The effect of direct interactions in steady state electrophoresis and thermophoresis of colloids

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Abstract
Applying a stochastic scheme we show how to obtain the density profile of a suspension of weakly interacting charged colloids in a steady state situation. The density profile corresponds to the set of macroions and depends of the electrophoretic velocity and the self-diffusion, as observed in experiments on dilute solutions of charged colloids. Our approach permits us to observe the deviation of the density profile from an ideal case when the pair interactions between the macroions are important and permits a better interpretation of such experiments. For the case of colloids with tuning interactions under a temperature gradient we obtain the behaviour of the collective diffusion and the thermal diffusion of the particles in terms of the volume fraction. This result could be important for understanding the boosting of DNA in thermocapillary traps.

1. Introduction

Our system is a set of colloids under both an external field and a temperature gradient. As a first case we study the system under an external electric field and at constant temperature, describing the dynamics of the suspension of charged colloids (macroions) in a steady state situation. Taking into account that colloids are Brownian particles, it is important to choose a stochastic approach to describe their dynamics; if additionally the system is out of equilibrium, the goal concerns an appropriate description of the interaction between the particles and the heat bath (a solvent which includes electrolytes). It was recently shown how the methods of non-equilibrium thermodynamics help one to obtain the intrinsic stochastic dynamics of non-equilibrium Brownian motion of interacting particles, described through Fokker–Planck

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equations [1, 2]. This scheme will establish a unified description of mass transport processes and structural properties of electrophoresis and thermophoresis in colloids. Following such methods it is easy to show that the Brownian motion of interacting colloids under a temperature gradient and an external field can be described by the following Fokker–Planck equation [3]:

$$\frac{\partial P^{(2)}}{\partial t} + \sum_{i=1}^{2} \mathbf{u}_i \cdot \frac{\partial P^{(2)}}{\partial \mathbf{r}_i} - \frac{1}{m}\frac{\partial V^{\text{eff}}}{\partial \mathbf{r}_1} \cdot \frac{\partial P^{(2)}}{\partial \mathbf{u}_1} - \frac{1}{m}\sum_{i=1}^{2}\frac{\partial V^{\text{ext}}}{\partial \mathbf{r}_i}\cdot\frac{\partial P^{(2)}}{\partial \mathbf{u}_i}$$
$$= \sum_{i=1}^{2}\frac{\partial}{\partial \mathbf{u}_i}\cdot\left[\overset{\leftrightarrow}{\beta}_{ij}\left(P^{(2)}\mathbf{u}_i + \frac{kT}{m}\frac{\partial P^{(2)}}{\partial \mathbf{u}_i}\right) + \frac{\overset{\leftrightarrow}{\gamma}_{ij}}{T_j}\frac{\partial P^{(2)}}{\partial T_j}\right]. \tag{1}$$

In the previous equation we identify direct (effective) short range interactions accounted for by V^{eff} (which includes the effect of electrolytes), hydrodynamic interactions quantified by the friction coefficients $\overset{\leftrightarrow}{\beta}$ (hydrodynamic friction), $\overset{\leftrightarrow}{\gamma}$ (thermal acceleration), together with the external forces—both thermodynamic (temperature gradient) and the conservative one—and their interrelations involved in the stochastic dynamic description. The average values for the conservative thermodynamic fields, namely, the density ρ_B, density of momentum $\rho_B\mathbf{u}_B$ and the density of energy $\rho_B\epsilon$, can be calculated through the corresponding integrations of the two-particle distribution function. Using the stochastic equation (1), together with some mathematical manipulations, and using the appropriate boundary conditions for the distribution function, we obtain the hydrodynamic equations for the Brownian particles [4]. We will show, in the following two sections, how the hydrodynamics contained in the mass and the momentum balance lead to the description of two different phenomena in colloids, electrophoresis and thermophoresis. In electrophoresis, for the particular case in which the flux of macroions, driven by the gradient of their concentration, is opposite to an external electric field we describe a steady state which produces a still concentration profile. Such a profile has been observed experimentally [7] and our approach permits an interpretation in terms of the electrophoretic velocity, the self-diffusion and the effective interaction between macroions. This is an extension of a recent interpretation of such experiments for a solution of non-interacting macroions [8]. When colloids are under an external temperature gradient, we describe the migration of particles driven by the variation of surface tension with respect to temperature. This phenomenon is accounted for by the thermal diffusion which is a cross effect predicted by irreversible thermodynamics.

2. Steady state electrophoresis of interacting macroions

Using the above stochastic equation, for an isothermal case and under an external electric field, we have a description of the Brownian motion, where the external force induces a systematic motion in the particles. If such a force is enough to surmount the Brownian motion, we observe that the particles have a terminal velocity as usually occurs in electrophoretic experiments. The physical phenomenon that we address is concerned with the fact that the force exerted over the macroions is small enough for one to consider that the Brownian motion is an important ingredient, such that the macroions obey Fick's law. In this situation we have a competition between two forces, namely, the usual one associated with the random movement due to the thermal fluctuations of the solvent that induces the migration of particles to a region of lower concentration and the motion induced by the electrical field over the macroions. When the two forces are in opposite directions, the particles only have thermal motion and their concentration profile is maintained as in a stationary state. This phenomenon has been successfully used for measuring properties of macroions, and on this basis electrophoretic cells have recently

been developed [7, 9]. To study this phenomenon, we obtain the momentum balance for the macroions in solution from equation (1):

$$\rho_B \frac{\partial \mathbf{u}_B}{\partial t} = -\nabla \cdot \overset{\leftrightarrow}{\mathbf{P}}_B - \overset{\leftrightarrow}{\beta} \cdot \rho_B \mathbf{u}_B - \rho_B \frac{\nabla V^{\text{ext}}}{m}. \tag{2}$$

The mathematical details of the derivation of the above hydrodynamic equation have been reported before [2, 3], and for the purpose of this paper we will only mention that the pressure tensor has two parts, $\overset{\leftrightarrow}{\mathbf{P}}_B(\mathbf{r}_1, t) = \overset{\leftrightarrow k}{\mathbf{P}}_B(\mathbf{r}_1, t) + \overset{\leftrightarrow \phi}{\mathbf{P}}_B(\mathbf{r}_1, t)$, the first term being a kinetic one which is similar to the one obtained in the kinetic theory of gases, $\overset{\leftrightarrow k}{\mathbf{P}}_B(\mathbf{r}_1, t) = \int P^{(1)}(\mathbf{u}_1 - \mathbf{u}_B)(\mathbf{u}_1 - \mathbf{u}_B) \, d\mathbf{u}_1$, and the second term being a potential contribution that accounts for the interaction between the particles, $\overset{\leftrightarrow \phi}{\mathbf{P}}_B(\mathbf{r}_1, t) = -\int \hat{\mathbf{r}} \hat{\mathbf{r}} \frac{\partial V^{\text{eff}}}{\partial r} r \int_0^1 P^{(2)} \, d\alpha \, d\mathbf{u}_1 \, d\mathbf{u}_2 \, d\mathbf{r}_2$, where $\int_0^1 P^{(2)} \, d\alpha = \int_0^1 P^{(2)}(\mathbf{r}_1 - [1 - \alpha], \mathbf{r}, \mathbf{u}_1, \mathbf{r}_1 + \alpha \mathbf{r}, \mathbf{u}_2, t)$ is the mathematical condition for the negligible variation of $P^{(2)}$ around the distance of separation between the particles. This condition permits one to express the probability density $P^{(2)}$ in a Taylor's expansion around the distance $\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$ between particles; hence the spatial gradient of $P^{(2)}$—which is related to the mean force between particles—has a small variation over the distance of interest, and allows us to keep only the lower term in the expansion and identify the pressure tensor in the momentum balance [5, 6]. The pressure tensor can be split into its irreducible parts, namely, $\overset{\leftrightarrow}{\mathbf{P}}_B(\mathbf{r}_1, t) = p \overset{\leftrightarrow}{\mathbf{I}} + \overset{\leftrightarrow}{\pi}$ where p is the hydrostatic pressure and physically represents the pressure exerted by the Brownian particles on the solvent, i.e., the osmotic pressure, and mathematically is a virial equation of state, namely, $p = \frac{\rho_B}{m} kT - \frac{2\pi}{3} (\frac{\rho_B}{m})^2 \int_0^\infty \frac{\partial V^{\text{eff}}}{\partial r} g(r) r^3 \, dr$ with $r = |\mathbf{r}|$, where it is important to emphasize that even if V^{eff} represents a pair interaction potential between the particles, it accounts for the effects of the solvent. Here $\overset{\leftrightarrow}{\pi}$ is the viscous tensor which we consider negligible since there is no shear acting upon the system and we consider an incompressible fluid. The trace of the pressure tensor permits one to obtain the hydrostatic pressure (osmotic pressure) which results in a virial equation of state with an effective interaction potential accounting for the effects of the solvent. If we neglect the effects of a velocity gradient, then we only account for the force due to the gradient of the osmotic pressure of the particles, and for long times, i.e., in the diffusive regime, the above momentum balance leads to the following relation:

$$\nabla \cdot \overset{\leftrightarrow}{\mathbf{P}}_B = -\overset{\leftrightarrow}{\beta} \cdot \rho_B \mathbf{u}_B - \rho_B \frac{\nabla V^{\text{ext}}}{m}; \tag{3}$$

defining the flux of particles as $\mathbf{j} = \rho_B \mathbf{u}_B$ we obtain the following relation:

$$\mathbf{j} = \mathbf{j}_{\text{diff}} + \mathbf{j}_{\text{el}} \tag{4}$$

where $\mathbf{j}_{\text{diff}} = -\overset{\leftrightarrow}{\mathbf{D}} \cdot \nabla \rho_B$ (Fick's law) and $\mathbf{j}_{\text{el}} = -\overset{\leftrightarrow}{\beta}^{-1} \cdot \frac{\rho_B}{m} \nabla V^{\text{ext}}$ (the flux of macroions due to the external force). The system reaches a steady state when the net flux is equal to zero, i.e., the thermodynamic force induced by the gradient of the osmotic pressure and the external force induced by the electric field are equal in magnitude but with opposite directions. This situation is accounted for by the relation $\mathbf{j}_{\text{diff}} + \mathbf{j}_{\text{el}} = \mathbf{0}$. Experimentally, as Godfrey describes, after applying the electric field the macroions move towards the semipermeable membrane: 'The macroions are stopped by the membrane, the concentration of macroions increases next to the membrane surface and the concentration gradient thus formed produced a diffusion-driven back-flow of macroions. In time, the macroion concentration gradient stabilizes; at every point in the gradient, macroion flow due to the electrical field is countered, exactly, by macroion flow due to diffusion'. This means that if we turn off the electric field, the macroions move in

a collective manner with an average velocity $\mathbf{u}_{el}$ defined by $\mathbf{j}_{el} = -\mathbf{j}_{diff} = \rho_B \mathbf{u}_{el}$. In this steady state and over the x, the last equation can be rewritten as the following differential equation:

$$-D\frac{\partial \rho_B}{\partial x} = \beta^{-1}\frac{\partial V^{ext}}{\partial x}\frac{\rho_B}{m} \tag{5}$$

or, alternatively,

$$-\frac{kT}{m}\left[1 - \frac{4}{3}\pi\frac{\rho_B}{mkT}\int_0^\infty \frac{\partial V^{eff}}{\partial r}g(r)r^3\,\mathrm{d}r\right]\frac{\partial \rho_B}{\partial x} = \frac{\partial V^{ext}}{\partial x}\frac{\rho_B}{m}, \tag{6}$$

where $g(r)$ is the usual equilibrium pair correlation function. We should note that the above equilibrium condition differs from the widely used equilibrium condition between electrostatic external force and the friction of the macroion in the solvent, namely, $Q_{eff}E = v_{el}f$ where Q_{eff} is the 'effective charge' of the particle, E the electric field and f the friction coefficient. The difference between u_{el} and v_{el} is that the first one is a collective macroscopic quantity that accounts for the interactions between macroions, while v_{el} corresponds to the velocity of just one macroion. This last equation should be solved in order to obtain the density profile, and the needed input is the pair correlation function which must be obtained for a particular model of interactions between the particles. In order to test our approach, and taking into account that in Godfrey's experiments the concentration of macroions is in the range 0.5–2 g l^{-1}, i.e. the system is diluted and weakly coupling from the electrostatic point of view [10], we use as an effective potential a hard core part plus a repulsive Yukawa tail:

$$V^{eff} = \begin{cases} \infty & \text{for } r/\sigma < 1 \\ \epsilon\dfrac{\exp[b(r/\sigma - 1)]}{r/\sigma} & \text{for } r/\sigma > 1. \end{cases} \tag{7}$$

Here ϵ and b play the role of effective parameters for fitting the experimental data. On the other hand, we solve the Ornstein–Zernike integral equation in the Fourier space by iteration [11] using the hypernetted-chain (HNC) closure. When the interactions between macroions are neglected, i.e., in the infinite dilution regime, we obtain from equation (6) the density profile

$$\rho_B(x) = \rho_B(x_0)\exp[u_{el}(x - x_0)D_0^{-1}], \tag{8}$$

where u_{el} is the electrophoretic velocity, D_0 the self-diffusion coefficient and $\rho_B(x_0)$ the density next to the membrane in the electrophoretic cell. We can consider this profile an ideal one, so any deviation from ideality could be due to the interactions between the particles (e.g., proteins). In figure 1 we reproduce the density profile (ideal case) observed by Godfrey [7] for bovine serum albumin (BSA). It is important to note that the same profile can be reproduced with the model of a soft repulsive potential mentioned above. As, in the ideal case, the interactions between the particles are neglected, the corresponding soft particles should have a small hydrodynamic radius (small effective diameter) in order to occupy the same volume fraction; i.e., if we have an ideal solution and a non-ideal one with the same density profile, then our approach will distinguish between these two systems.

3. Thermophoresis of interacting tunable colloids

When the colloidal system is under an external temperature gradient, the stochastic equation (1) leads to the hydrodynamic equations describing the macroscopic behaviour of this non-equilibrium situation. In the diffusive regime the flux of particles follows a dynamics similar (from the mathematical point of view) to that in the steady state electrophoresis, namely,

$$\mathbf{j} = -\overset{\leftrightarrow}{\mathbf{D}}\cdot\nabla\rho_B - \overset{\leftrightarrow}{\mathbf{D}}_T\cdot\frac{\nabla T}{T}, \tag{9}$$
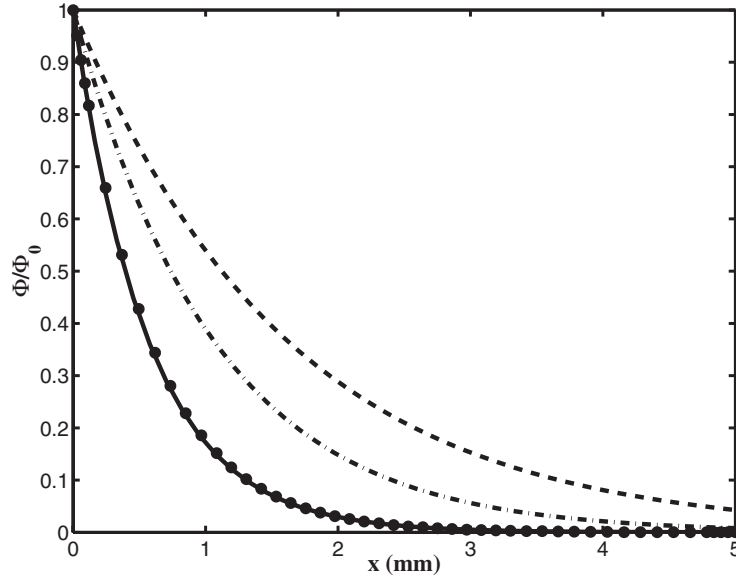
Figure 1. The density profile: $\frac{\Phi}{\Phi_0}$ represents the ratio of the volume fraction of macroions. Φ_0 corresponds to the density next to the membrane in the electrophoretic cell. The full curve (——) stands for the experiments of Godfrey, while the remaining discontinuous curves are for interacting particles. The dashed curve (- - - -) was obtained with $\epsilon = 0.1kT$ and the chain curve (— · —) was obtained with $\epsilon = 0.05kT$. The full circles ● fit the ideal profile with $\epsilon = 0.01kT$. All the curves are calculated for $b = 5$ and x denotes the distance along the direction of the electric field.

where $\overset{\leftrightarrow}{\mathbf{D}}_{\mathrm{T}}$ is the thermal diffusion described by the following expression:

$$\overset{\leftrightarrow}{\mathbf{D}}_{\mathrm{T}} = \overset{\leftrightarrow}{\boldsymbol{\beta}}^{-1} \cdot \rho_{\mathrm{B}} \overset{\leftrightarrow}{\boldsymbol{\gamma}} + \overset{\leftrightarrow}{\boldsymbol{\beta}}^{-1} \frac{kT}{m} \left[\rho_{\mathrm{B}} - \frac{2\pi\rho_{\mathrm{B}}^2}{3mk} \int_0^\infty \frac{\partial V^{\mathrm{eff}}}{\partial r} \frac{\partial g(r)}{\partial T} r^3 \, \mathrm{d}r \right]. \tag{10}$$

In this expression it is important to observe that $\overset{\leftrightarrow}{\boldsymbol{\gamma}}$ stands for the thermal acceleration, which has been shown to be the ratio of the thermal mobility and the usual collective mobility (sedimentation coefficient). One additional fact is concerned with the derivative of the pair correlation function with respect to the temperature.

In figure 2(a), using the Yukawa model, we reproduce the behaviour of the collective diffusion, observed in the light scattering experiments in microemulsions of Cazabat *et al* for a very low volume fraction. The decay of such a coefficient is a signature of the effective attractive interactions between particles; i.e., the particles are closer when the concentration increases. The slightly deviation between the theoretical and the experimental curve is due to the fact that the authors performed a linear fit over the experimental data. On the other hand, we are interested in the effect of the effective repulsive interactions in the transport of particles. The simplest way to investigate this is by changing the sign of the Yukawa potential; i.e., now we use $\epsilon > 0$. After doing this, we observe the result in figure 2(b), which shows an inverted behaviour of the coefficients in comparison with the previous case—namely, the thermal diffusion now decreases in a linear way and the collective diffusion shows a non-linear change increasing initially upwards to a maximum value and afterwards decreasing. We interpret such changes as a transition of the potential of mean force (pmf), defined as $W = -kT \ln(g(r))$, from repulsive to attractive interactions. In order to test this hypothesis we calculate the pmf for different volume fractions and we present our results in figure 3.
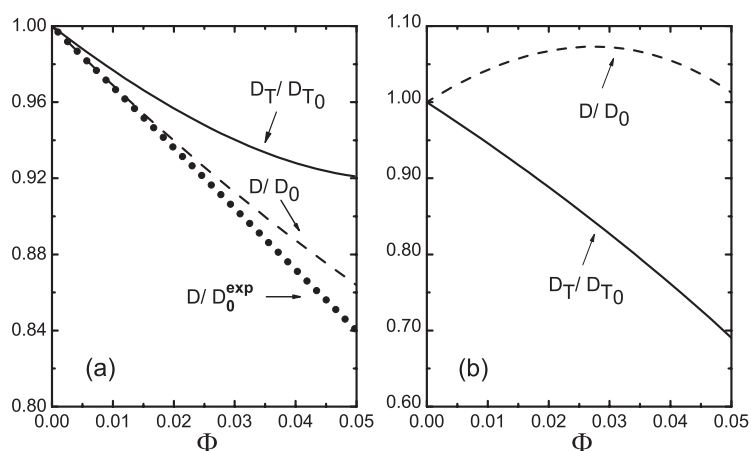
Figure 2. Collective D/D_0 (- - - -) and thermal D_T/D_{T_0} (———) diffusion for attractive (a) and repulsive (b) effective direct interaction between particles, where D_{T_0} is the thermal diffusion for one particle. In both cases the potential model was of Yukawa type with parameters $\epsilon = 0.66kT$ and $b = 2.9$. D/D_0^{exp} (●) is the experimental linear fit used by Cazabat *et al*.
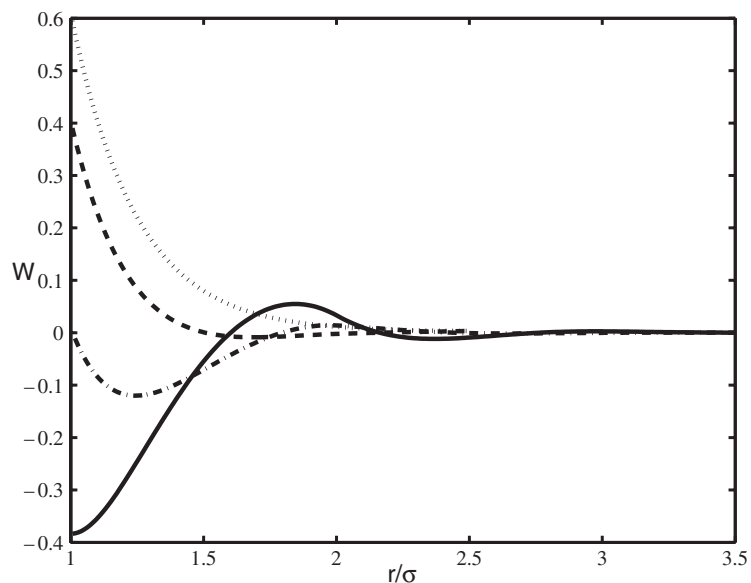

Figure 3. The pmf W shows a transition from a purely repulsive interaction ($\Phi = 0.01$; ······), a soft core with a small attractive well ($\Phi = 0.03$; - - - -), a hard core with a more developed attraction ($\Phi = 0.12$; — · —) and the fully entropic attraction ($\Phi = 0.2$; ———).

The changing in the behaviour of the pmf shows how the increasing of the diffusion corresponds to a purely repulsive pmf, and when the diffusion decreases the pmf initially shows an attractive well which eventually increases towards exclusivity until an attractive interaction arises at the contact point. This last phenomenon corresponds to an entropically driven attraction between particles.

4. Discussion

Using a stochastic description, compatible with the methods of irreversible thermodynamics, we describe the diffusive regime of a system composed of colloidal interacting particles either subject to an external electric field or under a temperature gradient. Both phenomena correspond to non-equilibrium stationary states; i.e., the relevant variables are time independent. In this regime the density profile of macroions is still in the electrophoretic experiment condition, while the temperature profile is fixed in the thermophoretic case. In order to test our approach, we obtain analytically the density profile observed in a steady state electrophoresis experiment for a dilute solution. When we account for the interaction between macroions, we find, as in the non-interacting case, an exponential decay of the density. This leads us to observe that the ideal density profile has an equivalent profile composed from soft repulsive particles. In this sense our scheme is useful for interpreting, in a more detailed manner, a steady profile of macroions in terms of the electrophoretic velocity, the self-diffusion and an appropriate interaction potential between particles. Our calculations were performed for the low concentration regime and the solvent was treated as a continuum. Including the discrete nature of the solvent, the electrostatic correlations [12] between the ions of the electrolyte solution and the asymmetry in the valence and the sizes of ions [13] would lead to a better description with a richer phenomenology, for example overcharging in colloids [14]. In the case of thermophoresis, the resulting expression for the collective diffusion and the thermal diffusion depend on the interactions between the colloids and on the equilibrium behaviour of the pair correlation function. Even if our approach were valid for any short range continuous potential, our procedure in this case would be to fit the parameters of an interaction potential with the Yukawa functional form. With this input we are able to reproduce the tendency of collective diffusion from experimental data for microemulsions in the low concentration regime. We used in this case undeformed droplets as a model of particles, such that we account for the variation of surface tension with respect to temperature as the main mechanism of the driving force for the migration of droplets along the temperature gradient. Analysing the potential of mean force we can interpret the effects of interactions in the collective diffusion when we use a soft repulsive potential. In this case the change of the behaviour of such a coefficient with respect to the volume fraction was driven at first energetically; afterwards, when it was due to an increasing of the volume fraction, we found that the attraction between particles was an entropic effect. In the case of the thermal diffusion it was interesting to note that in both cases, whether the tail of the direct interaction was repulsive or attractive, the coefficient showed a decay with respect to the volume fraction. However, with the attractive tail the thermal diffusion's behaviour changes and starts to be enhanced; it would be interesting to apply these results to other phenomena ranging across magnetic colloids [15], micelles [16], polymers [17], aerosols [18] and the trapping of DNA with a temperature gradient [19].

References

[1] Rubí J M and Mazur P 1998 *Physica* A **250** 253
[2] Mayorga M, Romero-Salazar L and Rubí J M 2002 *Physica* A **307** 297

[3] Mayorga M, Hernández-Flores O A and Romero-Salazar L 2003 *Recent Research Developments in Molecular Physics* ed S G Pandalai (India: Transworld Research Network) at press

[4] Mayorga M, Dominguez B and Romero-Salazar L 2002 *Mol. Phys.* **100** 3155

[5] Ferziger J H and Kaper H G 1972 *Mathematical Theory of Transport Processes in Gases* (Amsterdam: North-Holland)

[6] Irving J H and Kirkwood J G 1959 *J. Chem. Phys.* **18** 817

[7] Godfrey J E 1989 *Proc. Natl Acad. Sci.* **86** 4479

[8] Stigter D 2000 *J. Phys. Chem.* B **104** 3402

[9] Laue T M *et al* 1996 *J. Pharm. Sci.* **85** 1331

[10] Hansen J P and Lowen H 2000 *Annu. Rev. Phys. Chem.* **51** 209

[11] See for example: Lado F 1967 *J. Chem. Phys.* **47** 4828

[12] Levin Y 2002 *Rep. Prog. Phys.* **65** 1577

[13] Tanaka M 2003 *Phys. Rev.* E **68** 061501

[14] Quesada-Pérez M, González-Tovar E, Martín-Molina A, Lozada-Cassou M and Hidalgo-Álvarez R 2003 *Chem. Phys. Chem.* **4** 234

[15] Blums E *et al* 1998 *Phys. Fluids* **10** 2155

[16] Piazza R and Guarino A 2002 *Phys. Rev. Lett.* **88** 208302

[17] Zhang K J, Briggs M E, Gammon R W, Sengers J V and Douglas J F 1999 *J. Chem. Phys.* **111** 2270

[18] Chen S H 2002 *J. Aerosol Sci.* **33** 1155

[19] Braun D and Libchaber A 2002 *Phys. Rev. Lett.* **89** 1888103