly equal to \( S_{\text{ex}} \) but comprises of 80% of its value.\(^{13,22,34,37,38}\)

We find that as the PDI increases the difference between \( E_{\text{sim}} \) and \( E_{\text{eff}} \) and \( S_{\text{ex}} \) and \( S_{\text{eff}} \) increases. This clearly shows that as expected, with an increase in PDI the effective one component description of the system becomes less accurate. In Fig. 4 we plot both the dynamics and the effective one component rdf of the systems. We find that although the dynamics remains almost the same, with an increase in polydispersity the structure appears to soften. This artificial softening of the structure which has been observed earlier, leads to the increase in \( E_{\text{eff}} \) and \( S_{\text{eff}} \). Note that even for 5% polydispersity we find that the effective one component structure of the system fails to provide the correct value of the potential energy and the pair excess entropy. These results presented in Fig. 2 and Fig. 3 are not surprising but a confirmation of the observations made earlier.\(^{23,26}\)

B. Pseudo species and its dependence on degree of polydispersity

Describing the structure of a continuous polydisperse system can be challenging? Unlike in a discrete polydisperse system where each species has a finite number of particles and all of them have the same size, for a continuous polydisperse...
system the number of species is the same as the number of particles. However, let us assume that we describe a pseudo system where we divide the particles into M number of pseudo species (where $M < N$) in terms of the size of the particles. In doing so we bunch particles with similar but different sizes, in a group and assign an average size to them. This introduces disparity in the actual size and the assigned size of the particles and leads to an error in describing the properties of the system. An extreme case of that ($M = 1$) can be seen in Fig. 2 and Fig. 5. For a fixed $M$, the maximum difference in the actual diameter of a particle and its assigned average diameter is $\Delta \sigma / 2M$. Thus with an increase in $M$ this error reduces and at $M = N$ the pseudo system is exact. So the first question is can we describe the structure of a system in terms of an optimum number of species $M_0$, where $M_0 << N$ such that the structure can provide a correct estimate of the thermodynamic quantities? If we can then how does $M_0$ depend on the degree of polydispersity?

In Fig. 4(a) we plot $\frac{Q(\sigma)}{Q_{\text{sim}}}$ as a function of $M$, at two different temperatures for the different PDIs. For systems with a fixed value of PDI as we increase the value of $M$ the $E_2$ decreases and after a certain value of $M$, $E_2 \simeq E_{\text{sim}}$. We find that this is weakly temperature dependent. For this work, we consider that at $T = 1$ the minimum number of pseudo species for which $\left( E_2 - E_{\text{sim}} \right) / E_{\text{sim}} < 0.01$ is $M_0$. The value of $M_0$ is system dependent and as expected increases with the increase in PDI value as can be seen from Fig. 4(b).

FIG. 4: (a) Dynamics of systems at different PDIs. The overlap function is plotted against time. (b) Effective one component radial distribution function of the systems. Black square, red triangle, green circle and blue diamond represent a monodisperse system, 5% PDI, 10% PDI and 15% PDI, respectively. With an increase in PDI although the dynamics remains almost the same the structure shows a substantial softening. Here particles are interacting via IPL potential and the particle size distribution is given by $P_\Lambda(\sigma)$ (constant volume fraction distribution).

FIG. 5: Comparison between energy obtain from simulation, $E_{\text{sim}}$, and energy obtain from partial radial distribution functions, $E_2$ (Eq. 7). (a) Ratio of $E_2$ and $E_{\text{sim}}$ vs the number of pseudo species $M$ at $T=1.0$ and $T=0.5$ for different PDIs. (b) Relative error calculation between $E_{\text{sim}}$ and $E_2$, $(E_2 - E_{\text{sim}}) / E_{\text{sim}}$ plotted as a function of $M$ for different PDIs. Here particles are interacting via IPL potential and the particle size distribution is given by $P_\Lambda(\sigma)$ (constant volume fraction distribution).

Is the value of $M_0$ sensitive to the thermodynamic quantity that we calculate or is it universal? To answer this question we calculate the two body partial entropy for different values of $M$, where $M_0 < N$. For $M_0 < N$, the entropy remains almost the same. However, for large values of $M$, the entropy decreases and after a certain value of $M$, it becomes weakly temperature dependent. Thus with an increase in $M$ this error reduces and at $M = N$ the pseudo system is exact. So the first question is can we describe the structure of a system in terms of an optimum number of species $M_0$, where $M_0 < N$ such that the structure can provide a correct estimate of the thermodynamic quantities? If we can then how does $M_0$ depend on the degree of polydispersity?
we plot the variation of volume fraction distribution). This onset temperature can also be obtained from the change in the slope of the temperature dependence of the inherent structure energy and also other methods. As shown earlier the values of the onset temperatures obtained using these different methods are not exactly the same but they are in a similar range.

In Fig. 7 we plot the variation of $T_{cross}$ with $M$ for the different systems. For higher PDI, at small values of $M$, we cannot calculate $T_{cross}$, which implies that $S_2$ is far away from $S_{ex}$ and never crosses it as seen in Fig. 6. However, from our other estimates of onset temperature, we know that we are in a temperature range where these two forms of entropy should cross. As $M$ increases the two functions cross at some temperature $T_{cross}$. We find that initially $T_{cross}$ increases with $M$ and then after a certain value of $M$ it shows a saturation. The saturation of $T_{cross}$ is an indication of the saturation of $S_2$ w. r. t. $M$. We find that this saturation value of $T_{cross}$ is in a similar range as the estimated onset temperature using the method of inherent structure energy (see Sec III E). In this plot we also mark the $M_0$ values as obtained from the potential energy. We find that the $M$ value for which $T_{cross}$ saturates falls in the similar range as $M_0$. The values of $T_{cross}$ at $M = M_0$ and the $T_{onset}$ are given in Table I. Thus we show that the minimum number of pseudo species required to describe the potential energy of the system can also describe the two body excess entropy of the system.

The details of the $M_0$ values for the different systems are given in Table I. We also tabulate a quantity $\Delta\sigma = \frac{\Delta S}{\Delta M}$. We find that although $M_0$ is dependent on the PDI this quantity $\Delta\sigma$ is not. Note that when $M = M_0$, the maximum error in assigning a diameter to a particle is $\Delta\sigma$. Thus our study suggests that the thermodynamic properties of the system studied here are not sensitive to a change in diameter by $\Delta\sigma$ and for a constant volume fraction polydisperse system interacting via IPL potential when $\Delta\sigma \approx 0.036$ we can treat it as a monodisperse system.

Interestingly we find that when we plot the partial rdf for two consecutive pseudo species, $g_{11}(r)$ and $g_{22}(r)$ (here these

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**FIG. 6:** Excess entropy, $S_{ex}$, and pair excess entropy $S_2$. The latter is calculated at different values of $M$ (Eq.12). Dashed dot line represents $S_{ex}$ and solid lines represent $S_2$. (a) PDI 5% (b) PDI 10% (c) PDI 15%. Here particles are interacting via IPL potential and the particle size distribution is given by $P_1(\sigma)$ (constant volume fraction distribution).

**FIG. 7:** $T_{cross}$ vs $M$ plot for different PDIs. Initially, $T_{cross}$ increases with $M$ but after certain value of $M$, it saturates. For larger PDI the saturation takes place at a higher $M$ value. The vertical lines give the value of $M_0$ obtained from energy criteria. Here particles are interacting via IPL potential and the particle size distribution is given by $P_1(\sigma)$ (constant volume fraction distribution).
two species 1 and 2 have the largest and the second largest number of particles, respectively) for different values of $M$ then for $M = M_0$ the peaks of the two rdfs almost overlap (Fig. 8). Thus we can say that when the size difference of the two consecutive species are such that there is a large overlap between the radial distribution functions of two consecutive species then they can be treated as a single species.

**TABLE II:** The values of $M_0$ and $\Delta \sigma_0$ for different systems. We also provide the values of $T_{\text{cross}}$ at $M = M_0$ and for comparison we give the $T_{\text{onset}}$ values obtained from fitting the Inherent structure energy to two straight lines.

| Distribution | Potential | PDI$^a$ | $M_0$ | $\Delta \sigma_0$ | $T_{\text{cross}}(M_0)$ | $T_{\text{onset}}$ |
|--------------|-----------|--------|------|-----------------|--------------------------|------------------|
| $P_1(\sigma)$ | IPL       | 5%     | 5    | 0.036           | 0.42                     | 0.43             |
|              |           | 10%    | 10   | 0.036           | 0.33                     | 0.36             |
|              |           | 15%    | 15   | 0.036           | 0.26                     | 0.31             |
| $P_2(\sigma)$ | IPL       | 5%     | 4    | 0.043           | 0.43                     | 0.46             |
|              |           | 10%    | 14   | 0.043           | 0.35                     | 0.34             |
|              |           | 15%    | 21   | 0.043           | 0.28                     | 0.30             |
| $P_3(\sigma)$ | WCA       | 15%    | 20   | 0.027           | 0.58                     | 0.7              |
|              | LJ        | 15%    | 12   | 0.045           | 0.67                     | 0.81             |

C. Effect of the type of distribution on $M_0$ and $\Delta \sigma_0$

We next study the effect of the type of distribution on $M_0$ and $\Delta \sigma_0$. In Fig. 8 we compare the $M$ dependence of $T_{\text{cross}}$ for systems where polydispersity is described in terms of $P_1(\sigma)$ (constant volume fraction) and $P_2(\sigma)$ (Gaussian), for three different PDIs. In the same plot the $M_0$ values as obtained from the potential energy are also marked.

At the same PDI, the nature of saturation of $T_{\text{cross}}$ and also the value of $M_0$ are different for the two different distributions. Compared to the constant volume fraction distribution, the values of $M_0$ are higher for the Gaussian distribution. The reason behind this can be understood by comparing Fig. 4 and Fig. 2 (also see Table I). For the same PDI, the Gaussian distribution is wider compared to the constant volume fraction distribution. A closer observation tells us that the saturation of $T_{\text{cross}}$ is better for the CVF distribution when compared to the Gaussian distribution. Note that for the Gaussian distribution $M_0$ is higher (more number of species), and by nature towards the tail of the distribution the number of particles is less so the partial rdf for the largest and the smallest species are poorly averaged. We have seen that with an increase in system size the saturation improves (not shown here).

We find that when compared to CVF distribution, the $\Delta \sigma_0$ is marginally higher for the systems with Gaussian distribution (see Table I). Note that we divide a continuous polydisperse system into $M$ species in a way that the difference in diameter of two consecutive species is always separated by $\Delta \sigma_0$. This implies that the percentage error in calculating the size of the smaller particles is higher than that of the larger particles. Also, note that in constant volume fraction distribution the smallest particles are the largest in number thus by construction the error is maximum for the dominant species. On the other hand for the Gaussian distribution, the place where the percentage error is maximum the population of particles are the minimum. Thus compared to the Gaussian distribution for continuous volume fraction we need to go to marginally smaller values of $\Delta \sigma_0$. A way to increase $\Delta \sigma_0$ (decrease $M_0$) in CVF distribution can be to have a size dependent bin width such that the percentage error in describing the size of a smaller particle is the same as that of a larger particle.

![FIG. 8: The partial radial distribution function for the first two species for different values of $M$. (a) PDI 5% (b) PDI 10% (c) PDI 15%. For $M = M_0$ the rdf peak of the two consecutive species almost overlap. Here particles are interacting via IPL potential and the particle size distribution is given by $P_1(\sigma)$ (constant volume fraction distribution).](image-url)
we compare the rdf values for the first two species.

We plot for the WCA system the partial rdfs of $T$ for the WCA system and also the compared to the IPL system we need to go to higher values of $M$.

The partial radial distribution function for the first two species for different values of $M$. The particles are interacting via WCA potential and the polydispersity of the system is described by $P_1(\sigma)$ with 15% PDI.
study involves systems where the polydispersity is described in terms of different distributions (constant volume fraction and Gaussian) and the degree of polydispersity is varied. We also study the effect of the interaction potential.

We exploit the fact that the potential energy and the pair excess entropy can be described in terms of the partial radial distribution functions. First, we describe the system in terms of pseudo species. In the case of potential energy, we obtain the minimum number of pseudo species, $\sigma_0$ required to match the energy obtained from the partial rdf with that obtained from the simulation. For the entropy part, since the excess entropy and pair excess entropy are never equal, we calculate the temperature where they cross each other. Our earlier study shows that this $T_{\text{cross}}$ is an estimate of the onset temperature of supercooled liquids. We show that for a smaller number of species, the $T_{\text{cross}}$ varies with $M$ and as a function of species this temperature shows a saturation, suggesting a saturation of the pair excess entropy w.r.t $M$. This gives us a second estimation of $\sigma_0$ which we find is similar to that obtained from the potential energy.

Our study reveals that for a given system, it is possible to define a parameter $\Delta\sigma_0$ which gives the limiting width of the size distribution that can be treated as a monodisperse system. This limiting value primarily depends on the interaction potential. The softer the interaction potential the larger is the value of $\Delta\sigma_0$. Depending on the type of distribution this limiting width $\Delta\sigma_0$ translates into different values of PDI.

The present study clearly shows that even 1% polydispersity when treated as an effective monodisperse system will not provide us the correct structure of the liquid. This implies that when the effective one component structure is used to study the influence of polydispersity on some property, we have to be careful in decoupling the effect of this artificial softening of the structure from the actual effect of the polydispersity.

In our study, we have only considered the structure of the liquid and its effect on the thermodynamic quantities. We have not studied the role of the structure of a polydisperse system on the dynamics. However, Weysser et al studied the effect of polydispersity on the dynamics. They studied a system with constant polydispersity where $\Delta\sigma = 0.2$. According to their study, the dynamics can be well explained when the system is divided into 5 pseudo species. Thus according to their study, the $\Delta\sigma_0 = 0.04$ falls in a similar range as predicted here. Thus we can say that both thermodynamics and dynamics predict a similar structure. Note that $\sigma_0$ and $\Delta\sigma_0$ are independent of the system size which makes this pseudo neighbour description of a system more useful for larger systems.

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