Transport Properties of Inhomogeneous Fluid Mixtures[1]

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ABSTRACT

Explicit expressions for the transport coefficients of mixtures of dense, strongly inhomogeneous fluids are derived in terms of the equilibrium structure factors of such mixtures, in the framework of the nonequilibrium statistical mechanical theory suggested by the authors.

KEY WORDS: diffusion coefficients; fluids; inhomogeneous fluid mixtures; nonequilibrium statistical mechanics; transport coefficients; transport theory.

1. INTRODUCTION

The thermodynamic properties of dense, strongly inhomogeneous fluids (both gases and liquids), such as those at interfaces, or confined in narrow capillary pores of several molecular diameters in width, differ markedly from their counterparts for homogeneous (bulk) fluids. Such fluids and their mixtures (called below nanofluids or nanofluid mixtures) show new and modified phase transitions and transport properties, highly selective adsorption, spatially dependent structure properties, etc. Experimental investigation of thermodynamic properties of nanofluids and their mixtures are difficult, because of the complicated structure of the confined systems and interfaces, the many variables involved, and sensititvity of the properties to experimental conditions.

Although over the last decade there has been significant development in understanding equilibrium properties of inhomogeneous fluids, much less progress has been made in the case of transport properties. Such knowledge is very important both for basic and applied research, since many industrial processes are known to be limited by diffusion, selectivity and/or flow considerations.

Over the last few decades, several successful statistical mechanical approaches to microscopic theory of transport processes have been developed for homogeneous fluids (see, for example, Refs. 1 - 6). However, there have been few attempts to develop a statistical mechanical theory of transport processes in nanofluids, in particular in nanofluids of liquid-like density [7 - 9]. Recently the authors of this paper suggested a rigorous, nonequilbrium statistical mechanical approach [10 -14] to transport processes

in nanofluids and their mixtures. This approach incorporates and develops basic mathematical techniques and ideas featuring in nonequilibrium statistical mechanics of bulk fluids, including the representation of intermolecular interaction potentials as sums of hard-core repulsive and soft attractive contributions [6]. Also, the approach utilizes the authors' generalization of the Mori-Zwanzig projection operator method to establish kinetic and transport theories of nanofluids [10 - 13], and recently of nanofluid mixtures [14]. These theories tolerate any specific geometry of a confined system or interface (arbitrary pore shape, width, structure of pore walls; arbitrary form of an interface, etc.), and supply explicit expressions for transport coefficients of nanofluids and their mixtures. The derived transport coefficients are related to equilibrium structure properties (the densities, the pair and direct correlation functions) of the nanofluids or the nanofluid mixtures. The above theoretical results have been tested against nonequilibrium molecular dynamics (NEMD) simulation data for the shear viscosity of a simple nanofluid confined in narrow slit pores of about 5 molecular diameters in width [13]. The theory correctly predicts an increase in the shear viscosity of up to 50% due to confinement, and the oscillatory nature of the local shear viscosity. The agreement between the theoretical and NEMD data is within 1% to 5%.

2. TRANSPORT PROPERTIES OF NANOFLUID MIXTURES

In this paper we report our latest results on the transport coefficients of nanofluid mixtures. For further analytical details and explicit expressions for the viscosities and

thermal conductivities of nanofluid mixtures we refer readers to our recent paper [14]. However, the diffusion coefficients of the nanofluid mixtures are considered below in greater detail, in view of their importance in applications.

In what follows we consider a mixture of N fluid components composed of simple, structureless molecules in a confinement of arbitrary shape. The walls are formed by simple, structureless molecules, all of the same species, immovable from their positions in the walls, and thermostated at temperature T. Inhomogeneity of the nanofluid mixture is caused by the continuous external potential field, represented as a sum of short-range repulsive and long-range attractive contributions. The repulsive part describes hard-core-like interactions of the fluid molecules with the wall molecules forming the confinement. The attractive contributions are caused by both the long-range intermolecular interactions of the fluid molecules with the molecules of the walls, and an external potential field of a general nature. A similar representation can be used for the fluid-fluid molecule interactions by means of the Weeks, Chandler and Andersen (WCA) or Barker and Henderson (BH) methods. The repulsive contributions to all of the potentials of intermolecular interaction are assumed to be hard-core ones, with the effective diameters σ_{ij} specific to interactions of the i-th species molecules with those of the j-th species, and with the effective diameters σ_{iw} corresponding to the repulsive interactions of the i-th species molecules with those of the walls. The attractive parts of the potentials are expected to behave as r^{-n}, $n > 2$, at $r \to \infty$, where r is the distance between interacting molecules. The potentials of intermolecular interaction

are central and pairwise. In addition, we assume that there is no chemical reaction in the system.

At the above conditions we can use Eq. (4.1) of Ref. [14] for the diffusion velocity of the i-th component of the nanofluid mixture, and the generating expression for the tensorial diffusion coefficients, Eq. (4.3), derived there. This expression represents the local values of the tensorial diffusion coefficients of the nanofluid mixture in terms of its local equilibrium pressure, $\mathbf{P}(\mathbf{q})$ at the point $\mathbf{q}$. For the nanofluid mixture described above the equilibrium pressure can be written in terms of the equilibrium structure factors of the nanofluid mixture,

$$\begin{aligned}\mathbf{P}(\mathbf{q}) = \sum_{i=1}^{N}\sum_{j=1}^{N}\Big\{ & n_i(\mathbf{q})k_BT\left[\delta_{ij} + \frac{1}{4\pi}b_{ij}n_j(\mathbf{q})\int d\hat{\sigma}\, g_{ij}(\mathbf{q},\mathbf{q}-\sigma_{ij}\hat{\sigma})\right] \\ & - \frac{1}{6}n_i(\mathbf{q})n_j(\mathbf{q})\int_{\sigma_{ij}\hat{\sigma}}^{\infty} d\mathbf{r}\, g_{ij}(\mathbf{q},\mathbf{q}+\mathbf{r})\left[\frac{\partial\phi_{ij}(\mathbf{r})}{\partial\mathbf{r}}\cdot\mathbf{r}\right]|\mathbf{r}|^2\Big\}, \end{aligned} \tag{1}$$

where $\phi_{ij}(\mathbf{r})$ is the attractive part of the intermolecular interaction potential for the i-th and j-th components; k_B is Boltzmann constant; $n_i(\mathbf{q})$, $i = 1, \ldots, N$ are the equilibrium densities of the components; δ_{ij} denotes Kronecker's delta; $b_{ij} = \frac{2}{3}\pi\sigma_{ij}^3$; $g_{ij}(\mathbf{q},\mathbf{q}-\sigma_{ij}\hat{\sigma})$ and $g_{ij}(\mathbf{q},\mathbf{q}')$ are values of the pair correlation function calculated at different locations of the i-component and j-component molecules, $\hat{\sigma} = \sigma_x\mathbf{i} + \sigma_y\mathbf{j} + \sigma_z\mathbf{k}$ is the unit vector ($\sigma_x^2 + \sigma_y^2 + \sigma_z^2 = 1$); $\mathbf{i}, \mathbf{j}, \mathbf{k}$ are unit vectors of the directions of the adopted Cartesian system of coordinates; integration over $\hat{\sigma}$ is integration over the surface of the unit sphere, and the integral over $\mathbf{r}$ is a regular volume integral.

Using Eq. (1) one can derive from Eq. (4.3) of Ref. [14] the following expression

for the Fourier-image of the local tensorial mutual diffusion coefficient, $\hat{\mathbf{D}}_{i\alpha}(\mathbf{q},\omega)$,

$$\hat{\mathbf{D}}_{i\alpha}(\mathbf{q},\omega) = \Bigg\{ E_{i\alpha}(\mathbf{q}) + \sum_{k\neq i}^{N} \Omega_{ik}(\mathbf{q},\omega) E_{k\alpha}(\mathbf{q}) \hat{\mathbf{\Omega}}_{ik}(\mathbf{q})$$
$$+ \sum_{k\neq i}^{N} \sum_{l\neq k}^{N} \ldots \sum_{j\neq s}^{N} \Omega_{ik}(\mathbf{q},\omega)\Omega_{lk}(\mathbf{q},\omega)\ldots\Omega_{js}(\mathbf{q},\omega) E_{j\alpha}(\mathbf{q})$$
$$\times \hat{\mathbf{\Omega}}_{ik}(\mathbf{q}) \cdot \hat{\mathbf{\Omega}}_{lk}(\mathbf{q}) \cdot \ldots \cdot \hat{\mathbf{\Omega}}_{js}(\mathbf{q}) \Bigg\} \mathbf{I}, \tag{2}$$

where $\alpha = 1, \ldots, N$, ω is the frequency, m_i is the mass of a molecule of the i-th fluid component of the mixture, $\mathbf{I}$ is the unit matrix, and the rest of the notations are as follows,

$$\overline{\tau_{id}(\mathbf{q})} \equiv \frac{3\sqrt{\pi\beta m_i}}{2\sigma_{ii}^2} \tau_{id}(\mathbf{q}); \tag{3}$$

$$\tau_{id}^{-1}(\mathbf{q},\omega) \equiv \sum_{k\neq i}^{N} \frac{\sqrt{2m_k/m_i}\,\sigma_{ik}^2}{[1+m_k/m_i]^{1/2}\sigma_{ii}^2} \int d\hat{\sigma} n_k(\mathbf{q}-\sigma_{ik}\hat{\sigma}) g_{ik}(\mathbf{q},\mathbf{q}-\sigma_{ik}\hat{\sigma})$$
$$- \frac{\sqrt{2}\,\sigma_{iw}^2}{\sigma_{ii}^2} \int d\hat{\sigma} n_w(\mathbf{q}-\sigma_{iw}\hat{\sigma}) g_{iw}(\mathbf{q},\mathbf{q}-\sigma_{iw}\hat{\sigma}); \tag{4}$$

$$\tau_{id}^{*}(\mathbf{q},\omega) = \frac{\tau_{id}(\mathbf{q})}{[1 - i\omega\overline{\tau_{id}(\mathbf{q})}]}; \tag{5}$$

$$\Omega_{ik}(\mathbf{q},\omega) = \frac{3\sqrt{2} m_i \sigma_{ik}^2 n_i(\mathbf{q})}{[1+m_k/m_i]^{1/2}\sigma_{kk}^2 n_k(\mathbf{q})} \tau_{kd}^{*}(\mathbf{q},\omega); \tag{6}$$

$$\hat{\mathbf{\Omega}}_{ik}(\mathbf{q}) = \int d\hat{\sigma} n_k(\mathbf{q}-\sigma_{ik}\hat{\sigma}) g_{ik}(\mathbf{q},\mathbf{q}-\sigma_{ik}\hat{\sigma}) [\hat{\sigma}\hat{\sigma} - \frac{1}{3}\mathbf{I}]; \tag{7}$$

$$\begin{aligned} E_{il}(\mathbf{q}) \;=\; & \frac{1}{\beta} \{ \delta_{il} + \frac{1}{2\pi} n_i(\mathbf{q}) b_{il} \int d\hat{\sigma} g_{il}(\mathbf{q},\mathbf{q}-\sigma_{il}\hat{\sigma}) \\ & + \frac{1}{4\pi} \sum_j n_i(\mathbf{q}) n_j(\mathbf{q}) \int d\hat{\sigma} \frac{\partial g_{ij}(\mathbf{q},\mathbf{q}-\sigma_{ij}\hat{\sigma})}{\partial n_l(\mathbf{q})} \\ & - \frac{\beta}{3} n_i(\mathbf{q}) \int_{\sigma_{il}\hat{\sigma}+\mathbf{q}}^{\infty} d\mathbf{q}'' |\mathbf{q}''|^2 \mathbf{q}'' \cdot \frac{d\phi_{il}(\mathbf{q}'')}{d\mathbf{q}''} g_{il}(\mathbf{q},\mathbf{q}'') \\ & - \frac{\beta}{6} \sum_j n_i(\mathbf{q}) n_j(\mathbf{q}) \int_{\sigma_{ij}\hat{\sigma}+\mathbf{q}}^{\infty} d\mathbf{q}'' |\mathbf{q}''|^2 \mathbf{q}'' \cdot \frac{d\phi_{ij}(\mathbf{q}'')}{d\mathbf{q}} \frac{\partial g_{ij}(\mathbf{q},\mathbf{q}'')}{\partial n_l(\mathbf{q})} \} \;; \end{aligned} \tag{8}$$

The expression (5) defines the diffusion relaxation time specific to the i-th component.

The diffusion coefficients of Eq. (2) come into Eq. (4.3) of Ref. 14 with the gradients of the equilibrium densities of the components, which are not all linearly independent. The dependent component density can be excluded upon usage of Eq. (1). This leads to the final expression for the theoretical diffusion coefficients of the nanofluid mixture,

$$\left[\hat{\mathbf{D}}_{il}(\mathbf{q},\omega)\right]_T = \frac{3\tau^*_{id}(\mathbf{q},\omega)\rho_l(\mathbf{q})}{2\sigma^2_{ii}n_i(\mathbf{q})\rho(\mathbf{q})}\sqrt{\frac{\pi\beta}{m_i}}\left[\hat{\mathbf{D}}_{il}(\mathbf{q},\omega) - \frac{P_l(\mathbf{q})}{P_m(\mathbf{q})}\hat{\mathbf{D}}_{im}(\mathbf{q},\omega)\right], \tag{9}$$

where $P_l(\mathbf{q}) = \sum_{i=1}^N E_{il}(\mathbf{q})$, and m is the index of the linearly dependent density. The diffusion coefficients of Eq. (9), in their turn, are not linearly independent, and satisfy the condition

$$\sum_i m_i n_i(\mathbf{q})[\hat{\mathbf{D}}_{il}(\mathbf{q},\omega)]_T \;=\; 0\,, \tag{10}$$

which follows from the restriction $\sum_{i=1}^N m_i n_i(\mathbf{q})\mathbf{V}_i(\mathbf{q},\omega) = 0$ on the diffusion velocities of the components, $\mathbf{V}_i(\mathbf{q},\omega)$. At zero frequency, $\omega = 0$, from Eqs. (9) and (10) one can derive the local values of the frequency-independent diffusion coefficients of the nanofluid mixture.

2.1. Phenomenological diffusion coefficients of nanofluid mixtures

The local values of the phenomenological diffusion coefficients $\hat{\mathbf{D}}^p_{il}(\mathbf{q})$ are defined by the expression for the mass flux of the i-th component, $\mathbf{J}^p_i(\mathbf{q})$,

$$\mathbf{J}^p_i(\mathbf{q}) \;=\; m_i n_i(\mathbf{q})\mathbf{V}_i(\mathbf{q})$$

$$= -\sum_{l\neq m} \hat{\mathbf{D}}^p_{il}(\mathbf{q}) m_l \cdot \frac{\partial n_l(\mathbf{q})}{\partial \mathbf{q}} - \hat{\mathbf{D}}^T_l(\mathbf{q}) \left(\frac{\partial \ln T(\mathbf{q})}{\partial \mathbf{q}} \right) , \tag{11}$$

where $\hat{\mathbf{D}}^T_l(\mathbf{q})$ is the thermal diffusion coefficient, and the dot $\cdot$ denotes the inner product. On the other hand, the theoretical diffusion coefficients are proportionality coefficients between the diffusion velocities and the gradients of the densities of the components,

$$\mathbf{V}_i(\mathbf{q},\omega) = -\sum_{l\neq m} \left[\hat{\mathbf{D}}_{il}(\mathbf{q},\omega) \right]_T \cdot \frac{\partial n_l(\mathbf{q})}{\partial \mathbf{q}}.$$

Substitution of the result (9) calculated at $\omega = 0$ into the definition (11) leads to the relation

$$\hat{\mathbf{D}}^p_{il}(\mathbf{q}) \;=\; \frac{m_i}{m_l} n_i(\mathbf{q}) \left[\hat{\mathbf{D}}_{il}(\mathbf{q}) \right]_T \tag{12}$$

between local values of the theoretical and phenomenological diffusion coefficients.

2.2. Binary diffusion in nanofluid mixtures

In the case of weak inhomogeneity of the nanofluid mixture the terms with sums in the right hand side of Eq. (2) can be neglected, and from Eqs. (2), (9), (4), (5), and (10) it follows that the theoretical diffusion coefficient of the binary mixture, $[\hat{\mathbf{D}}_{12}(\mathbf{q})]_T$, at $\omega = 0$ is

$$[\hat{\mathbf{D}}_{12}(\mathbf{q})]_T \;=\; \frac{4D^*_{12}(\mathbf{q}) n(\mathbf{q}) \beta m_2 n_2(\mathbf{q})}{n_1(\mathbf{q}) \int d\hat{\sigma} n_2(\mathbf{q}-\sigma_{12}\hat{\sigma}) g_{12}(\mathbf{q}, \mathbf{q}-\sigma_{12}\hat{\sigma}) \rho(\mathbf{q})} \left[E_{12}(\mathbf{q}) - \frac{P_2(\mathbf{q})}{P_1(\mathbf{q})} E_{11}(\mathbf{q}) \right] \mathbf{I} \,,$$

where (13)

$$D^*_{12}(\mathbf{q}) = \frac{3\sqrt{2\pi k_B T}}{16\pi\sigma^2_{12} n(\mathbf{q}) \sqrt{m_{12}}} \quad \text{and} \quad m_{12} \;=\; \frac{m_1 m_2}{m_1 + m_2}.$$

$E_{il}(\mathbf{q})$ is given by Eq. (8), and $P_l(\mathbf{q})$ is defined below Eq. (9).

From Eqs. (13) and (12) one can derive the following relation between the two phenomenological diffusion coefficients of the binary mixture of nanofluids,

$$\hat{\mathbf{D}}^p_{12}(\mathbf{q}) \;=\; \left[\frac{m_1 P_2(\mathbf{q})}{m_2 P_1(\mathbf{q})}\right]\left[\frac{n_2(\mathbf{q})\int d\hat{\sigma} n_1(\mathbf{q}-\sigma_{12}\hat{\sigma}) g_{12}(\mathbf{q},\mathbf{q}-\sigma_{12}\hat{\sigma})}{n_1(\mathbf{q})\int d\hat{\sigma} n_2(\mathbf{q}-\sigma_{12}\hat{\sigma}) g_{12}(\mathbf{q},\mathbf{q}-\sigma_{12}\hat{\sigma})}\right]\hat{\mathbf{D}}^p_{21}(\mathbf{q}). \tag{14}$$

In the particular case of a binary mixture of bulk fluids this expression reduces to

$$\hat{\mathbf{D}}^p_{12} \;=\; \left[\frac{m_1 P_2}{m_2 P_1}\right]\hat{\mathbf{D}}^p_{21},$$

where $\hat{\mathbf{D}}^p_{12}$ is the homogeneous reduction of the corresponding phenomenological coefficient, Eq. (12), expressed in terms of the theoretical diffusion coefficient (13) calculated for the homogeneous mixture. This relation has been originally discovered in Ref. 17 for a binary mixture of hard spheres in the framework of the Chapman - Enskog method. Here we have generalized this result, and proved that the same relation also holds for a binary mixture of any bulk fluids, provided their intermolecular interaction potentials can be divided into a sum of hard-core repulsive and soft attractive contributions.

From the results of Ref. 14 it follows that the diffusion coefficients of the nanofluid mixture depend strongly on the equilibrium pressure of the mixture, which in the above case depends explicitly on the attractive part of the intermolecular interaction potentials (see Eq. (1)). This also means, that the values of the diffusion coefficients are very sensitive to a particular approximation of the equilibrium pressure of the nanofluid mixture. In this respect the diffusion coefficients differ significantly

from the viscosities and thermal conductivity coefficients of such mixtures, Eqs. (3.24) - (3.26), (3.32) of Ref. 14, which do not depend on the equilibrium pressure explicitly.

3. CONCLUSIONS

Calculation of the transport coefficients based on Eqs. (3.24) - (3.26), (3.32) of Ref. 14 and the above equations (13), (9), (2) require data on equilibrium structure factors of the nanofluid mixtures, in particular on the number densities of the components $n_i(\mathbf{q})$, the contact values of their pair correlation functions, $g_{il}(\mathbf{q}, \mathbf{q} - \sigma_{il}\hat{\sigma})$. These coefficients also depend on the effective hard-core diameters, σ_{il}, evaluated for the intermolecular interaction potentials, which are divided into a sum of hard-core repulsive and soft attractive contributions. Such intermolecular interaction potentials have to be obtained from more realistic intermolecular interaction potentials (e.g., the Lennard-Jones model potentials) by means of Weeks, Chandler, and Andersen (WCA) [15] or Barker and Henderson (BH) [16] methods. The WCA method supplies hard-core diameters σ_{il}^{WCA} which depend on both the temperature and the equilibrium number densities of the components of the mixture, whereas the BH procedure leads to σ_{il}^{BH}'s that depend only on temperature. From a dynamical point of view the differences between collisional encounters described by the model potentials of this theory and more realistic ones are small.

In order to avoid calculation of σ_{il}'s for every local set of values of $n_i(\mathbf{q})$, $i = 1, \ldots, N$, one can use the BH choice of hard-core diameters, which do not depend

on the densities of the components or the density of the mixture. In the case of the nanofluid mixtures confined in narrow capillary pores this seems to be the best choice for the hard-core diameters.

The structure properties of the nanofluid mixtures can be obtained by direct equilibrium computer simulations. These results can be expressed in dimensionless form, and as such are valid for any σ_{il} and $n_i(\mathbf{q})$. Another possibility is to determine the structure by analytical means from integral equations of equilibrium statistical mechanics, and/or in the framework of density functional theory. For practical purposes direct computer simulation data seem to be more useful, as they should reflect the structure of a particular nanofluid system in greater detail.

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REFERENCES

1. J. Karkheck and G. Stell, J. Chem. Phys. bf 75: 1475 (1981).
2. S.A. Rice and P. Gray, *The Statistical Mechanics of Simple Fluids*, (Interscience, New York, 1965).
3. A.R. Altenberger, J.S. Dahler, and M. Tirrell, J. Chem. Phys., **86**: 2909 (1987).
4. H.T. Davis, in *Advances in Chemical Physics*, Vol. XXIY, I. Prigogine and S. Rice, eds. (Elsevier, The Netherlands, 1973), p.257.
5. G. Stell, J. Karkheck, and H. van Beijeren, J. Chem. Phys. **79**: 3166 (1983).
6. W. Sung and J.S. Dahler, J. Chem. Phys.**80**: 3025 (1984).
7. H.T. Davis, Chem. Eng. Commun. **58**: 413 (1987).
8. T.K. Vanderlick and H.T. Davis, J. Chem. Phys. **87**: 1791 (1987).
9. I. Bitsanis, T.K. Vanderlick, M. Tirrell, and H.T. Davis, J. Chem. Phys. **89**: 3152 (1988).
10. L.A. Pozhar and K.E. Gubbins, J. Chem. Phys. **94**:1367 (1991).
11. L.A. Pozhar and K.E. Gubbins, J. Chem. Phys. **99**: 8970 (1993).
12. L.A. Pozhar, *Transport Theory of Inhomogeneous Fluids* (World Scientific, Singapore, 1994).
13. E. Akhmatskaya, B.D. Todd, P.J. Daivis, D.J. Evans, K.E. Gubbins, and L.A. Pozhar, J. Chem. Phys. **104**: 4684 (1997).

14. L.A. Pozhar and K.E. Gubbins, Phys. Rev. E, in press.

15. J.D. Week, D. Chandler and H.C. Andersen, J. Chem. Phys. **54**: 5237 (1971).

16. J.A. Barker and D. Henderson, J. Chem. Phys. **47**: 4714 (1967).

17. M.K. Tham and K.E. Gubbins, J. Chem. Phys. **55**: 268 (1971).