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1990 J. Phys.: Condens. Matter 2 5849

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A test of the timescale separation in solutions containing interacting Brownian-type particles

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Received 2 January 1990, in final form 17 April 1990

Abstract. Theoretical work has shown that the timescale separation required for the application of the Smoluchowski, Fokker–Planck and Langevin equations to interacting Brownian particles in concentrated liquid solutions may not exist. In particular, it was suggested that the current autocorrelation function of the Brownian particles may not decay sufficiently quickly in comparison with the intermediate scattering function at appropriate wave vectors. Here, molecular dynamics (MD) calculations are performed for ‘hard–soft–sphere’ liquid solutions containing Brownian-type particles of large mass and volume. The mass and volume ratio are varied systematically. The MD results indicate the following: (i) for solutions of equally sized particles, the current autocorrelation function of the massive particles decreases sufficiently quickly compared with the intermediate scattering function, thus ensuring timescale separation; (ii) massive particles of large volume diluted among light and small particles show a time decay of the current autocorrelation function, which approaches that of the intermediate scattering function. However, the similarity of the two correlation functions reduces with increasing mass ratio. Hence, for asymptotic conditions timescale separation can be expected.

1. Introduction

A few years ago Masters [1] showed that the timescale separation required for several fundamental kinetic equations, such as the Fokker–Planck or Smoluchowski equations, may not be valid for interacting Brownian particles in concentrated liquid solutions. As the latter equations are predominantly used to treat interacting Brownian particles [2] theoretically—for instance, in polymer solutions—it is of particular interest to know when the necessary timescale separation is no longer valid.

Masters showed in his study that the relevant time correlation functions (TCFs) are the intermediate scattering function, $F(\mathbf{k}, t)$ and the longitudinal current autocorrelation, $C_1(\mathbf{k}, t)$. These functions should decay on sufficiently different timescales to guarantee the applicability of the Smoluchowski, Fokker–Planck and Langevin equations. Why timescale separation is necessary for the use of these equations is reviewed in the work of Masters, so we can omit derivations here.

Our purpose is to show quantitatively the time behaviour of $F(\mathbf{k}, t)$ and $C_1(\mathbf{k}, t)$ of heavy or heavy and large particles in solution with light and small particles of a liquid model system.

2. The model solutions and the molecular dynamics calculations

Systems of ‘hard–soft spheres’ (HSS) were considered for the molecular dynamics (MD)

Table 1. Hard–soft-sphere interaction parameters.

$\sigma_{12} = 3.400 \times 10^{-10}$ m; see table 2
 $\varepsilon/k_B = 120$ K; $k_B =$ Boltzmann's constant

Table 2. System parameters of the solutions studied.

System	N_1	N_2	$(N/V)\sigma_x^3$	m_1 (amu)	m_2/m_1	σ_{22}/σ_{11}	$(\sigma_{22}/\sigma_{11})^3$	Comments
A1	246	10	0.800	40.00	16	1	1	$\sigma_{12} = \frac{1}{2}(\sigma_{11} + \sigma_{22})$
A2	246	10	0.800	40.00	25	1	1	
	251	5	0.800	40.00	25	1	1	$T^* = Tk_B/\varepsilon = 1$
B1	246	10	0.3757	31.25	8	2	8	$N_2 =$ number of Brownian-type particles
	251	5	0.3757	31.25	8	2	8	
	241	10	0.4085	31.25	8	2	8	
B2	246	10	0.3757	22.86	16	2.52	16	$(N_1 + N_2 = N)$
B3	246	10	0.3757	20.41	25	2.92	25	
	251	5	0.3757	20.41	25	2.92	25	
	246	10	0.3211	20.41	25	2.92	25	

Table 3. Technical details of the MD Calculations.

Number of particles (N)	256 500	Number of runs	$\left\{ \begin{array}{l} 25 (N = 256) \\ 3 (N = 500) \end{array} \right.$
Integration time-step	0.5×10^{-14} s		
Number of steps per run	1.8×10^5		
Computation time per 1000 steps (Cyber 205)			$\left\{ \begin{array}{l} 14.4 (N = 256) \\ 34.0 (N = 500) \end{array} \right.$
$NVEp$ ensemble; $V =$ total volume, $E =$ total energy, $p =$ total momentum (Stoermer–Verlet integration scheme)			

calculations. The interaction of the particles was assumed to be of the form

$$u_{\alpha\beta}(r) = \varepsilon(\sigma_{\alpha\beta}/r)^{42}$$

where α, β indicate the interaction between species, $u_{\alpha\beta}(r)$ denotes the potential energy depending on the separation, and ε and $\sigma_{\alpha\beta}$ denote the energy and volume parameters, respectively. The interaction parameters are listed in tables 1 and 2 for the solution types considered herein. Use of the HSS system has a lot of advantages [3]: for example, the temperature is a scaling parameter, the HSS system approximates the HS system well and there are no problems due to cut-off separations. Solutions containing total numbers of particles of 256 and 500 were considered. Of these particles 5 or 10 were chosen as Brownian-type molecules. A reduced density of $n^* = \sigma_{11}^3 N/V = 0.8$ was chosen for the isotopic mixtures (systems A) corresponding to liquid density. For solutions with different volume ratios of the particle species, we fixed the reduced density in the one-fluid approximation: $n_x^* = \sigma_x^3 N/V$, where σ_x^3 is defined by the expression

$$\sigma_x^3 = \sum_{\alpha=1, \beta=1}^2 x_\alpha x_\beta \sigma_{\alpha\beta}^3 \quad x_\alpha = \text{mole fraction.}$$

Because of the bulky particles we chose a density smaller than the liquid density in these cases to facilitate equilibration of the MD system. The influence of the density upon the results was, however, tested. A compilation of all the systems and parameters studied is given in table 2.

Our MD calculations were performed in the manner extensively discussed in [4]. Some useful details of the present calculations are summarised in table 3. Note, however, that we consider here collective, wave-vector-dependent quantities for which MD runs of 10^5 time-steps are required in order to achieve a statistical accuracy of 0.01–0.03 for the normalised time correlation functions to be discussed here.

3. Scattering functions considered for the MD calculations

The intermediate scattering function $F(\mathbf{k}, t)$ is defined by the spatial Fourier transform of the van Hove function [5]. Denoting by $\rho_{\mathbf{k}}$ the Fourier component of the local density $\rho(\mathbf{r}, t)$, we may write

$$\rho_{\mathbf{k}} = \sum_{i=1}^N \exp(-i \mathbf{k} \cdot \mathbf{r}_i(t)) \quad (1)$$

where \mathbf{k} denotes the chosen wave vector and \mathbf{r}_i the space coordinate of a particle i of the N -particle system. $F(\mathbf{k}, t)$ is then the autocorrelation function (ACF) of the time-dependent Fourier component of the local density:

$$F(\mathbf{k}, t) = (1/N) \langle \rho_{\mathbf{k}}(0) \rho_{-\mathbf{k}}(t) \rangle \quad (2)$$

where $\langle \rangle$ denotes the equilibrium ensemble average.

Analogous defining expressions hold for the so-called current ACF, $C(\mathbf{k}, t)$, which is given by the Fourier components of the local current in the following way. Denoting the local velocity by $\mathbf{v}(\mathbf{r}, t)$ we obtain the Fourier component from the expression:

$$\mathbf{j}_{\mathbf{k}}(t) = \sum_{i=1}^N \mathbf{v}_i(t) \exp(-i \mathbf{k} \cdot \mathbf{r}_i(t)). \quad (3)$$

Considering only that component of the current $\mathbf{j}_{\mathbf{k}}$ that lies in the direction of the wave vector, say the z direction, we may write the longitudinal current ACF as follows:

$$C_1(\mathbf{k}, t) = (k^2/N) \langle j_{\mathbf{k}}^z(0) j_{-\mathbf{k}}^z(t) \rangle. \quad (4)$$

The transverse part of the current ACF, $C_t(\mathbf{k}, t)$, contains information about visco-elastic modes and will therefore not be treated here.

For a two-component system the total scattering function is composed of three partial terms. Denoting these partial functions by $F^{\alpha\beta}(\mathbf{k}, t)$ for the intermediate scattering function, we have [5]

$$F(\mathbf{k}, t) = F^{11}(\mathbf{k}, t) + 2F^{12}(\mathbf{k}, t) + F^{22}(\mathbf{k}, t)$$

where we sum solely over particles of kind N_1 or N_2 in (1) and (3) to calculate the partial functions $F^{\alpha\beta}$; ($\alpha, \beta = 1, 2$). Analogous expressions hold for $C_1(\mathbf{k}, t)$. We are interested in the partial correlation functions concerned with the Brownian particles, which we choose to denote by F^{22} or C_1^{22} in the following.

4. MD results and discussion

4.1. The wave vector range considered for scattering functions

Masters [1] studied in his work a wave vector range around R_0^{-1} for $F^{22}(\mathbf{k}, t)$ and $C_1^{22}(\mathbf{k}, t)$, where R_0 is the radius of the Brownian particle. Our systems A1–A2

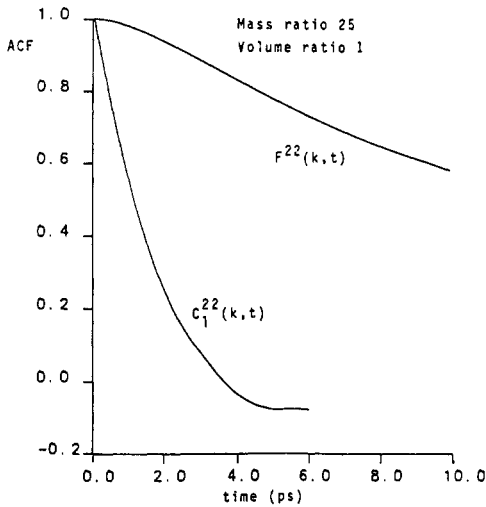


Figure 1. $F^{22}(k, t)$ and $C_1^{22}(k, t)$ as a function of time. $k\sigma_{11} = 1.59$. System A2. $T^* = 1$, $n_r^* = 0.8000$.

Table 4. Ratio of the decay times up to $1/e$ of $F^{22}(k, t)$ and $C_1^{22}(k, t)$ for systems A1–B3.

System	N_1	N_2	n_r^*	$k\sigma_{11}$	$\tau_{F^{22}}/\tau_{C^{22}}$
A1	246	10	0.8	1.6	19 ± 2
A2	246	10		1.6	18 ± 2
	246	10		0.92	19 ± 3
	246	5		1.6	18 ± 3
B1	246	10	0.3757	1.17	6.5 ± 0.5
	251	5		1.57	6.0 ± 0.5
	246	10		0.92	6.5 ± 0.5
	246	10	0.4085	1.55	7.5 ± 1.0
B2	246	10	0.3757	1.12	8.5 ± 0.5
B3	246	10	0.3757	1.07	9.0 ± 0.5
	251	5		1.07	8.5 ± 0.5
	490	10		1.07	8.0 ± 1.0
	490	10		0.4	8.0 ± 1.0
	246	10	0.3211	1.02	7.5 ± 1.0

contain massive and fluid particles of the same radius, so we selected wave vectors with $|\mathbf{k}|\sigma_{11} \approx 2$ to compare with the findings of Masters. For the systems B1–B3, in which the volume of the massive particles changes, we chose wave vectors with $|\mathbf{k}|\sigma_{11} \approx 1$, since the bulkiest particles occurring in the systems have about three times the radius of the liquid particles. Hence the chosen $k\sigma$ -range does indeed correspond to that considered by Masters. However, it is, of course, far away from the hydrodynamic region. We shall return to this point in our final discussion of the results.

4.2. Systems A1–A2 with equally sized particles

The solutions of particles of the same size, of mass ratios 16 and 25—the isotopic systems—undoubtedly showed the timescale separation required for the above-mentioned kinetic equations to be valid. We display as an example $F^{22}(k, t)$ and $C_1^{22}(k, t)$ of system A2, which has the largest mass ratio, in figure 1. Evidently, the time decay of C_1^{22} is much more rapid than that of F^{22} . In table 4 we compare the decay times of both functions up to the value $1/e$ for systems A1 and A2. The results are convincing

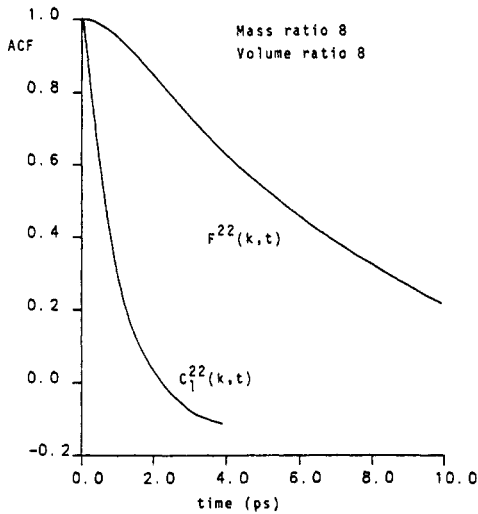


Figure 2. As in figure 1, but for system B1. $k\sigma_{11} = 1.17$. $T^* = 1$, $n_x^* = 0.3757$.

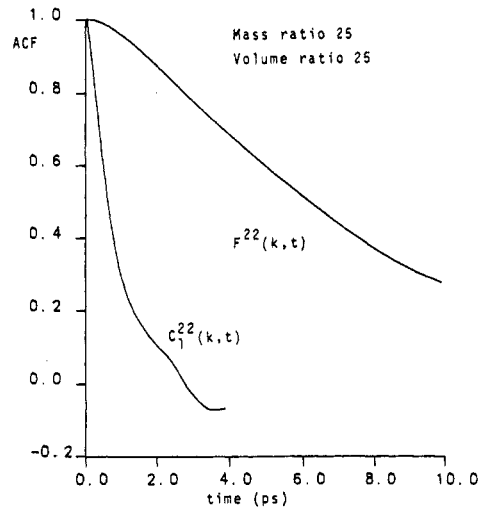


Figure 3. As figure 1, but for system B3. $k\sigma_{11} = 1.07$. $T^* = 1$, $n_x^* = 0.3757$.

and reveal a timescale factor of about 20. As the timescale difference remains constant for increasing mass ratio and is furthermore independent of the dilution, our findings should also hold for macroscopic systems of this type [6].

We have additionally checked the results for different k -values. Although for significantly smaller k , the form of F^{22} and C_1^{22} alters appreciably, the finally determined ratio of the decay times does not depend on the k -value, as table 4 shows.

4.3. Systems B1–B3, containing particles of different volume and mass

The scattering functions $F^{22}(k, t)$ and $C_1^{22}(k, t)$ of the solutions B1 and B3 are shown as examples in figures 2 and 3. Although the time decay differences are not as strong as in systems A1 or A2, the time decay of C_1^{22} is still much steeper than that of F^{22} . This becomes more evident from table 4, where we have summarised the ratio of the decay times up to $1/e$ for all the three systems B1–B3. While for system B1 with a particle volume ratio of 8 the decay time ratio amounts to 6.5, it increases to a value of 9 for the system B3 with the largest volume ratio, 25.

Hence in contrast to the findings for systems A1 and A2, the decay time ratio of F^{22} and C_1^{22} grows with increasing volume ratio. Thus for macroscopic systems of this type, we can expect that timescale separation will hold, justifying the application of such kinetic equations as the Fokker–Planck and Langevin equation.

We have again investigated the influence of the chosen k -value, the dilution, and the total density upon the decay time ratio, $\tau_{F^{22}}/\tau_{C_1^{22}}$. Table 4 contains additionally some of these results. While wave vector and dilution effects are completely negligible, the total density changes $\tau_{F^{22}}/\tau_{C_1^{22}}$ slightly in the range considered in our study.

However, as increase of the density leads to enhanced $\tau_{F^{22}}/\tau_{C_1^{22}}$ ratios, our conclusions would hold even more strongly for higher densities than studied by us.

5. Discussion and conclusions

Our MD calculations do not support the theoretical estimates of Masters [1], which appeared to show that for concentrated liquid solutions of Brownian particles the

timescale separation between the intermediate scattering function and the longitudinal current autocorrelation function of the Brownian particles may not exist.

The MD calculations presented herein do not really model macroscopic solutions of Brownian particles.

Neither the extremely high dilution nor the huge volume and mass ratio between the liquid and the Brownian particles possible in macroscopic systems can be achieved in MD calculations. However, the trends found in our study undoubtedly indicate that large particle–volume ratios together with large mass ratios lead to timescale separation. A large mass ratio alone suffices as well to produce timescale separation. Thus we may conclude that timescale separation between $C_{\parallel}^{22}(\mathbf{k}, t)$ and $F^{22}(\mathbf{k}, t)$ persists up to macroscopic systems, and the predicted breakdown is not likely to occur. Consequently application of kinetic equations like the Smoluchowski equation to liquid solutions of interacting Brownian particles is justified with respect to the existence of very different timescales.

Acknowledgments

We thank U Antoinette for typing and B Hoheisel for producing the plots. We are grateful to the ‘Rechenzentrum der Ruhr-Universität Bochum’ for allocating a large amount of computer time on the Cyber 205 vector machine to us.

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