Local structure and density fluctuations in confined fluids

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A B S T R A C T

Spatial confinement modifies the microscopic structure of dense fluids, thereby inducing for example structural forces between the confining walls. However, confinement also modifies the fluids' density fluctuations, resulting in more elusive but equally important effects. In this brief review it is shown that both of these phenomena are naturally analyzed using the confined fluid's pair densities, which have recently become also experimentally accessible. Two particular topics are discussed, namely, the mechanisms of oscillatory density profiles and ensuing solvation forces in dense confined fluids as well as the behavior of liquids in solvophobic confinement.

1. Introduction

At microscopic length scales the continuum description of dense fluids such as liquids or colloidal dispersions breaks down, and their granular structure must be taken into account explicitly. In bulk the microscopic structure is routinely characterized in terms of the pair density, which describes the temporally averaged local density around a central particle [1]. The importance of pair densities is twofold: first, they provide a formal connection between the fluid's microscopic interactions and its macroscopic, thermodynamic properties. Second, they are experimentally accessible by scattering techniques, thereby allowing quantitative comparison between experiment and theory at a high level of sophistication. As a consequence, pair densities are today the most important quantities for characterizing bulk fluids.

In the case of a dense fluid confined between two solid walls at close separation the situation is more complicated, with the pair densities being both anisotropic and depending on the central particle's position between the walls. In the overwhelming majority of studies the microscopic structure is instead characterized in terms of the fluid's density profile across the confining slit, i.e., in terms of a singlet density distribution [2]. The resulting oscillatory density profiles of dense fluids in narrow confinement are often used to rationalize oscillatory solvation forces [3], and are hence well known by the colloid and interface community. However, explicit consideration of pair densities in confinement facilitates mechanistic analysis of the confined fluid's properties, such as solvation forces [4] or diffusivity [5], and is hence worth the extra effort. Here I will review some recent and future directions of research on confined fluids at the level of pair densities, with an emphasis

on phenomena of importance within the field of colloid and interface science.

The outline of this brief review is as follows. First, I will introduce the concept of pair densities in spatial confinement. As an illustrative example, I will next use the pair densities to outline a conceptually simple mechanistic analysis of oscillatory density profiles and solvation forces in thin fluid films. In the limit of short wall separations the latter give the depletion forces [6], which were the topic of a recent special issue [7]. Finally, I will introduce the ensuing density fluctuations in a confined open system. In particular, I discuss means to quantify how liquids (including water) meet extended solvophobic (hydrophobic) interfaces. This phenomenon, in turn, is of importance for example in hydrophobic assembly [8].

2. Local structure of confined fluids

Let us begin the discussion by defining the density profile and pair densities of a dense simple fluid between planar solid walls at short separation, which is in equilibrium with a bulk fluid reservoir. The situation is schematically presented in Fig. 1, with the particles (which can be atoms, molecules, or colloidal particles alike) depicted as spheres. Spatial confinement induces microscopic ordering of the fluid constituents into layers parallel to the confining walls. This ordering is typically characterized by the density profile $n(z)$ across the confining slit, as shown to the right. Note that $n(z)$ gives the distribution of particles across the slit, but does not provide the positions of neighboring particles.

At the next level of sophistication we consider a central particle, depicted by the yellow sphere in the figure. We may now pose the question, what is the density locally around the central particle? The answer is given by the pair density $n(z)g(\mathbf{r}, \mathbf{r}')$, with g denoting the pair distribution function, $\mathbf{r}'$ the position of the central particle, $\mathbf{r}$ the position

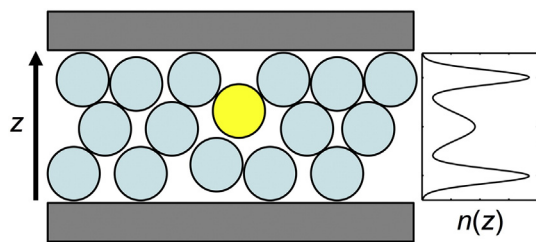E-mail address: kim.nygard@chem.gu.se.

Fig. 1. Schematic of a dense fluid confined between planar solid walls at short separation. The fluid orders into layers parallel to the confining walls, which can be quantified by the density profile $n(z)$ across the confining slit as shown to the right. The yellow sphere depicts a central particle at position $\mathbf{r}'$, and the pair density describes the local density at position $\mathbf{r}$ around the central particle.

where the local density is measured, and z the coordinate of $\mathbf{r}$ perpendicular to the confining walls. Note that whereas in bulk the pair density is isotropic and only depends on the distance from the central particle, in confinement it is both anisotropic and dependent on the central particle's position in the slit (see, e.g., Refs. [4,9] for illustrative examples). As a consequence ng is significantly more complex in confinement than in bulk, explaining why the former has been studied explicitly only seldom.

The theoretical schemes for explicit studies of confined fluids at the level of pair densities ng are rather mature, including integral-equation theories [4,10,11], classical density functional theory [12,13], and mode-coupling theory [14,15**]. Simulations of pair densities in dense confined fluids have also recently become feasible [13]. However, since the practical computations have been conceived as complicated and expensive, it is only recently that theoretical studies at this level of sophistication have become more common. Studies of interest to the colloid and interface community include, but are not limited to, ion–ion correlations in electrolytes near charged surfaces [16], depletion potentials [17], tunable assembly of charged fluids between dielectric walls [18*], reentrant glass transitions in confined fluids [19*], and fluid inclusions in porous matrices [20].

The traditional experimental approach to study pair densities of dense fluids is scattering, as already alluded to in the introduction, which provides the pair density in reciprocal space in terms of a structure factor [1]. However, while studies on bulk systems have been routinely carried out for about half a century, experiments on confined fluids have been hampered by minute sample volumes and the presence of the confining walls. This problem was recently overcome, when we reported the first scheme for probing pair densities of confined fluids, based on x-ray scattering from colloid-filled nanofluidic containers [21]. Within this scheme the pair densities are probed in terms of an anisotropic structure factor [9],

$$S(\mathbf{q}) = 1 + \frac{1}{N}\int n(\mathbf{r})n(\mathbf{r}')[g(\mathbf{r},\mathbf{r}')-1]e^{i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')}d\mathbf{r}d\mathbf{r}', \qquad (1)$$

where $\mathbf{q}$ is the scattering vector, N the number of particles in the slit, and the integrations are performed over the whole space between the walls. Most importantly, the thus obtained experimental structure factors have been found to be in semi-quantitative agreement with ab initio theoretical calculations [22*], providing experimental verification of the strong anisotropy in the pair densities of dense confined fluids predicted twenty years earlier [4]. I note in passing that this confinement scheme has also been used to control the assembly of anisotropic nanoparticles [23].

The experimental studies have to date been carried out using colloidal dispersions as model systems. While such an approach allows quantitative comparison with statistical mechanics calculations and facilitates mechanistic analysis, chemical specificity is inevitably sacrificed by the use of model systems. A highly challenging but extremely important continuation of these studies would thus be to

extend the methodology to molecular liquids, including 'hot topics' such as nanoconfined ionic liquids [24,25] and water in hydrophobic confinement [26,27**]. I note that the first promising experimental results on structure factors of confined molecular liquids have been recently reported [28*], although more development work is still needed in order to carry out these extremely challenging experiments reliably.

3. Oscillatory density profiles and solvation forces

Having introduced pair densities in dense confined fluids, I turn to the first example of this brief review — a conceptually simple and formally exact approach for mechanistic analysis of oscillatory density profiles and solvation forces.

Let us begin by considering again the schematic presentation of Fig. 1. The central particle at $\mathbf{r}'$ interacts with the confining walls and all other particles in the system. These interactions can be cast in the form of the potential of mean force, which is the free energy of interactions. By definition the potential of mean force $w(z)$ is related to the number density profile $n(z)$ across the slit via $n(z) = n_b \exp[-\beta w(z)]$, with n_b denoting the bulk number density, $\beta = (k_BT)^{-1}$, k_B Boltzmann's constant, and T the absolute temperature. The fluid in the slit geometry exhibits isotropy parallel to the confining walls. For mechanistic analysis of the density profile, it is thus sufficient to consider the normal component of the mean force, $F(z) = -dw/dz = k_BTd\ln n/dz$, which can be determined using the principal components of the mean force in the upward ($F_\uparrow$) and downward ($F_\downarrow$) directions, $F(z) = F_\uparrow - F_\downarrow$ [13,29]. A key observation here is that we can determine the principal mean force components $F_\uparrow$ and $F_\downarrow$ using the confined fluid's pair densities, and hence analyze the mechanisms of oscillatory density profiles and solvation forces.

To illustrate the concept of principal mean force components, I exemplify them in Fig. 2(a) for a dense hard-sphere fluid confined between hard planar walls. For theoretical details and more examples, see Ref. [29]. Since $F(z) = F_\uparrow - F_\downarrow \propto d\ln n/dz$, maxima and minima in $n(z)$ are observed for vanishing $F(z)$ (i.e., $F_\uparrow = F_\downarrow$) and a positive (negative) $F(z)$ corresponds to a positive (negative) dn/dz. By integrating the net force $F(z)$ of panel (a) one thus obtains the density profile $n(z)$ of panel (b). From $n(z)$ one can further determine the pressure in the slit, and hence the net force acting on the confining walls. However, by analyzing the force components separately one can also understand the mechanisms leading to the oscillatory density profile, and subsequently the oscillatory solvation force by carrying out the analysis as a function of slit width [29]. Note that this scheme is formally exact and can also be applied to simple fluids exhibiting soft interactions, such as Lennard-Jones or screened Coulomb potentials.

For completeness I also present in Fig. 2(c) the potential of mean force $w(z)$, i.e., the free energy of interactions. The small values of $|w(z)| \lesssim k_BT$ directly imply that (i) the instantaneous local structures are continuously changing and (ii) the temporally averaged local structures, and hence many of the confined fluid's ensuing properties, are rather sensitive to weak particle-wall interaction potentials comparable to the thermal energy k_BT.

In the particular case of Fig. 2, namely a dense hard-sphere fluid in hard planar confinement, the principal force components are only slightly perturbed by the presence of the opposite wall; $F_\uparrow$ (and $F_\downarrow$) is to a good approximation given by the corresponding force component at a single solid–fluid interface [29]. As a result, we can understand the slit-width dependence of $n(z)$ qualitatively (or even semi-quantitatively) simply by a translation of $F_\downarrow$ with respect to $F_\uparrow$. This is a rather surprising finding which provides a novel, conceptually simple approach to understand oscillatory density profiles and ensuing solvation forces.

Here I have discussed a model system – a dense hard-sphere fluid between planar hard walls – but eventually this kind of analysis should be extended to more realistic systems. For example, oscillatory solvation forces in ionic liquids [24], which are determined by a complicated
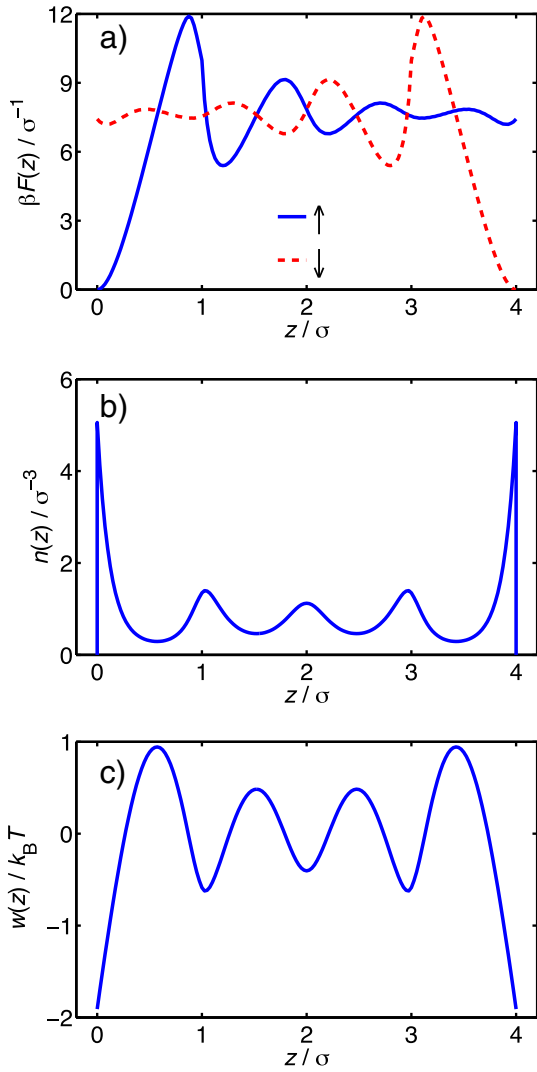
Fig. 2. (a) Principal mean force components in upward ($F_{\uparrow}$) and downward ($F_{\downarrow}$) directions, determined for a dense hard-sphere fluid between hard planar walls using the theory of Ref. [29]. Data are shown for a reduced slit width available for particle centers, $L = H - \sigma = 4.0\sigma$, where H is the wall separation and σ the particle diameter. The confined fluid is kept in equilibrium with a bulk reservoir of number density $n_b = 0.75\sigma^{-3}$. (b) Resulting number density profile $n(z)$ across the confining slit. (c) Corresponding potential of mean force $w(z)$ across the confining slit.

interplay between energetic and entropic effects, are presently attracting significant interest. These systems are rather complex, and in order to obtain a better understanding it would be highly useful to apply a mechanistic analysis similar as outlined above.

4. Density fluctuations and solvophobicity

So far I have discussed static properties of confined fluids, viz. temporally averaged density distributions and solvation forces (for dynamic aspects of solvation forces, see Ref. [30]). However, spatial confinement also modifies the fluid's density fluctuations, with important implications within the field of colloids and interfaces. For a schematic presentation of density fluctuations in confinement, see Fig. 3. Hence I turn to the second example of this review — confined fluids' density fluctuations and solvophobicity.

An open system exhibits fluctuations in the number of particles N [31], and these can be probed using scattering techniques. For bulk fluids this relation is given by $\lim_{q \to 0} S_b(q) = (\langle N^2 \rangle - \langle N \rangle^2)/\langle N \rangle = (k_B T/n_b)(\partial n_b/\partial \mu)_T$, where a constant temperature is assumed and the isotropic bulk structure factor is denoted by $S_b(q)$, the mean number
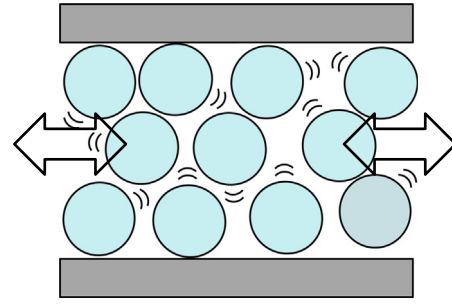

Fig. 3. Schematic of density fluctuations in a dense confined fluid. There is a continuous exchange of particles between the open confinement and the bulk reservoir, resulting in fluctuations in the number of particles in the slit.

of particles in the (open) system by $\langle N \rangle$, the fluctuation in number of particles by $\sqrt{\langle N^2 \rangle - \langle N \rangle^2}$, and the chemical potential by μ [1]. A similar result can be obtained for confined fluids, although now the fluid's density fluctuations depend on the slit width H [32]. The long-wavelength limit of the anisotropic structure factor of Eq. (1) then becomes [33*]

$$\lim_{\mathbf{q} \to 0} S(\mathbf{q}) = \left(\frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle} \right)_{H,T} = \frac{k_B T}{n_H} \left(\frac{\partial n_H}{\partial \mu} \right)_{H,T}, \qquad (2)$$

where n_H denotes the average number density of particles in the slit. This is a beautiful result of statistical thermodynamics, which provides a formally exact relation between density fluctuations and thermodynamic response functions of confined fluids, on the one hand, and scattering experiments, on the other hand. This approach was very recently applied to confined colloidal suspensions [33*], demonstrating the possibility to directly determine density fluctuations of spatially confined fluids by scattering experiments.

To highlight the importance of density fluctuations in confinement, let us consider how water meets extended hydrophobic interfaces. This is obviously an important question in the field of colloid and interface science, providing a basis for phenomena such as hydrophobic assembly [8]. Based on extensive theoretical and simulation studies, a picture has emerged where water exhibits a density depletion near extended hydrophobic interfaces, akin to the liquid–vapor interface [8,26]. However, quantitative experimental characterization of the minute density depletion – known as the hydrophobic gap – has proven challenging [34–37]. Moreover, a straightforward relation between the microscopic hydrophobic gap and the macroscopic contact angle remains unsolved [38].

Recent studies have provided further insight into the problem. First, the hydrophobic gap is accompanied by enhanced density fluctuations of the liquid [8,26], and these provide an alternative approach to characterize how water meets extended hydrophobic interfaces. It has indeed recently been shown that a properly defined local compressibility $\chi(z) \equiv [\partial n(z)/\partial \mu]_{H,T}$, or equivalently local density fluctuations, provides a far better measure of the connection between microscopic structure and contact angle than does the density profile [39*]. Second, the enhanced density fluctuations are not limited to water close to hydrophobic interfaces, but are also observed for simpler liquids, such as Lennard-Jones fluids near saturation in the vicinity of solvophobic interfaces [39*]. Finally, recent simulations of water near hydrophobic interfaces evidence a continuous critical drying transition [40**], providing a rationale for the enhanced density fluctuations of water near hydrophobic interfaces (or other liquids near solvophobic interfaces) observed in simulation studies [27**,41,42]. Experimental verification of these theoretical and simulation results is, however, still missing.

How can the hypothesis of continuous critical drying of water (or simpler liquids) near hydrophobic (solvophobic) interfaces be verified

experimentally? A possible solution is given by Eq. (2), according to which the long-wavelength limit of $S(\mathbf{q})$ yields an integral of the local compressibility $\chi(z)$; for sufficiently narrow slits $\lim_{\mathbf{q}\to 0} S(\mathbf{q})$ is sensitive to density fluctuations near the confining walls, thus allowing experimental verification of the theoretically predicted divergence of density fluctuations in hydrophobic (or solvophobic) confinement. At the moment such experimental studies could be carried out following Ref. [33*] using liquid-like colloids, and I foresee experiments addressing the nature of solvophobicity in the near future. However, eventually this experimental approach will also be applicable to molecular liquids [28*], and I look forward to experimental verification for water in hydrophobic confinement.

Finally, I conclude with a speculative open question. Tunable interactions allow controlled assembly of colloidal systems. As an illustrative example, confinement of binary liquid mixtures close to their bulk critical point leads to highly temperature-sensitive critical Casimir forces between the walls [43], which are today used for reversible assembly of colloidal particles [44]. The above discussion on solvophobicity raises an interesting question: is it possible to tune the solvophobic interactions by a suitable choice of model fluid [45*], thereby providing an alternative method for controlled colloidal assembly?

5. Summary and outlook

I have briefly reviewed some recent research on confined fluids at the fundamental level of pair densities, with an emphasis on phenomena of importance in the field of colloid and interface science. These kind of studies are now entering a very exciting phase, since they can finally be carried out both theoretically and experimentally. While my discussion here focused on simple model systems, I expect that similar analysis also can shed light on the behavior of more complicated fluids, such as nanoscopically confined ionic liquids and water in hydrophobic confinement.

Acknowledgments

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