Energy polydisperse 2d Lennard–Jones fluid in the presence of flow field

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Abstract. The behaviour of energy polydisperse 2d Lennard–Jones fluid (in thin-film geometry) is studied subjected to linear flow field using molecular dynamics simulations. By considering neutral and selective substrates, we systematically explore the effect of flow field on particle ordering as well as response of the system. It is shown that particle density profile, spatial organisation as well as local particle identity ordering in the film are affected. Furthermore, we observe flow-induced melting associated with a decrease of effective interaction parameter, $⟨\epsilon_{\text{eff}}⟩$, which characterises local neighbourhood identity ordering. In terms of macroscopic response, the systems exhibit both shear thinning and shear thickening, and shear thinning exponent decreases with increasing temperature and eventually attains Newtonian fluid-like behaviour at sufficiently high temperature. The onset of shear thinning is governed by the time scale of structural relaxation of the strongly attractive particles. It is found that the qualitative behaviour of the one-component LJ-fluid and energy polydisperse fluid with neutral substrates are similar in many respects, while the one with selective substrate shows differences. In the case of energy polydisperse system, the effect of having different substrate types is significantly manifested in the density profile near the interface, effective interaction parameter and in viscosity.

Keywords. Fluids; energy polydisperse; MD simulation; rheology; shear thinning.

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1. Introduction

Multicomponent fluids are very common in nature, where degree of polydispersity is often attributed to the distribution of particle sizes. The particle size variation has an important role in the glass-forming ability of the colloidal fluids. In experiments, polydispersity offers a means to avoid crystallisation and thus allows one to study very high viscous fluids [1,2]. Application of these materials demands understanding their physics and our ability to manipulate them for industrial processing. Various equilibrium aspects of size polydisperse systems (e.g., packing, thermodynamics, etc.) have been discussed in earlier works [3–15]. Polydispersity is also very common in biological systems, where a cell contains large amount of different types of macromolecules that differ in their shape, size and interactions, leading to interesting dynamical behaviour and geometry-controlled kinetics [16–21]. In our recent work [22,23], a model complex fluid characteristic of biological systems (named APD fluid) was introduced, where we focussed on interaction multiplicity, i.e. energy polydispersity among the constituents – a minimal physical model in which all particles are different in the sense that their interaction parameters are chosen at random from a given distribution. The results of our earlier work on statics and dynamics of APD fluid close to solidification transition are briefly discussed below.

In an energy polydisperse fluid, although the particles have random interactions, the local self-organisation shows that the particles relax into a non-random state characterised by the clustering of particles according to the values of their pair interaction parameters which become more pronounced as temperature is decreased throughout the fluid region. This particle identity ordering has consequences in the particles’ dynamical behaviour. For example, when particle identity ordering sets in, different types of particles find themselves in different local environments and thus show distinct diffusion coefficients. It is important to note that size polydispersity leads to entropic effects associated with packing a large number of dissimilar
objects in an efficient way, thus increasing the number of available configurations, whereas interaction polydispersity affects the weights of different configurations through neighbourhood identity ordering (NIO). The effect of particle size disparity in the NIO in APD fluid is considered recently, where it is shown that enhancement of NIO is possible by changing the size ratio [24]. This energy polydisperse fluid model is also closely related to lattice models of glass with particles of many types [25,26]. Furthermore, several aspects of the system, viz., identity ordering and metastable cluster, and effect on tensile strength (where a multicomponent solid shows limiting tensile strength that far exceeds the corresponding one-component solids) are reported in refs [27,28]. On the other hand, Ingebrigtsen and Tanaka investigated the effect of energy polydispersity on the nature of Lennard–Jones liquids in 3D [29], where they showed that energy polydisperse LJ liquids are Roskilde-simple liquids [30]. Although APD fluid is an idealised system, it can capture some of the important features of multicomponent systems, e.g., multicomponent metallic alloys and complex fluids in terms of the self-organising property in the liquid state upon cooling [31,32].

The presence of flow field, on the other hand, can induce many interesting phenomena in complex fluids, e.g., shear thinning/thickening of suspensions and shear-induced phase transition. There is large volume of work on the rheological studies of colloidal dispersion and soft-matter in general [33–38]. Recent advances in the field allow access to the microscopic structural changes during the process and thus gives better understanding of the mechanical response of these complex fluids. In the present paper, non-equilibrium aspects of the idealised multicomponent system (APD model) in the fluid state is addressed, where we study the system subjected to a linear flow field. In particular, we investigate the effect of flow field on particle distribution in the film, spatial ordering of particles and local identity ordering. Also, macroscopic response is studied by measuring stress components and hence shear viscosity. Finally, the role of substrate quality on the aforesaid quantities of the fluid is also investigated by considering two types of substrates (non-selective and selective substrates) described in the following section.

Our paper is organised as follows: In §2, we present the model and simulation details. Particle distribution in the film through density profile is reported in §3.1, particle ordering and flow-field induced melting in §3.2, and macroscopic response in §3.3. Finally, in §4 we summarise and discuss the results of this work.

2. Model and simulation details

We consider $N = 2500$ coarse-grained particles in two dimensions which are confined by two all-atom walls in slit geometry of width $D = 46\sigma$ (and channel length $= 80\sigma$), where $\sigma$ is the particle diameter [39]. Thus, the reduced number density of the system $\rho^* \approx 0.68$, where the system behaves as liquid at high temperature. As shown in figure 1 the system is periodic along X-axis and non-periodic in the Y direction. All the particles have the same mass $m$ and size $\sigma$ which are set to unity. In this model, all the particles interact via the Lennard–Jones (LJ) potential which is cut-off and shifted to zero at $r_c = 2.5\sigma$.

$$U_{ij}(r) = 4\epsilon_{ij}[(\sigma/r)^{12} - (\sigma/r)^{6}],$$

(1)

Here, $\epsilon_{ij}$ and $r$ are the interaction strength and separation between a pair of particles $i$ and $j$ respectively. In order to introduce energy polydispersity, we assign interaction parameter $\epsilon_i$ to each particle $i$ which is drawn randomly from a uniform distribution in the range $1–4$, where the value of interaction strength $\epsilon_i$ defines the particle identity, see figure 1a. Between particles $i$ and $j$, the interaction strength is given by $\epsilon_{ij} = \epsilon_i\epsilon_j$ (following Lorentz–Berthelot anzatz [40]). The distribution $P(\epsilon_{ij})$ is shown in figure 1b, where the most probable value $\epsilon_{ij}^{\text{max}} = 2.0$ and mean $\bar{\epsilon}_{ij} = 2.42$. As a reference system, we simulate a one-component (1C) LJ system at the same density with interaction parameter $\epsilon_{ij} = 2.5$ (mid-point of the interval 1–4).

The rigid wall atoms (having the same size as that of the fluid particles) are arranged in a square lattice with lattice constant $\sigma$. Two types of walls are considered: (i) non-selective walls (ns wall), where there is no preferential interaction between the wall and fluid particles, and we set the fluid–wall interaction strength $\epsilon_{\text{fluid–wall}} = 2.5$ for all particle types and (ii) selective walls (s-wall), where the interaction strength between the fluid particles and walls depend on the particle type. For example, $i$th fluid particle with interaction parameter $\epsilon_i$ interacts with the wall with interaction strength $\epsilon_{\text{fluid–wall}} = \sqrt{\epsilon_i \epsilon_{\text{wall}}}$. For the wall particles, we set $\epsilon_{\text{wall}} = 1.0$, and since $1 \leq \epsilon_i \leq 4$ we have $1 \leq \epsilon_{\text{fluid–wall}} \leq 2$. In both the wall types, fluid–wall interaction cut-off distance is set to $r_c = 2.5\sigma$.

In this study, we do not consider the case of ns-wall made by setting $r_c = 1.12\sigma$ (i.e., purely repulsive case). Various interaction strengths present in the system are summarised in table 1.
Figure 1. (a) Uniformly distributed $\epsilon_i$ and (b) the corresponding distribution of $\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}$. Solid line in (b) corresponds to the analytical expression of the distribution of the product of two uniformly distributed random numbers. (c) Typical equilibrium configuration of the APD system (with non-selective confining walls) relaxed at temperature $T = 1$. A flow field is subjected along the $X$-direction (with velocity gradient along the $Y$-direction). Confining walls move along with the fluid. Particles are coloured according to their interaction parameter $\epsilon_i$ in the range 1–4 (see colour scale bar). Wall particles are coloured green here and in the remaining figures.

Since we are interested in studying the effect of flow field, particles are given additional velocities along the $X$-direction whose magnitude changes linearly with $y$ position as follows:

$$ v(y) = \frac{2v_0}{D} \left( y - \frac{D}{2} \right) , $$

where $y$ varies from 0 to $D$, as shown in figure 1. Furthermore, the upper and lower walls are given velocity of magnitude $+v_0$ and $-v_0$, respectively, thereby fixing the shear rate

$$ \dot{\gamma} = \frac{2v_0}{D} . $$

Table 1. Pair-wise interaction strength among the species.

| Between $i$ and $j$ | Strength $\epsilon_{ij}$ | Nature of interaction |
|---------------------|--------------------------|-----------------------|
| Fluid–fluid polydisperse | Attractive (strength varies) |
| Fluid–wall 2.5 (a) | Attractive (strength same) |
| Fluid–wall polydisperse (b) | non-selective wall case |
| Wall–wall 1.0 | Attractive (strength varies) |
|                     | selective wall case |
|                     | Repulsive |

When a shear velocity is applied, the wall moves as a whole and the relative positions among the wall particles are maintained. Also, it is important to note that by imposing linear flow profile and moving the walls with the same velocity as the outermost fluid layer, we neglect the slipping near walls.

We carried out MD simulations in NVT ensemble using the open source simulation package LAMMPS [41]. The equations of motion are integrated using Velocity-Verlet algorithm with a time-step of $\delta t = 0.005\tau_{LJ}$, where $\tau_{LJ} = \sigma (m/\epsilon)^{1/2} = 1$ is the LJ time (we take $\sigma = m = 1$ and define $\epsilon = 1$ as the lower bound on $\epsilon_{ij}$). All the physical quantities are expressed in LJ reduced units [42].

Using Langevin thermostat we maintain the temperature of the system [42], where the thermostat modifies Newton’s equation of motion of the $i$th particle according to

$$ m \frac{d^2 \mathbf{r}_i}{dt^2} = -\frac{\partial U}{\partial \mathbf{r}_i} - \zeta \frac{d\mathbf{r}_i}{dt} + \mathbf{f}_i , $$

where $\mathbf{r}_i$ is the position of the particle $i$, $\zeta$ is the friction coefficient (assumed to be the same for all particles), $U$ is the sum of all the pair potentials $U_{ij}$ ($i \neq j$) and $\mathbf{f}_i$ is a random external force with zero mean and second moment proportional to the product of temperature $T$ and $\zeta$. The friction coefficient is fixed at $\zeta = 1/\tau_d = 1/50\tau_{LJ}$ ($\tau_d$ is the viscous damping time). Since there is streaming velocity along the $X$-direction, the temperature of the system is calculated by subtracting the streaming velocity before we compute the kinetic energy.

We equilibrate the systems at high temperature and then bring the system down to the desired temperature and relax for about $2.5 \times 10^4\tau_{LJ}$ followed by shear for $5 \times 10^5\tau_{LJ}$ (corresponding to 100 million MD steps) to steady-state in which the ensemble-averaged (potential) energy remains constant in time. All the data reported in this work were obtained in the stationary regime and averaged over 15 replicas with each replica having a different set of interaction parameters $\epsilon_i$ values (uniformly distributed in the range 1–4).
3. Results

For the bulk APD system in equilibrium (at the same $\rho^*$) [22,23], the phase diagram differs from that of a pure one-component (1C) fluid [14], where in 1C system (at the same density) it passes through the triple point and thus goes directly from the fluid to the solid–gas coexistence region upon cooling [43,44]. The liquid–solid transition takes place within a narrow temperature range in which the mean interaction energy decreases sharply upon cooling from the liquid to solid–fluid coexistence region. The transition temperature is estimated to be $T^* \approx 1.0$ for both APD and 1C systems (for bulk systems), and interesting dynamical differences are observed close to $T^*$.

It is known that the presence of substrate can suppress or enhance the onset of solidification and thus shift the transition temperature to lower or higher values. For example, simulation study of freezing and melting of Lennard–Jones methane confined within the slit pores by Miyahara and Gubbins showed that when the adsorbate–wall interactions were weaker than the adsorbate–adsorbate interactions, the freezing temperature is significantly lower than in the bulk, as reported in most of the experiments for silica pores [45]. In contrast, a large increase in the freezing temperature is observed for strongly attractive materials, such as porous carbons. No appreciable change in the freezing temperature is observed when the adsorbate–adsorbate and adsorbate–wall interactions have similar strength. A detailed investigation is necessary to understand the effect of confinement on the solidification transition of APD fluids by varying the parameters such as density, film thickness, etc., and we leave this task for a future study. However, for the current work, approximate values of $T^*$ is located for the confined systems by performing heating/cooling cycles and using the procedure detailed in ref. [22].

For the considered density, it is observed that $T^*$ deviates from that of the bulk (albeit very small) and follow the trend: $T^*_{\text{bulk}} \approx 0.98 < T^*_{\text{s-w}} \approx 0.997 < T^*_{\text{ns-w}} \approx 1.01$. Since the walls are attractive to fluid particles, elevation of $T^*$ compared to the bulk is expected. However, as defined above, ns-wall attracts all the particles with the same strength and s-wall, depending on particle type, attracts particles with different strengths. Consequently, particle enrichment near the walls is more for ns-wall type and thus we expect the particles to solidify at a higher temperature, and for stronger fluid–wall interaction, $T^*$ is expected to increase even further. Since our interest is in the fluid phase, we focus our attention to $T \geq T^*$ (otherwise stated clearly).

Figure 2. Typical configurations of the 1C (upper panel), APD systems with non-selective walls (middle panel) and selective walls (lower panel) in the steady state for shear rate $\dot{\gamma} \approx 0.0087$ for $\delta \approx -0.1$, 0 and 0.1. Particles are coloured according to their $\epsilon_i$ values (see colour scale bar).

Figure 3. Laterally averaged particle density $\langle \rho \rangle$ as a function of the normalised distance $y/D$ for three different values of $\delta$ and shear rate $\dot{\gamma}$ indicated in the figure. The walls are located at $y = 0$ and $y = 1$.

3.1 Density profile

In figure 2, we show the typical steady-state configurations of the systems when $\dot{\gamma} = 0.0087$ and $\delta \approx -0.1, 0, 0.1$, where

$$\delta \equiv \frac{T - T^*}{T^*}.$$  

The particles are homogeneously distributed in the film for $\delta > 0$, while voids are present for lower values of $\delta$. In APD systems, the particles with large $\epsilon_i$ values clump together forming a core and smaller $\epsilon_i$ particles surrounding it. To understand the steady-state particle
distribution in the film, we calculate the laterally averaged density, \( \langle \rho \rangle \), at different positions (i.e., distance \( y \) from the walls) of the film and compare with 1C system. The density \( \langle \rho \rangle \) is calculated by dividing the film into several layers and the particle density is calculated in each layer. The density profiles of 1C and APD systems obtained at three different values of shear rates are shown in figure 3.

As expected, above the transition temperature the particle distribution is homogeneous and hence \( \langle \rho \rangle \) is flat in the bulk, and also no shear rate dependence of the density profile is observed (see figure 3 for \( \delta \approx 0.1 \)). However, the effect of non-selective/selective-wall types on the density profile is reflected in the fluid–wall interface region, where \( \langle \rho \rangle \) is higher (and hence particle enrichment) for APD with non-selective walls, while it is lower (and hence particle depletion) for the APD system with selective walls. Particle enrichment near the interface region is also observed for 1C system. As for lower temperatures (\( \delta \approx -0.1, 0 \)), the differences in the profiles are enhanced both in bulk and interface regions. Here, the density profiles of both 1C and APD (ns-wall) systems show that the density is lower in the bulk than near the interfaces, while the trend is opposite for APD systems with s-wall. However, the density profiles become homogeneous with the increase in shear rate. On the other hand, a quick look at the lateral average profile of energy \( \langle \epsilon_i \rangle \) for the APD system reveals a pattern similar to the density profile, i.e., \( \langle \epsilon_i \rangle \) is higher near the interface for the ns-wall system and lower for the s-wall system indicating aggregation of higher \( \epsilon_i \) particles in the interface region for the ns-wall system (see figure 4).

A more detailed analysis of local particle identity ordering together with the spatial organisation of particles in the film is discussed in the following section.

### 3.2 Particle ordering and shear-induced melting

To characterise the spatial organisation of particles, we calculate the radial distribution function (RDF) defined as

\[
g(r) = \frac{1}{\rho_0 N} \sum_i \sum_{j \neq i} \frac{\epsilon(r - r_{ij})}{\delta(r - r_{ij})},
\]

where \( \rho_0 \) is the particle number density in the system and \( r_{ij} = r_i - r_j \) is the distance between the \( i \)th and \( j \)th particles. Since the systems under investigation are confined, we use the method outlined in ref. [46] for the correct computation of \( g(r) \) for systems confined to a finite volume. The key idea of the method is to use an analytic solution for the intersection volume between the spherical shell and the sample volume.

In figure 5, comparison of \( g(r) \) profiles for 1C and APD systems obtained at \( \delta \approx 0 \) are shown for three different values of shear rates. For both the systems, weakly developed higher-order peaks corresponding to the onset of (short-range) hexagonal packing observed at very small \( \dot{\gamma} \) value (see figure 5a), is gradually transformed to liquid-like ordering upon increasing \( \dot{\gamma} \). Such shear-induced melting and distortion of \( g(r) \) when subjected to shear flow in simple liquids were observed in earlier works [47–49]. The associated effects in the transport coefficients due to structural reorganisation is discussed in §3.3. For small shear rates, it is clear from the figure that the difference in \( g(r) \) between the two APD systems is insignificant and compared to 1C
Figure 6. Radial distribution function for 1C (first row), APD ns-wall (second row) and APD s-wall (third row) when \( \dot{\gamma} \approx 0.00087, 0.0087, 0.026 \).

system the amplitude of maxima is relatively low. The difference between the APD and 1C systems however vanishes at high shear rates (see figure 5c).

On the other hand, it has been a challenge theoretically to determine the microstructure in the presence of the flow field. Recently, Banetta and Zaccone calculated the RDF as a solution to the Smoluchowski diffusion–convection equation [50]. For low-density 12-6 LJ fluid, they observed that in RDF the depth of the undershoot, the height of the peak and the slope of \( g(r) \) before and after the maximum, increase with the attraction parameter (equivalent to lowering temperature at fixed interaction strength). A plot of \( g(r) \) near the first peak is shown in figure 6 for 1C and APD systems. The observed trend is consistent with the observation made by Banetta and Zaccone. Furthermore, different \( g(r) \) curves corresponding to different \( \delta \), approach each other in the limit of high shear rate.

Another aspect of particle ordering is the identity of neighbouring particles. Neighbourhood identity ordering is quantified by means of effective interaction parameter \( \epsilon_{eff}^i \), defined as

\[
\epsilon_{eff}^i = \frac{1}{n_b} \sum_{j=1}^{n_b} \epsilon_{ij},
\]

where the sum over \( j \) goes over all the \( n_b \) neighbouring particles within a cut-off radius \( r_c = 1.7 \) which roughly corresponds to the minimum between the first and the second peaks of the radial distribution function. The value of \( \epsilon_{eff}^i \) varies in the range of 0 (for no neighbours within \( r_c \)) to 4 (all neighbour particles having \( \epsilon_i = 4 \)).

Figure 7. Typical steady-state configurations of the APD systems shown for three different values of shear rates \( \dot{\gamma} \approx 0.0026, 0.0087, 0.026 \) at (a) \( \delta \approx 0 \) and (b) \( \delta \approx 0.1 \). Particles are coloured according to their effective interaction parameter \( \epsilon_{eff}^i \) values. See colour scale bar for \( \epsilon_{eff}^i \) values.

In figure 7, we display the systems under shear, where particles are coloured according to their \( \epsilon_{eff}^i \), shown for different shear rates at \( \delta = 0, 0.1 \). One can see in the figure, for both selective and non-selective wall types, that there are regions of high \( \epsilon_{eff}^i \) surrounded by regions of low \( \epsilon_{eff}^i \) values. For \( \delta \gg 0 \), particles are homogeneously distributed in the film (as discussed above) and smaller regions of relatively high \( \epsilon_{eff}^i \) values are observed, and as \( T \to T^* \) (from above) high \( \epsilon_{eff}^i \) regions gets bigger.
To gain further insight, we proceed to understand the spatial ordering of particles’ identity at different locations of the film characterised by laterally averaged $\langle \epsilon_{i}^{\text{eff}} \rangle$ profile and $\epsilon_{i}^{\text{eff}}$ distributions as shown in figures 8 and 9 respectively. We observe that the laterally averaged $\epsilon_{i}^{\text{eff}}$ profile closely follows that of the corresponding $\langle \epsilon_{i} \rangle$ profile shown in figure 4. For both APD systems, at a given temperature, when we increase shear rate the spatial distribution of particles as well as the effective identity becomes homogeneous throughout the film indicated by the flattening of the curve and thus the effect of substrate quality is insignificant at high shear rates (see $\langle \epsilon_{i}^{\text{eff}} \rangle$ profiles for $\delta \approx -0.1$ and 0 in the figure).

For $\delta > 0$, where the system is in a fluid state, the profile is independent of $\dot{\gamma}$ (except for small differences close to the walls at small shear rates). On the other hand, $\epsilon_{i}^{\text{eff}}$ distributions show that as shear rates increase, the peak position is shifted to a lower value. The mean value $\langle \epsilon_{i}^{\text{eff}} \rangle$ at different shear rates is plotted in figure 10 for APD systems. Below the transition temperature, $\langle \epsilon_{i}^{\text{eff}} \rangle$ slightly increases with increasing $\dot{\gamma}$ and then decreases beyond a threshold value as indicated in the figure for $\delta \approx -0.1$. The decrease of $\langle \epsilon_{i}^{\text{eff}} \rangle$ with increasing shear rate is observed for all the temperatures considered. However, at high temperature (see $\delta \approx 1.5$ in the figure) the shear rate dependence of $\langle \epsilon_{i}^{\text{eff}} \rangle$ is very weak. It is expected that the curves for relatively small $\delta$ (i.e., close to transition temperature $T^*$) will approach that of the high temperature of the respective systems at sufficiently high $\dot{\gamma}$ values, where the applied mechanical shear dominates over the interparticle interaction and the local identity ordering is completely destroyed. Between the two APD systems, no qualitative difference is observed, but only a quantitative difference, i.e., for a given shear rate $\langle \epsilon_{i}^{\text{eff}} \rangle$ is relatively high for the APD system with ns-wall. The observed decrease in mean effective interaction parameter with increasing shear rate is associated with the structural changes in the system and is consequently reflected in the macroscopic response of the system discussed in the following section.

### 3.3 Macroscopic response

When mechanical shear is introduced to simple fluids, a wide variety of interesting effects such as shear-induced ordering and phase transition, and non-Newtonian rheological behaviour, i.e., shear thinning or shear thickening, are observed [47–49,51–53]. For the present APD fluid system also, the rheological behaviour or the macroscopic response under shear is studied. In particular, we calculate shear viscosity $\eta_{xy}$ defined as

$$\eta_{xy} = \frac{\sigma_{xy}}{\dot{\gamma}},$$

where $\sigma_{xy}$ is the shear stress, to see whether there is any qualitative and quantitative differences among the systems. In general, shear viscosity is related to the shear
Shear viscosity $\eta_{xy}$ against the imposed steady shear rate $\dot{\gamma}$ for the APD systems with (a) non-selective wall and (b) selective wall at different values of reduced temperatures $\delta$. (c) Typical steady-state configurations during (i) first shear thinning, (ii) shear thickening, (iii) second shear thinning corresponding to the points marked (i)--(iii), respectively, in the curve of figure (b) inset for $\delta = -0.1$. Fluid particles are coloured according to the value of $\langle \epsilon_{i}^{\text{eff}} \rangle$ (see colour scale bar).

Figure 12. Comparison of shear viscosity $\eta_{xy}$ profiles among different systems indicated in the figure for (a) $\delta = -0.1$, (b) $\delta = 0$ and (c) $\delta = 0.1$.

Figure 11. Shear viscosity $\eta_{xy}$ against the imposed steady shear rate $\dot{\gamma}$ for the APD systems with (a) non-selective wall and (b) selective wall at different values of reduced temperatures $\delta$. (c) Typical steady-state configurations during (i) first shear thinning, (ii) shear thickening, (iii) second shear thinning corresponding to the points marked (i)--(iii), respectively, in the curve of figure (b) inset for $\delta = -0.1$. Fluid particles are coloured according to the value of $\langle \epsilon_{i}^{\text{eff}} \rangle$ (see colour scale bar).

where $\alpha = 0$ for the Newtonian fluid and $\alpha \neq 0$ for the non-Newtonian fluid. Fluids with $\alpha < 0$ show shear thinning and $\alpha > 0$ show shear thickening.

Typical shear viscosity profiles of the APD systems for temperature close to $T^*$ is shown in figure 11. For $T < T^*$ (i.e., $\delta < 0$ in the figure), it is observed that the shear viscosity $\eta_{xy}$ decreases with increasing $\dot{\gamma}$ (shear thinning) which is followed by an increase in $\eta_{xy}$ on further increasing $\dot{\gamma}$ (shear thickening) and finally a decrease again at high $\dot{\gamma}$ values (second regime of shear thinning). The shear thickening happens in a relatively short range of $\dot{\gamma}$, and the onset of shear thickening shifts towards smaller $\dot{\gamma}$ values as $T \to T^*$, e.g., at $\delta = -0.1$ the onset is observed at $\dot{\gamma} \approx 0.013$ for APD with s-wall, see (i) marked point in figure 11b. Note that the onset of shear thickening also corresponds to the decrease in average interaction parameter $\langle \epsilon_{i}^{\text{eff}} \rangle$, see the asterisk marked point in figure 10 for APD with s-wall at $\delta = -0.1$, and thus reflects the structural as well as local particle identity ordering changes with increasing shear rate. Steady-state configurations of the systems around the shear thickening region is shown in figure 11c. It is evident from the configurations that before the onset of shear thickening no major identity reorganisation takes places and thus $\langle \epsilon_{i}^{\text{eff}} \rangle$ is roughly constant (e.g., see figure 10 for $\delta < 0$). Comparison of figure 10c(i) and figure 10c(ii) clearly shows that a strong spatial and identity ordering happens during the shear thickening, where we see particle clustering (i.e., formation of a denser phase composed predominantly of high-$\epsilon_{i}^{\text{eff}}$ particles). Shear thinning and thickening behaviour is prevalent in a wide variety of dense suspensions, e.g. in concentrated colloidal systems [34–38]. The associated microstructural changes observed for the APD fluid are very similar to that of the colloidal systems, i.e., with increasing shear rate the particles become organised in the flow and hence reduce the viscosity (shear thinning), and at sufficiently high shear rates, strong hydrodynamic coupling between particles dominates over random ones leading to the formation of hydrocluster – a transient concentration fluctuation that is driven and sustained by the applied shear field [34,38]. The second regime of shear thinning (observed for $\delta < 0$), which is understood as a manifestation of the finite elasticity of the particles [34], corresponds to gradual melting and hence decrease in $\langle \epsilon_{i}^{\text{eff}} \rangle$ leading to a completely disordered fluid phase. When $\delta \geq 0$ only one regime of shear thickening is observed and shear viscosity weakly depends on the shear rate, i.e., $\eta_{xy} \sim \dot{\gamma}^0$.

In figure 12, we show comparison among the systems at three different temperatures. Both shear thinning and shear thickening is observed for temperature slightly
below $T^*$. As shown in figure 12a, for $\delta = -0.1$, at very small shear rates all systems show $\eta_{xy} \sim \dot{\gamma}^0$, and first shear thinning (i.e., $\eta_{xy} \sim \dot{\gamma}^{-\alpha}$) sets in above a threshold value $\dot{\gamma}_c \approx 0.0026$ with $\alpha \approx 1$ for APD/ns-wall system and $\dot{\gamma}_c \approx 0.0044$ for 1C system. Typically, non-Newtonian behaviour sets in for $\gamma \tau \geq 1$ with $\tau$ the relevant relaxation time scale \[51\]. Here, the time scale corresponding to the onset of shear-thinning transition is roughly estimated to be $\tau_c \approx 1/\dot{\gamma}_c \approx 384\tau_{LJ}$ (APD/ns-wall) and $250\tau_{LJ}$ (1C) at $\delta \approx -0.1$. From the APD system in equilibrium (and no confinement), reported in ref. [23], it is known that this heterogeneous system shows a broad distribution of relaxation times, where the large (small) $\epsilon_i$ particles have the large (small) relaxation times, and the difference $\Delta \tau$ increases with lowering temperature. Typically, at $\delta \approx -0.1$, the relaxation time due to diffusion $\tau$ is found to be in the range 100–200 in LJ units (for large $\epsilon_i$ particles) which is of the same order of magnitude as $\tau_c$, while $\tau \approx 1$ for smallest $\epsilon_i$ particles. These observations suggest that the onset of shear thinning is governed by the time scale of structural relaxation of the largest $\epsilon_i$ particles which form the long-lived cluster in the sense that the time taken for such particles to completely change the identity of neighbouring particles in a cage (formed by the neighbouring particles) is the longest. For the APD system with the s-wall, first shear thinning sets in at a slightly lower value ($\dot{\gamma} \approx 0.0017$) and continues up to $\dot{\gamma} \approx 0.01$ with exponent $\alpha \approx 0.33$.

Comparing the values of exponent $\alpha$, it is clear that the first shear thinning is relatively strong for 1C and APD systems with the ns-wall, and the onset value $\dot{\gamma}_c$ is smallest for the APD with the s-wall and largest for the 1C system. Upon increasing $\dot{\gamma}$ further, shear thickening is observed followed by second shear thinning with exponent $\alpha \approx 0.78$ for all the systems. We note that as $\delta \rightarrow 0$ the onset of the first shear thinning shifts towards smaller value of $\dot{\gamma}$. For $\delta \geq 0$, the only shear thinning is observed with exponent $\alpha \approx 0.42$ (see figure 12b). As $\delta$ becomes positive and gets larger (i.e., fluid phase further away from $T^*$) the exponent $\alpha \rightarrow 0$ and shows Newtonian-like behaviour for all the systems.

### 4. Conclusion

We have studied the effect of linear flow field on the spatial and particle identity ordering, density profiles, and macroscopic response of a multicomponent fluid model. All the particles in the system are different in the sense that different particles have different values of interaction parameter $\epsilon_i$ drawn from a uniform distribution. In equilibrium, this multicomponent fluid model system exhibits local self-organisation and clustering of particles according to their identity, i.e. a non-random state, leading to different dynamical properties for different particle types. When the system is subjected to steady flow field, depending on the shear rate, it displays various interesting features. We focussed on temperature close to the solidification transition and investigated the system at various shear rates considering non-selective and selective substrate types. The results are briefly summarised below.

The particle density profiles of the two APD systems are significantly different, e.g., the density profile for the APD with s-wall is maximum in the bulk and minimum near the substrates. But, there is particle enrichment near the interface and hence higher density than the bulk value in the case of APD with ns-wall. As we increase the shear rate, particle density becomes homogeneous and no difference is seen between the two APD systems in the bulk. However, close to the substrate, significant difference in the density is observed even at high shear rates. It is interesting to note that the density profiles of APD (ns-wall) and 1C systems are very similar.

Further study of the radial distribution function reveals that this homogenisation is related to the shear-induced melting, where higher-order peaks (corresponding to hexagonal packing) in $g(r)$ disappears at high shear rates. Apart from structural changes, one of the main concern of this study is to understand how the neighbourhood identity ordering is affected due to shear. As detailed in §3.2, the neighbourhood identity ordering is characterised through $\epsilon_i^{eff}$. The laterally averaged profiles of $\epsilon_i^{eff}$ (or $\epsilon_i$) closely follow that of the corresponding density profiles, and high-density regions predominantly consists of $\epsilon_i^{eff}$ (or $\epsilon_i$) particles (see figure 8). At high shear rates (or relatively high temperature), homogeneous particle distribution is observed (except for small deviations near the substrates). Furthermore, the $\epsilon_i^{eff}$ distribution shows that the mean of the distribution is shifted to lower values with increasing shear rates and hence $(\epsilon_i^{eff})$ also decreases. We found only quantitative difference between the systems with selective and non-selective substrates, i.e., $(\epsilon_i^{eff})$ for system with selective walls is consistently higher in the range of $\dot{\gamma}$ considered. It is clear from this observation that the local particle identity ordering is affected by the quality of substrates and it is reflected in the global average quantity (i.e., selective substrate type leads to higher value of $(\epsilon_i^{eff})$).

Finally, we looked at the behaviour of shear viscosity, $\eta_{xy}$, for both systems. Below the transition temperature, both energy polydispersed and 1C systems show shear-thinning as well as shear-thickening regimes, and
shear thickening is more pronounced as we go below the transition temperature. Shear thickening is also associated with transient increase of \( \langle \epsilon_{\text{eff}} \rangle \). Shear thickening is followed by shear thinning again leading to shear-induced melting at high shear rates. Exponent characterising shear thinning varies with the system and depends on temperature. It is important to point out that APD fluid with selective (non-selective) substrate has the shear viscosity below (or above depending on \( T \)) that of 1C fluid indicating that by tuning the substrate or wall properties, one can tune the shear viscosity of this multicomponent fluid.

In conclusion, we present a comprehensive study on the effect of flow field on the energy polydisperse fluid, an idealised multicomponent fluid model in 2D. We believe that the results of this work, in addition to complex fluids in general, is also of relevance in understanding e.g. particle organisation in high entropy alloys. A possible extension of the current work is to be considered, e.g., other distribution types of interaction parameter, and extension to 3D.

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