

Virtual Nanofabrication of Electronic Materials

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ABSTRACT

A rigorous statistical mechanical theory of inhomogeneous fluids and molecular dynamics simulations are used to predict characteristic features of transport processes and the corresponding transport coefficients for a number of model nanoscale systems in terms of the system equilibrium structure factors. The obtained results confirm that the PG-theory supplies accurate characterization of transport processes in nanosystems and can be effectively used as a basis for software development to control 3D nanoscale materials processing.

Keywords: statistical mechanics, nanosystems, transport properties, molecular simulations.

1 INTRODUCTION

Recent advances in materials processing rely upon atomic/molecular deposition on structured surfaces (i.e. surfaces considered at the molecular/atomic level) and other nanoscale manipulations with spatially inhomogeneous systems (such as groups of atoms, molecules, molecular clusters, interfacial systems, or nanofluids, etc.). Structure of such nanosystems and transport processes within them (i) differ dramatically from those specific to their spatially homogeneous counterparts; (ii) are highly sensitive to the surface structure, composition, chemistry and topology of the nanosystems, and (iii) define the outcome of nanomaterials processing, including physical properties of nanomaterials and their spatial molecular structures.

During the last decade Pozhar and Gubbins [1] have developed the first rigorous and at the same time tractable statistical mechanical theory (PG-theory) that describes the transport processes in strongly inhomogeneous systems (including nanosystems). Among other advances, the PG-theory suggests unambiguous and explicit expressions for the transport coefficients and relaxation times in terms of the equilibrium structure factors (the density and correlation functions) of the systems. This permits to predict a change in the nature and outcome of a transport process with a change in the surface/fluid structure and suggests a reliable way of materials processing control. In particular, this approach can be applied to processing of electronic materials at the nanolevel to ensure their desired spatial structure and properties. Means to facilitate this advance involve development of the theory-based, simulations-

added, computationally undemanding and affordable software for virtual design of advanced materials.

In this work the PG-theory is used to study transport processes and the corresponding transport coefficients for about 20 model nanoscale systems each of which is composed of about 200 to 300 "fluid" molecules confined in slit and zeolite-like pores built of about 400 to 2000 "wall" molecules and possessing the width from about 3 to 10 molecular diameters. The equilibrium structure factors of these nanosystems (required as input data by the PG-theory) may be obtained from the equilibrium statistical mechanical considerations or simulated using the EMD technique. This latter technique is used in this work to account for the surface structure effects in detail, and the nanofluid and nano-surface structure factors are analysed and used to calculate "local" values of the PG-theoretical transport coefficients. The "local" PG-transport coefficients so obtained are further used to derive simplified correlations for and to calculate the corresponding system-average values of the system transport coefficients. These theoretical data are analysed in conjunction with the NEMD simulations data and known experimental results for all of the considered systems. The correspondence between these three data sets confirms reliability of the PG-approach.

2 FLOWS OF NANOFLUIDS

In the case of a nanofluid confined in a slit pore with the inhomogeneity in the z -direction (that is orthogonal to the wall planes) the major terms in a general expression for the "local" PG-viscosity of a nanofluid reduces significantly to the formula

$$\eta(z) = \eta_b \{ 4\pi n^*(z) \tau_\eta^*(z) [1 + \pi \beta^{*0}(z)]^2 + \frac{16}{5} \pi n^*(z) \beta^{*0}(z) \}, \quad (1)$$

where $\eta_b = (5/16 \sigma^2) (m / \pi \beta_B)^{1/2}$, $\beta_B = 1/(k_B T)$, k_B is the Boltzmann constant, T denotes temperature, m is the mass of a fluid molecule, σ and σ_{fw} are the diameters of the hard-core parts of the fluid-fluid and fluid-wall intermolecular interaction potentials, respectively; $n^*(z) = n(z)\sigma^3$ and $n_w^*(z) = n_w(z)\sigma_{fw}^3$ denote the dimensionless equilibrium number densities, $n(z)$ and n_w , of the nanofluid and the confinement. The dimensionless quantity

$$\tau_{\eta}^*(z) = \left\{ 2\pi \left[v^*(z) + \frac{1}{3} v_1^*(z) + \sqrt{2} v_2^*(z) \right] \right\}^{-1} \quad (2)$$

is proportional to the viscous relaxation time and incorporates two essentially “fluid” contributions,

$$v^*(z) = \int_0^{\pi} d\vartheta \sin \vartheta n^*(z - \sigma \cos \vartheta) g(z, z - \sigma \cos \vartheta), \quad (3)$$

$$v_1^*(z) = \int_0^{\pi} d\vartheta \sin \vartheta [n^*(z - \sigma \cos \vartheta) - n^*(z)] g(z, z - \sigma \cos \vartheta), \quad (4)$$

and the contribution due to “direct” fluid-wall intermolecular interactions,

$$v_2^*(z) = \int_0^{\pi} d\vartheta \sin \vartheta n_w^*(z - \sigma_{fw} \cos \vartheta) g_{fw}(z, z - \sigma_{fw} \cos \vartheta), \quad (5)$$

where $g(z, z - \sigma \cos \vartheta)$ and $g_{fw}(z, z - \sigma_{fw} \cos \vartheta)$ are the contact values of the equilibrium fluid-fluid and fluid-wall pair correlation functions (PCFs), respectively, and ϑ is the angle between the vector connecting the centres of mass of the interacting molecules and the positive z -direction. Finally,

$$\beta^*(z) = \int_0^{\pi} d\vartheta \sin^3 \vartheta \cos^2 \vartheta n^*(z - \sigma \cos \vartheta) g(z, z - \sigma \cos \vartheta). \quad (6)$$

In what follows we omit the star “*”, assuming that all quantities are reduced. We consider flows of model nanofluids confined in structured slit pores where fluid-fluid and fluid-wall intermolecular interactions were both modelled either with the WCA repulsive potential (the WCA systems) or with

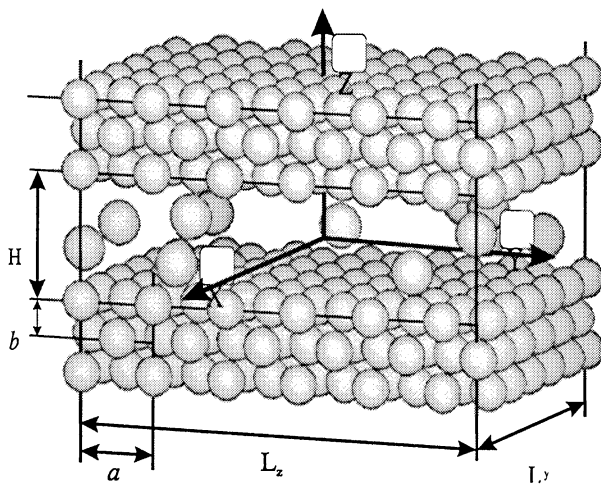


Figure 1. Slit pore geometry.

the LJ potential (LJ systems). The system geometry is pictured in Fig. 1. The equilibrium molecular dynamics simulation method (see Refs. [2] and [3] for the procedure details) was used to determine the densities and pair correlation function contact values of the model nanofluids that are required to calculate the “local” PG-viscosity of Eq. (1). The reduced potential parameters of the intermolecular interactions and molecular masses m were set equal to unity, $\epsilon = \sigma = \sigma_w = m = 1$. The pore wall structures, the average fluid number densities, $n = 0.442$; 0.603 , and the average wall number density, $n_w = 0.85$, were chosen to incorporate the simulation conditions of the two nanofluid systems considered previously [2]. The reasons for doing so include comparison of our and earlier results specific to the two systems considered previously (namely, the LJ and WCA nanofluids confined in the pore of $H = 5.1\sigma$ in width). The fluid and wall average densities are defined in a standard fashion, as the ratio of the total number of the fluid or wall atoms to the corresponding pore space or wall volumes they occupy, respectively. Similar to our earlier simulations, for the EMD simulations we used a fifth order Gear predictor-corrector algorithm with the reduced time steps $\Delta t = 2 \times 10^{-5}$ and $\Delta t = 2 \times 10^{-4}$. The periodic boundary conditions were applied in all three directions. The considered system parameters are collected in Table 1.

Pore width H/σ	Fluid average number density, $n\sigma^3$	Temperature, $k_B T/\epsilon$	Simulation box sizes, $L_x/\sigma = L_y/\sigma$	Parameter a/σ	Parameter b/σ	Number of fluid particles, N
3.2	0.442	0.729	13.026	2.368	0.638	240
	0.442	0.729	11.152	2.028	0.870	176
	0.442	0.729	10.636	1.933	0.958	160
	0.603	0.958	11.152	2.028	0.870	240
4.1	0.442	0.729	12.866	2.339	0.654	300
	0.603	0.958	12.894	2.344	0.651	411
5.1	0.442	0.729	12.637	2.298	0.678	360
	0.603	0.958	10.820	1.967	0.924	360
7.0	0.442	0.729	12.456	2.265	0.698	480
	0.603	0.958	10.664	1.934	0.952	480

Table 1. Parameters of studied systems.

The obtained EMD densities and the PCFs’ contact values were used further in Eqs. (2) – (6) to calculate the “local” PG-theoretical viscosity (1) for the studied systems. Here we stress the point that this viscosity is intrinsically non-local, as can be seen from Eqs. (1) – (6), as it includes integration (over the direction angles ϑ) of the PCFs’ contact values dependent on the positions of the particles

centres located at the positions $(z-\sigma \cos\theta)$, and the corresponding densities. Therefore, the label “local” is used to distinguish between the viscosity at a position z within the fluid and its pore-average value that is found by integration of Eq. (1) over the pore width H and subsequent division of the result by H . A typical “local” PG-theoretical viscosity and density of the LJ-fluid are plotted in Fig. 2.

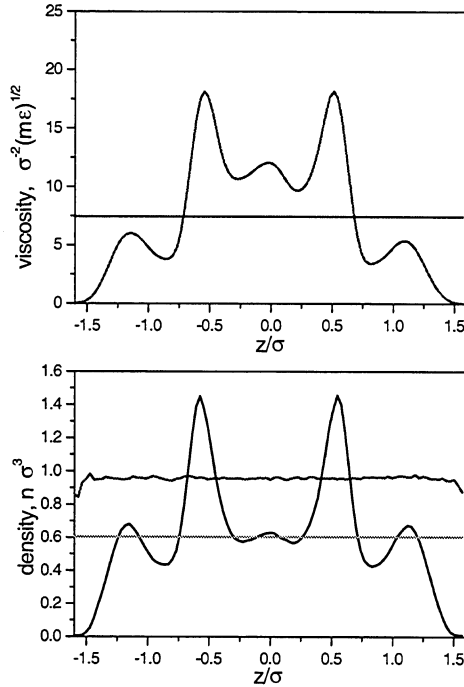


Figure 2. Top: the PG-theoretical viscosity for the LJ fluid confined in the pore of $H=3.2\sigma$ in width at $\langle n\sigma^3 \rangle = 0.603$ and temperature $k_B T/\epsilon = 0.958$. Curve: Eq. (1) with the EMD-simulated PCFs. Straight line: the corresponding pore-average PG-theoretical viscosity. Bottom: the corresponding number density (curve), average number density (lower line) and temperature (upper line).

To evaluate the theoretical results the Poiseuille flow of the studied nanofluids was recreated using the NEMD simulations method (a dimensionless force, $F=0.02$, acting in the y -direction was applied to the center of each fluid particle to generate the Poiseuille flow). A typical velocity profile obtained after about 7×10^8 time steps and the corresponding density profile are shown in Fig. 3. The oscillating velocity profile confirms theoretical expectation [1] and differs markedly from a parabolic one that is typical for the bulk fluids. The number of picks on the velocity profile corresponds to the number of fluid layers accommodated within a pore (and reflected by the density profile). These results confirm again the PG-theoretical predictions and previous NEMD findings (obtained for the nanofluids in slit nanopores of $H=5.1\sigma$) that the “standard” evaluation of the local viscosity as the ratio of the flow direction-bound pressure tensor component to the flow rate

can not be applied as it leads to negative and infinite values of the viscosity due observed extremal values and inflections of the velocity profile. This means that NEMD method does not provide an “independent” opportunity to evaluate the local viscosity of nanofluids. However, some useful information on the pore-average viscosity can be extracted from the NEMD data upon consideration that in the case of the Poiseuille flow of bulk fluids between two parallel walls separated by the distance H a well known correlation between the average flow velocity, u_p , and the pressure gradient, dp/dy , leads to the expression

$$\eta_p = \frac{H^2}{12 u_p} \frac{dp}{dy}, \quad (7)$$

where η_p - fluid viscosity and the parabolic velocity profile is assumed. In the NEMD simulation case $dp/dy = \langle n\sigma^3 \rangle F$,

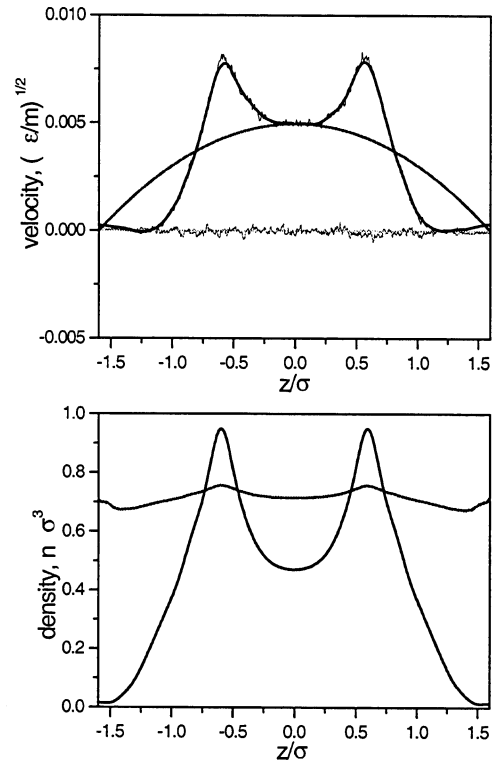


Figure 3. Top: the WCA fluid NEMD velocity profile at $\langle n\sigma^3 \rangle = 0.442$ and $k_B T/\epsilon = 0.729$ for the pore of $H=3.2\sigma$ in width, and its parabolic fit. Curve: the smoothed velocity component in the y -direction of the flow; fluctuations: the velocity components in the x and z directions orthogonal to the flow direction; fluctuations about the curve: the actual NEMD data. Bottom: the NEMD density and temperature.

where $\langle n\sigma^3 \rangle$ indicates the pore-average fluid density. Of course, in the case of nanofluids the correlation (7) can only be considered as heuristic. However, if one fits the

nanofluid velocity profile with a parabolic fit so that the pore-average fluid velocity specific to the observed NEMD oscillating velocity profile coincides with that specific to the parabolic feet, one can use Eq. (7) to evaluate the pore-average NEMD viscosity heuristically. Success of such an evaluation depends significantly upon a magnitude of the deviation between the actual NEMD velocity profile and its parabolic fit. The results of such an NEMD-heuristic evaluation and the corresponding PG-theoretical pore-average viscosity values are plotted in Fig. 4 for the case of the lower average fluid density, $\langle n\sigma^3 \rangle = 0.442$. The agreement between these sets of the pore-average viscosity values is extremely good and lies within 30% of the NEMD-heuristic values. [It has to be noted here that the expected accuracy of the PG-EMD theoretical viscosity values is about 40% due to the statistical errors of the EMD-based PCF-calculations used to determine the PG-theoretical viscosity.]

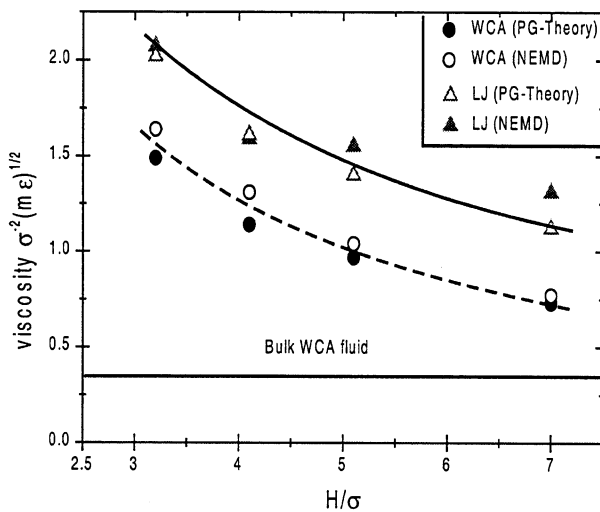


Figure 4. The pore-average theoretical and NEMD-heuristic viscosity, Eqs. (1) and (7), respectively, of the pore nanofluids at $\langle n\sigma^3 \rangle = 0.442$ and $k_B T/\epsilon = 0.729$ as a function of pore width H . Curves are a guide for an eye. Straight line: the bulk WCA fluid viscosity at the same temperature and density.

This agreement suggests that Eq. (7) can be used to evaluate the pore-average viscosity of nanofluids from the NEMD data in the case of the pore-average fluid densities up to 0.442 with the accuracy over 70%. At higher pore-average fluid densities a deviation between the NEMD velocity profile and its parabolic fit can be over 100%, and the accuracy of the correlation (7) decreases to 30 %.

3 DIFFUSION IN NANOFLUIDS

In addition to the flows of nanofluids in slit nanopores we studied self diffusion [4] in the LJ-nanofluids confined in nanopores composed of two channels of a square cross-section connected via a central octahedron-like unit, Fig. 5,

using both the PG-theoretical/EMD and NEMD methods. Once again, the results obtained by both methods agree very well (see discussion in Ref. 4).

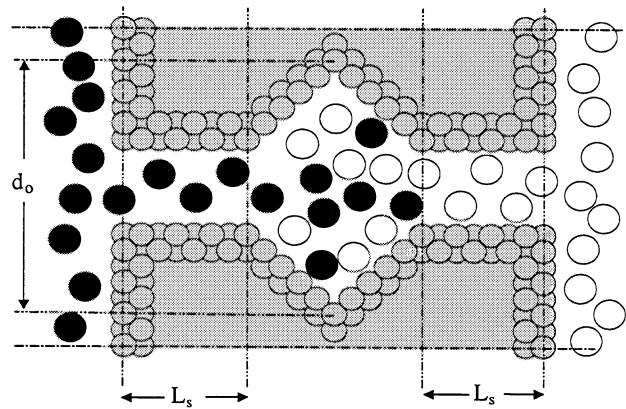


Figure 5. Self-diffusion: model system side view. The axial half length, L , of the composite pore is $L_s + 2.5\sqrt{2}\sigma_w$; the square channel: $L_s = 3.5\sqrt{2}\sigma_w$; channel width: $d_s = 3\sqrt{2}\sigma_w$. The central unit ("octahedron"): maximum dimension $d_o = 8\sqrt{2}\sigma_w$. The pore system is composed of two dense face-centered cubic layers of immobile atoms. The ratio of the fluid to wall atom diameters, σ/σ_w , is 3.8.

4 CONCLUSIONS

The unified PG-theory/EMD simulations method provides physically sound, reliable approach to and accurate data on transport processes in nanosystems.

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