Microscopic theory for anisotropic pair correlations in driven binary mixtures

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Received 20 April 2012, in final form 28 May 2012
Published 31 October 2012
Online at stacks.iop.org/JPhysCM/24/464115

Abstract
A self-consistent microscopic approach to calculate non-equilibrium pair correlations in strongly interacting driven binary mixtures is presented. The theory is derived from the many-body Smoluchowski equation for interacting Brownian particles by employing Kirkwood’s superposition approximation as a closure relation. It is shown that the pair correlations can exhibit notable anisotropy and a strong tendency to laning in the driving direction. Furthermore, there are strong indications that pair correlations are characterized by a long-range decay along the drive. The theoretical results are in good quantitative agreement with the complementary Brownian dynamics computer simulations.

(Some figures may appear in colour only in the online journal)

1. Introduction

It is a great theoretical challenge to predict structural and dynamical correlations for a strongly interacting classical system by using the interparticle interaction forces as the only input. Most conventional approaches, such as liquid integral equations [1], density functional [2, 3], or mode coupling theory [4] focus on correlations in equilibrium. The use of a microscopic theory for predicting correlations in non-equilibrium regimes is, however, much more difficult—only a few attempts have been made so far. The most advanced theories were constructed for colloidal particles which perform completely overdamped Brownian motion in a solvent. Non-equilibrium states in colloidal dispersions can be conveniently created by applying and controlling external driving forces, and the trajectories of the individual particles can be observed in real space [5, 6].

The dynamical density functional theory (DDFT) [7–9] is one of the microscopic theories describing correlations in Brownian systems out of equilibrium. However, DDFT assumes that the pair correlations in non-equilibrium are the same as those in an appropriate equilibrium reference system. Therefore, DDFT does not make self-consistent predictions for non-equilibrium pair correlations. One should also mention successful generalizations of mode coupling theory [10–13] to treat dynamical correlations in shear flows (which represent a special non-equilibrium case). Recently, mode coupling theory has also been applied to microrheology, where a single particle is dragged through a suspension [14]. Finally, there is a systematic theory for the change of pair correlations, based on the many-body Smoluchowski equation and developed by Szamel and co-workers [15, 16], see also [17].

Binary mixtures of oppositely driven colloidal particles or ions represent an ideal model system to study non-equilibrium phenomena in strongly interacting systems. When the driving force is sufficiently strong, one can observe the formation of lanes, which is considered as a prototype of a non-equilibrium transition [18, 19]. Lanning of driven colloids has been confirmed in subsequent investigations [20–22] and was found to occur—apart from colloids—in a variety of other systems including complex plasmas [23], ions in membranes [24], granulates [25, 26], pedestrians [27–29], social insects [30] and bacteria as well as cells and artificial microswimmers [31]. There have been attempts to describe lanning with a microscopic DDFT [32, 33], but such an approach needs a phenomenological current term which could only be grossly justified.
In this paper, we present a self-consistent microscopic approach for non-equilibrium pair correlation functions in the steady state of driven binary mixtures. The theory is based on the many-body Smoluchowski equation for interacting Brownian particles [34], and employs Kirkwood’s superposition approximation as a closure relation [35–37]. We solve the derived equations numerically for a 2D case and demonstrate that the pair correlations exhibit notable anisotropy and a strong tendency to laning in the driving direction. Furthermore, there are strong indications that pair correlations are characterized by a long-range decay along the drive. The theoretical results are in good quantitative agreement with the complementary Brownian dynamics computer simulations.

The paper is organized as follows. In section 2 we describe the model. The theory and the simulation technique are discussed in sections 3 and 4. Results for the pair correlations are presented in section 5. Finally, in section 6 we briefly summarize the implications and outlook for future work.

2. The model

We consider an equimolar binary mixture of species A and B, consisting in total of 2N particles. The particle coordinates are denoted with

\[ \{r_1^A, \ldots, r_N^A, r_1^B, \ldots, r_N^B\} \equiv \{r_{2N}\}, \]

where the upper index indicates the species and the lower index is its number. The interaction \( V_{ij}^{AB} \) between two particles with coordinates \( r_i^\alpha \) and \( r_j^\beta \) is described via a spherically symmetric pair potential,

\[ V_{ij}^{AB} \equiv V(|r_i^\alpha - r_j^\beta|), \]

with \( \alpha, \beta \in \{A, B\} \) and \( i, j \in \{1, \ldots, N\} \). Our theoretical equations derived below are in principle valid for \( V(|r|) \) of arbitrary form (e.g., for hard-sphere, Yukawa, or soft-sphere interactions), but in this paper we only present results for a Gaussian soft core potential [38].

The system is brought into a non-equilibrium steady state by applying an external driving force acting on individual particles, \( \mathbf{F}_{\text{ext}} \). For all particles the absolute value of the force is the same and equal to \( F \), but species A and B are driven in opposite directions,

\[ \mathbf{F}_{\text{ext}}^{\alpha} = \begin{cases} +Fe_y & \text{for } \alpha = A, \\ -Fe_y & \text{for } \alpha = B, \end{cases} \]

where \( e_y \) is the unit vector along the y-axis.

The trajectories \( r_i^\alpha(t) \) of individual particles in the Brownian dynamics regime are governed by the fully overdamped Langevin equation [39],

\[ \xi \dot{r}_i^\alpha = F_i^\alpha(|r_{2N}|) + \mathbf{f}_i^\alpha(t), \]

where \( \xi \) is a friction coefficient. Here, the total systematic force \( F_i^\alpha \) is a superposition of the pair interactions and the external force. The random force \( \mathbf{f}_i^\alpha(t) \) is Gaussian, with zero mean and second moments governed by the fluctuation-dissipation theorem [1],

\[ \mathbf{f}_i^\alpha(t) \sim 0, \]

\[ \mathbf{f}_i^\alpha(t)\mathbf{f}_j^\beta(t')^\top = 2\xi k_B T \delta_{ij} \delta(t-t')\mathbb{I}, \]

where the bar denotes a noise average, \( T \) is the system temperature, \( \delta_{ij} \) is the Kronecker symbol, \( \delta(t) \) is the Dirac delta function and \( \mathbb{I} \) is the unity matrix.

In the following we employ the mean interparticle distance \( a \) (to be defined later) as a suitable length scale and the thermal energy \( k_B T \) as an energy scale. We use the Brownian time \( \tau_B = a^2/D_0 \) as a time scale, with \( D_0 = k_B T/\xi \) being the short-time self-diffusion coefficient. In these units, the strength of the external force can be expressed in terms of a dimensionless Péclet number

\[ \text{Pe} = \frac{Fa}{k_B T}. \]

For \( \text{Pe} = 0 \), the system is in equilibrium, in a completely mixed state with isotropic fluid partial densities. Starting from this mixed configuration, a finite drive \( \text{Pe} > 0 \) leads to a non-equilibrium situation, where the system develops towards an anisotropic steady state after a certain relaxation period. Below we focus on the pair correlations in this non-equilibrium steady state.

3. Theory

The essential quantities studied here are the partial pair correlation functions in the steady state, which are defined as

\[ g_{\alpha\beta}(\mathbf{r}, \mathbf{r}') \equiv 4/\rho^2 \left\langle \sum_{i,j=1}^{N} \delta(|\mathbf{r}_i^\alpha(t) - \mathbf{r}_i^\beta(t)|)\delta(|\mathbf{r}_j^\alpha(t) - \mathbf{r}_j^\beta(t)|) \delta(\mathbf{r}' - \mathbf{r}_i^\beta(t)) \right\rangle, \]

where \( \rho \) is the total number density (of both species), \( \alpha, \beta \in \{A, B\} \) and \( \langle \cdots \rangle \) denotes a time or configurational average in the steady state. Since we are away from any freezing transition and macroscopic pattern formation, we assume that the steady state is homogeneous. Then translational invariance implies that

\[ g_{\alpha\beta}(\mathbf{r}, \mathbf{r}') = g_{\alpha\beta}(\mathbf{r}' - \mathbf{r}), \]

while the spherical symmetry is naturally broken due to the external drive. For the self-correlations there is spatial inversion symmetry,

\[ g_{\alpha\alpha}(\mathbf{r}) = g_{\alpha\alpha}(-\mathbf{r}). \]

In symmetric mixtures, there is another underlying symmetry upon the swap of the particle species: the equations of motion remain invariant upon the transformation \( (F \rightarrow -F, A \leftrightarrow B) \), which implies

\[ g_{BB}(\mathbf{r}) = g_{AA}(\mathbf{r}), \]

\[ g_{BA}(\mathbf{r}) = g_{AB}(-\mathbf{r}). \]
for asymmetric mixtures, such as, e.g., colloid–polymer mixtures [40].

For a microscopic description we now introduce the many-body probability density \( \Psi([r_{2N}], t) \). The quantity \( \Psi([r_{2N}], t) \, dr^{2N} \) represents the probability of finding the system at time \( t \) in the infinitesimal element \( dr^{2N} \) around the state \([r_{2N}]\). In order to construct a theory for the anisotropic steady state pair correlations we start from the Smoluchowski equation, which is stochastically equivalent to the Langevin equations [41] and reads as

\[
\frac{d\Psi([r_{2N}], t)}{dt} = D_0 \sum_{i=1}^{N} \sum_{a=A,B} \nabla_i \cdot \left[ x_i \nabla_i \Psi([r_{2N}], t) \right] - \frac{F}{k_B} \Psi([r_{2N}], t), \tag{8}
\]

where \( \nabla_i \) is the gradient operator with respect to \( r_i \).

By integrating out a certain number of degrees of freedom in equation (8) we obtain an equation for the reduced probability density. This procedure yields a set of hierarchical equations, which can be associated with the Bogolyubov–Born–Green–Kirkwood–Yvon (BBGKY) hierarchy (cf. [1]). By retaining the coordinates of two particles—either of the same or of different species—and taking into account that in the steady state the partial time derivative vanishes, we obtain the following equations for self- and cross-correlations, respectively:

\[
k_B T (\Delta^2_i + \Delta^2_j) g_{AA}(r^2_i - r^2_j) = -2 \nabla_i \cdot \left[ \nabla_i (\nabla_i V_{12}^{AA}) g_{AA}(r^2_i - r^2_j) \right] - \frac{\rho}{2} \sum_{i=1,2} \nabla_i \int d^3 r_i \nabla_i (\nabla_i V_{12}^{AA}) g_{AA}(r_i^2, r_i^2, r_i^2) - \frac{\rho}{2} \sum_{i=1,2} \nabla_i \int d^3 r_i \nabla_i (\nabla_i V_{12}^{AA}) g_{AA}(r_i^2, r_i^2, r_i^2) \tag{9}
\]

and

\[
k_B T (\Delta^2_i + \Delta^2_j) g_{AB}(r^2_i - r^2_j) = -2 \nabla_i \cdot \left[ \nabla_i (\nabla_i V_{12}^{AB}) g_{AB}(r^2_i - r^2_j) \right] - \frac{\rho}{2} \sum_{i=1,2} \nabla_i \int d^3 r_i \nabla_i (\nabla_i V_{12}^{AB}) g_{AB}(r_i^2, r_i^2, r_i^2) - \frac{\rho}{2} \sum_{i=1,2} \nabla_i \int d^3 r_i \nabla_i (\nabla_i V_{12}^{AB}) g_{AB}(r_i^2, r_i^2, r_i^2) + F \nabla_i (\nabla_i V_{12}^{AB}) g_{AB}(r^2_i - r^2_i), \tag{10}
\]

where \( \Delta_i^2 \) is the Laplace operator with respect to \( r_i^2 \). These equations are exact but not closed, since they involve the triplet correlation functions defined via

\[
g_{\alpha\beta\gamma}(r, r', r'') = \frac{1}{\rho^3} \left\{ \sum_{i,j,k=1}^N \delta(r - r^\alpha_i) \delta(r' - r^\beta_j) \delta(r'' - r^\gamma_k) \right\},
\]

where \( \alpha, \beta, \gamma \in [A, B] \). The non-equilibrium triplet correlations are in general not known; even in equilibrium they are highly nontrivial [42].

Here we propose a closure relation based on the traditional Kirkwood superposition approximation (KSA) [37] which becomes asymptotically exact for low densities [43]. For our non-equilibrium situation, we supplement this closure with a symmetrization postulate borrowed from the study of polymeric liquids [36]. The symmetrized Kirkwood closure reads

\[
g_{\alpha\beta\gamma}(r_1, r_2, r_3) \approx \tilde{g}_{\alpha\beta}(r_2 - r_1) \tilde{g}_{\alpha\gamma}(r_3 - r_1) \tilde{g}_{\beta\gamma}(r_3 - r_2), \tag{11}
\]

where the bar denotes a symmetrized pair correlation.

\[
\tilde{g}_{\alpha\beta}(r) = \frac{1}{2}(g_{\alpha\beta}(r) + g_{\beta\alpha}(r)). \tag{12}
\]

The symmetrization allows us to preserve the principal inversion symmetry of self-correlations. This operation (degenerate in equilibrium mixtures) becomes nontrivial in the driven regime, when cross-correlations are no longer symmetric, see equation (7).

The resulting closed but approximate equations for the two independent steady state correlations \( g_{AA}(r) \) and \( g_{AB}(r) \) then read

\[
k_B T \Delta g_{AA} = -\nabla \left[ \nabla (V V) g_{AA} \right] - \frac{\rho}{2} \nabla \left[ (K_{AA} * g_{AA}) g_{AA} \right] - \frac{\rho}{2} \nabla \left[ (K_{AB} * \tilde{g}_{AB}) g_{AB} \right]. \tag{13}
\]

\[
k_B T \Delta g_{AB} = -\nabla \left[ (V V) g_{AB} \right] - \frac{\rho}{2} \nabla \left[ (K_{AB} * \tilde{g}_{AB}) g_{AB} \right] - \frac{\rho}{2} \nabla \left[ (K_{AB} * \tilde{g}_{AB}) g_{AB} \right] + F \nabla (V V) g_{AB}. \tag{14}
\]

where \( K_{\alpha\beta} \equiv K_{\alpha\beta}(r) = (V V)(r))g_{\alpha\beta}(r) \) and \( \tilde{K}_{\alpha\beta}(r) = (V V)(r))\tilde{g}_{\alpha\beta}(r) \) are auxiliary functions, \( V \) and \( \Delta \) are the operators with respect to the relative coordinate \( r \), and \(*\) denotes the convolution of the functions \( f_1(r) \) and \( f_2(r) \)

\[
(f_1 * f_2)(r) = \int dr' f_1(r')f_2(r - r').
\]

The two coupled nonlinear integro-differential equations (13) and (14) cannot be solved analytically for \( F \neq 0 \) and finite \( \rho \). We have therefore employed a Picard and Krasnoselskij fixed point iteration scheme (see, e.g., [44–46]) to solve them numerically, where analytical solutions in the limit \( \rho \to 0 \) were used as inputs for the fixed point iterations. Results obtained with this numerical procedure for a 2D problem are discussed in section 5.

4. Computer simulations

We have performed Brownian dynamics computer simulations to verify the proposed theory. In this paper, the results are limited to a 2D case, which is sufficient for the basic comparative analysis of pair correlations.

The simulations with \( 2N = 50\,000 \) particles were performed in a quadratic box with periodic boundary
Figure 1. Equilibrium pair distribution functions of the Gaussian particle fluid. The pair interaction potential is given by equation (15) and the results shown are for (a) $V_0 = 50k_B T$, $\sigma^2 = 0.3a^2$ and (b) $V_0 = 300k_B T$, $\sigma^2 = 0.1a^2$. The solid lines represent results obtained from Brownian dynamics simulations and the dashed lines are theoretical results calculated from our microscopic theory. The distance is in units of the mean interparticle distance $a$.

Figure 2. Contour plots of the self-correlation function, $g_{AA}(x,y)$, for (a) $Pe = 4$ and (b) $Pe = 32$. The left panel shows theoretical results (numerical solution of equations (13) and (14)) and the right panel represents Brownian dynamics simulations. The interaction parameters are $V_0 = 300k_B T$ and $\sigma^2 = 0.1a^2$.

conditions. We used a simple first-order forward time algorithm [47, 48] to solve equation (1) for all particles. The mean interparticle distance $a$ (which sets the Brownian time $\tau_B$) was identified as $a = \rho^{-1/2}$, where $\rho = 2N/A_0$ is the total number density expressed via the simulation area $A_0$. We used a finite time step $\Delta t$ which was carefully adjusted to the magnitude $Pe$ of the driving force. For equilibrium simulations we set $\Delta t = 10^{-3}\tau_B$, while in non-equilibrium simulations with $Pe > 1$ a reduced time step of $\Delta t = 10^{-3}\tau_B/Pe$ was employed to give reliable trajectories. Starting from an initial equilibrium configuration, the external force was instantaneously switched on and the system relaxed to the steady state in about $50\tau_B$. Afterwards, statistics were taken over a time period of $50\tau_B$ which turned out to be sufficient to accumulate spatially resolved data for the anisotropic steady state pair correlations.

5. Results

In the following we present results obtained for a Gaussian interaction potential. The use of this interaction, which
Figure 3. Contour plots of the cross-correlation function, $g_{AB}(x, y)$, for the same parameters as in figure 2.

The non-equilibrium self-correlation functions $g_{AA}(x, y)$ obtained for $Pe = 4$ and 32 are presented in figure 2. Both theoretical and simulation data are shown in contour plots over the $(x, y)$-plane. First, the correlations are anisotropic and the anisotropy clearly increases with the driving force. For larger $Pe$, the probability that particle pairs are aligned along the drive is dramatically enhanced. Second, there is a good agreement between simulation and theory.

For more detailed comparison between theory and simulation, in figure 4 we show the longitudinal distributions, $g_{AB}(0, y)$, plotted along the driving field. Again, we can see that the qualitative features seen in the simulations are generally well reproduced by the theory. Interestingly, the cross-correlations $g_{AB}(0, y)$ exhibit a long-range depletion tail of $B$-particles (in the wake of the $A$-particle). The oscillations

\begin{equation}
V(|r|) = V_0 e^{-|r|^2/\sigma^2},
\end{equation}

where $V_0$ is the potential amplitude and $\sigma$ quantifies the interaction range. We have used combinations $V_0 = 50k_B T$ and $\sigma^2 = 0.3a^2$, or $V_0 = 300k_B T$ and $\sigma^2 = 0.1a^2$, both ensuring states far away from the freezing transition [38].
Figure 4. Longitudinal self- and cross-correlation functions, $g_{AA}(0, y)$ (left panel) and $g_{AB}(0, y)$ (right panel), respectively, plotted for (a) $Pe = 4$, (b) $Pe = 16$, and (c) $Pe = 32$. The arrows indicate the direction of the driving force (for the particle at the center).

6. Discussion and outlook

In this paper we proposed a self-consistent approach to calculate non-equilibrium pair correlations in driven binary mixtures. The approach is obviously not limited to symmetric mixtures: our principal aim here was to demonstrate that the proposed microscopic theory adequately represents the onset and development of laning, and the symmetry was only utilized in order to minimize the number of degrees of freedom and, hence, to simplify the numerical treatment of the problem. What is even more important, the theory could also be applied to time-dependent driving forces, which would allow us to tackle the fundamental problem of banding in oscillating fields [5, 55–57].

The direct comparison between theory and simulations shows that all equilibrium results as well as self-correlations $g_{AA}(r)$ in non-equilibrium regimes agree very well. On the other hand, the cross-correlations $g_{AB}(r)$—which exhibit strong asymmetry—reveal significant deviations, as one can see in the right panel of figure 4. We suppose that these deviations reflect disadvantages of the symmetrized KSA employed in our theory: artificial ‘downstream’ oscillations might well be caused by the enforced symmetry in three-particle distributions, due to mirroring of ‘upstream’ oscillations. Therefore we believe that for sufficiently strong driving forces, where the symmetry in $g_{AB}(r)$ naturally increases due to the growth of long lanes, the agreement between theory and simulations should improve as well.

We note that in this paper we only considered steady states at relatively small forces, due to complications arising in the numerical analysis. In future, we plan to investigate the role of stronger forces and implement numerics on much occurring in the tail of the theoretical curve can possibly be attributed to the symmetrization used in the KSA.

Finally, we studied a long-range behavior of the correlations at a rather strong drive ($Pe = 24, 36, 44$). For this purpose, in the simulations we calculated one-dimensional slice cuts of the correlation functions with a very high amount of statistics. Figure 5 illustrates how the correlations decay towards unity. The (nearly) linear curves seen in the double logarithmic plots suggest that the pair correlations themselves exhibit inverse-power-law tails $\propto y^{-\rho}$ at large distances, with $\rho$ between 1 and 2. Similar behavior of pair correlations upon differential motion of species is well known, e.g., from microrheology, where the motion of a probe particle through a compressible fluid induces a dipolar asymptote [51] (see also [52–54]). We note, however, that in the latter case power-law decay at large distances is predicted for $Pe \ll 1$, while for $Pe \gg 1$ exponential decay is expected again.
larger lattices (in order to suppress boundary effects in the employed Fourier methods; such undesired effects can strongly influence the long-distance tails of the correlation functions).

In fact, the asymptotic behavior of the correlation functions at large distances is of fundamental importance, because it could shed light on many important issues of self-organization in driven systems. In particular, the inverse-power-law decay of $g_{\alpha\beta}(r)$ towards 1.0 could be indicative of (approaching) divergence in the structure factors $S_{\alpha\beta}(k)$, associated with diverging correlations along the driving field (e.g., the decay $\propto r^{-p}$ of pair correlations could in principle result in a divergence when $p < 2$ in the 2D case or $p < 3$ in the 3D case—depending on the angle). The existence (or nonexistence) of such a divergence could help us to clarify the long-standing issue of whether the laning can indeed be considered as a non-equilibrium phase transition (occurring at a certain critical field) or it is merely a structural crossover [58]. Thus, the asymptotic behavior of pair correlations undoubtedly requires separate careful investigations.

Finally, we would like to point out that the laning is a topological process. For instance, if we consider a pair of lanes of one species separated by a lane of another species, then their mutual development could be very different in 2D and 3D systems: if the separating lane is infinite the other two lanes will never merge in the former case, while in the latter case merging is not inhibited. Therefore, the development of laning, the very existence of a hypothetical phase transition and, of course, its order [5, 58] could be primarily affected by the dimensionality of the experimental setup.

Acknowledgments

We thank J Chakrabarti and J Horbach for helpful discussions. This research was supported by the DFG within SFB TR6 (project C3) and by the European Research Council under the European Union’s Seventh Framework Programme (FP7/2007–2013)/ERC Grant agreement 267499.

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