CONFINED FLUIDS:
STRUCTURE, PROPERTIES AND PHASE BEHAVIOR

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I. Introduction

Reduction of the size of a sample of a substance to the nanometer scale endows it with properties and behavior that are different from those of the bulk material. It is not just the isolated nanosample of a material that has properties different from the same bulk material; interaction with the walls that confine a sample in a small volume further alters its properties and behavior. These changes in behavior arise when the range of molecular interaction and the length scale associated with position correlation in the material are similar to the length scale of the confinement. The changes in behavior are manifest in the structures of the equilibrium phases that are supported and the transitions between those phases, and in the dynamical properties of the nanosystem. The domains of stability of the structures in the confined system and the transitions between them, and the transport properties of the system, depend on the commensurability of the several length scales. Understanding the interplay of the several length scales is a challenge to experimentation, simulation and the molecular theory of fluids and phase transitions. Development of that understanding opens the door to better exploitation of many real-world physical and biological phenomena and industrial processes, some examples of which are properties of liquids in porous media [1] as in underground petroleum recovery [2], transfer of ions through biological ion-channels [3-5], transport of neutral molecules through zeolites and membrane channels [6], lubrication [7], and more.

In this paper we limit ourselves to a review of the thermodynamic properties of pure (one-component) substances that are confined in slits or cylindrical pores, examples of which are shown in Figs. 1.1-1.3 [8,9].

![Figure 1-1. Nanopore (left) and nanoslit (right)](image-url)
Current studies of the equilibrium properties of confined fluids are quite extensive, covering many kinds of fluids and fluid mixtures. Rather than attempt to survey this vast field we have limited our discussion to two exemplary systems, namely confined colloid suspensions and confined water. Confined colloid suspensions serve as experimentally accessible surrogates for molecular systems, because their equilibrium properties can, by virtue of the MacMillan-Mayer theory [10], be mapped into the properties of confined molecular systems. They provide very useful information about the properties of the simplest confined monoatomic and compact molecular fluids under conditions in which the role of the walls is to define the geometry of confinement, but little else. In contrast,
studies of nanoconfined water address issues associated with the role of anisotropic bonding in the liquid, and the importance of the liquid-wall interaction, in the determination of structure in a confined system.

Well-defined nanochambers for encapsulating various molecules in their interiors are available in the form of carbon nanotubes (Figure 1.2) with diameters in the range 1-100 nanometers [11,12] and the mobile synthetic crystalline material 41 (MCM-41), which has hexagonal one-dimensional tubes arranged in a hexagonal structure (Figure 1.3); the pore diameter can be adjusted up to 20 nm. In addition to these systems a variety of other nanometer scale structures are produced and used for confinement of fluids. Amongst these are uniform arrays produced using nanoimprint lithography over large areas (100 mm wafers), as proposed by Cao et al. [13]. The nanofluidic channels in this fabricated system can be further narrowed and sealed, resulting in channels with a cross section as small as 10 nm by 50 nm.

It is generally found that fluids confined between two walls with small separation become ordered into layers that have lateral internal ordering as well as transverse ordering between layers. That is, the density distribution of a fluid confined to a narrow slit is inhomogeneous. Comparable ordering occurs in fluids confined to other nano-geometries, such as cylinders, and this ordering is the subject of numerous theoretical and computational studies [14-40]. Typically, nanoslit walls have non-negligible influence on both the energy and the entropy of the enclosed fluid. The influence on the fluid energy arises from both the direct wall-molecule interaction and the truncation of interactions between molecules in the fluid in the direction of confinement [41]. If the wall is smooth its influence on the fluid entropy is associated with the inhomogeneous density distribution generated by the excluded volume constraints imposed by the walls [42-45]. If the wall is structured, the molecule wall interaction will generate some ordering of the fluid structure adjacent to the wall, and thereby affect the fluid entropy. In nanoconfined systems, as well as in inhomogeneous macroscopic fluid systems, the local density and pressure are important descriptors of the state of the system, and the pressure is a tensor with components $P_{ij}$, where $i, j = x, y, z$. In a simple molecular fluid confined in a nanoslit with smooth rigid walls the pressure tensor is diagonal with components $P_{ii}$ ($i = x, y, z$), but the component normal to the walls, $P_{zz}$, is different from the transverse components $P_{xx}$ and $P_{yy}$ noting that $P_{xx} = P_{yy}$. The pressure that is exerted on all parallel $zx$- and $zy$-planes is the same, but the pressure on each point on the $zx$- and $zy$-planes depends on $z$ [18]. In a simple molecular fluid confined in a cylindrical nanopore with smooth walls the pressure is also a diagonal tensor with components $P_{ii}$ ($i = r, \theta, z$). The normal component, $P_{rr}$, is exerted on the $\theta z$-plane and the transverse component, $P_{zz}$, is exerted on the $r \theta$-plane.

A one-component simple molecular fluid in a nanotube or a nanoslit may exist in a one-phase, a two-phase or a three-phase state, depending on the values of the independent variables that define the state of the system. For a macroscopic sample of fluid two independent variables, such as temperature and pressure, determine the state of the system. For a nanoconfined fluid these do not suffice due to the appreciable effect of the walls. Consequently, thermodynamic property relations in nanoconfined systems are also functions of the geometry and internal structure of the system under consideration. In contrast to the behavior of large systems, the thermodynamic properties and property
relations of a particular confined system will generally vary in different environments [46-48].

As will be seen below, we focus attention on the structure of different phases found in confined systems, and on the character of phase transitions between structures. In a macroscopic (strictly infinite) system, the signature of a first order phase transition is a discontinuity in a thermodynamic function. In a nanosystem that singularity is smoothed, and under certain circumstances may not occur. However, both experimental studies and computer simulations of small systems, some as small as clusters of a few atoms or molecules, reveal phenomena that resemble phase transitions in large systems and suggest the occurrence of what appear to be multiple stable phases of matter [46-48]. The formulation of the principles underlying thermodynamic property relations in small systems raises both theoretical and experimental issues [48]. While we can have controlled mass (closed) nanosystems, the finite size of such systems and the large ratio of surface to volume suggests that the definitions of extensive and intensive variables, and their separate roles in the theoretical description, must be examined carefully [47-51]. We expect that thermodynamic property relations in a nanoconfined system will be a function of the character of the walls, the geometry of confinement and the internal structure of the system under consideration. As a result, to develop a molecular representation and predict the behavior of a nanosystem an appropriate ensemble must be defined. It has been suggested [51,52] that these small systems be characterized as non-extensive, with the test for non-extensive character being the non-additivity of the system entropy [53].

The most widely studied phase transition in small/nano systems is the vapor-liquid transition known as capillary condensation. The earliest study of capillary condensation is due to Derjaguin [54]. Later Bangham [55] developed the thermodynamic description of the hysteresis loop in capillary condensation, and in 1947 Hill [56] formulated the statistical mechanics of capillary condensation and hysteresis. Many other investigators have worked on various aspects of capillary condensation, including Hirst [57], Everett and Haynes [58], Shahraeeni and Or [59], and very recently Berim and Ruckenstein [60].

An experimental observation of evaporation of water inside a sealed multi-wall carbon nanotube (MWCNT) has been reported by Gogotsi et al. [61] (Figs. 1.4 and 1.5). Typically, the inner diameter of a MWCNT is up to 10 nm and the wall thickness can exceed the inner diameter. The sealed MWCNTs containing water (and possibly some impurities like CO₂ and CH₄) used in this experiment were synthesized hydrothermally; some contain segregated liquid and gas phases with well-defined interfaces observable clearly under a transmission electron microscope. The experiments show that a MWCNT does not leak even when heated in the high vacuum environment of the transmission electron microscope column. The pressure inside the nanotube at room temperature was estimated to be up to 30 MPa, and we note that high pressure increases the solubility of CO₂ and CH₄ impurities in water and, possibility, the wettability of the inside-wall of the carbon nanotube. Fragmentation of the phases is observed in these samples as the temperature is raised.

Fragmentation of a system into many small parts is a characteristic feature associated with a phase transition in a small system. It is similar to boiling in a macroscopic (infinite) system but has new features arising from the contributions arising
from the importance of fluctuations in a small system. In the typical case it is observed that before evaporation a liquid in a nanosystem also exhibits dispersion of small pieces of the liquid phase in the gas phase. Figure 2.5 displays clearly the fragmentation of water during its evaporation inside the nanotube. Dispersion of one fluid phase into another occurs when the ratio of viscous to capillary forces exceeds a critical value that depends on the interfacial tension, the viscosity ratio between dispersed and continuous phases, pressure, and temperature [62,63]. A finite, small system undergoing a first order phase transition fragments loses its homogeneity and develops global density fluctuations. In a macroscopic system for which conventional thermodynamics is valid, the phase transition is usually analyzed by considering two infinite homogeneous regions that separate via action of an external gravity field. Then the two phases exchange energy and particles through an interface [48]. Fragmentation has been interpreted as a first order phase transition in a finite system; this interpretation was originally developed for nuclear processes, and it has been advanced theoretically and via simulations by several investigators [48,62-70].

Figure 1.4. First order phase transition of water inside a MWCNT [61]. Note the fragmentation of the liquid phase as the temperature is increased [48].

Figure 1.5. Fragmentation in the first order water-water vapor transition inside a MWCNT. These figures correspond to the same experiment as shown by Figure 1.4 [61,71]
In recent years many investigators have studied the solid-liquid phase transition in both unconfined and confined nanosystems [72-76]. The experimental studies have shown that in confined nanosystems the melting and freezing points of pure compounds are different from one another, they are less than the bulk system values, and there exists a hysteresis loop in the melting/freezing transition. We will illustrate and discuss these matters using, as examples, confined colloid suspensions and confined water. An example of a simple molecule freezing and melting hysteresis loop is found in nano-confined gallium (Ga, Mw = 69.7, mp = 303K, bp = 2477K)[72]. Di Cicco produced submicrometric Ga droplets confined in epoxy resin and studied the melting and freezing of the droplets by combining energy-dispersive x-ray diffraction, x-ray absorption fine structure, and single-energy x-ray absorption [see also: 75-81]. The constrained gallium liquid droplets were found to undercool to 150 K before freezing. It was also shown that the melting point of the gallium droplets was depressed to 254 K (see Figure 1.6).

![Figure 1.6. Melting and freezing changes of nanoconfined gallium. Upper panel: Temperature scan of the absorption coefficient at constant energy showing a clear hysteresis loop. Melting and freezing are indicated by arrows labeled as m and f, respectively. Lower panel: Derivative of the temperature scan shown in the upper panel [72].](image-url)
II. Macroscopic description of nanoconfined fluids

II.A. A simple equation of state

The ratio of surface to volume of a nanoconfined system, and the overwhelming importance of the fluid-wall interaction, require modification of the standard representation of the state of a confined system. Amongst other consequences, excluded volume effects in a nanoconfined fluid force the fluid to be inhomogeneous in space, and the pressure to be different in different directions. For a nanoconfined simple molecular fluid the pressure tensor, \( \mathbf{P} \), is diagonal with components \( P_i, \ i = x, y, z \). It is convenient to characterize the nanoconfined fluid using the total number of enclosed molecules, \( N \), the chemical potential of the molecules, \( \mu \), the wall-molecule interaction energy per unit area, \( u_w \), and the area of the confining walls, \( A_w \). The equation of state of the confined fluid depends on the geometry of the nanoconfinement under consideration and the nature of the walls. Arguably the simplest equation of state of a nanoconfined fluid is an extension of the bulk fluid van der Waals equation of state

\[
\left(P + \frac{a}{V^2}\right)(V - b) = RT
\]  

(2.1)

with values of the parameters \( a \) and \( b \) that vary with the size of the system [20]. Using the van der Waals equation of state Keshavarzi [20] derived the following expressions for the components of the pressure tensor of a confined fluid in a nanotube with radius \( r \):

\[
P_{zz}^* = \frac{T^*}{V^* - 1} - \frac{1}{V^{*2}} + \frac{2u_{w}^*N_w^*}{r^*}\ln V^*
\]  

(2.2)

\[
P_{yy}^* = \frac{T^*}{V^* - 1} - \frac{1}{V^{*2}} + \frac{2u_{w}^*N_w^*}{N^{1/2}r^*}
\]  

(2.3)

with \( P^* = P a / b, T^* = k_B T b / a, V^* = V / N b, u_{w}^* = u_w b^{5/3} / a \) and \( r^* = r / b^{1/3} \). Similar expressions are obtained for the components of the pressure tensor of a confined fluid in a nanoslit. The pressure as a function of volume for a van der Waals fluid in a nanopore and in a nanoslit is shown in Figure 2.1.
Figure 2.1. Pressure tensor components of a nanoconfined van der Waals fluid as a function of the volume inside a nanotube and a nanoslit at $T^* = 0.25$ and at various values of $y = u_w^* N_w / r^*$. Note that in the nanoslit the values of $P_{yy}^*$ and $P_{macro}^*$ are graphically indistinguishable [20].

The equations of state shown in Figure 2.1 display loops associated with a first order phase transition; use of the Maxwell equal areas construction leads to the coexistence curves shown in Figs. 2.2-2.4. We call the reader’s attention to the sensitivity of the coexistence curve to the shape of the confining volume and the interaction with the walls. Figures 2.3 and 2.4 reveal that the critical temperature and critical volume of a confined van der Waals fluid vary with the size and shape of the confining volume; they increase as the size of the confining volume increases [7].

Figure 2.2. The coexistence curves for the nanoconfined van der Waals fluid inside a nanotube and a nanoslit for various $y = u_w^* N_w / r^*$ values, compared with the coexistence curve for the bulk van der Waals fluid [20].
Figure 2.3. The ratio of critical temperature of a van der Waals fluid in a nanotube/nanoslit relative to the bulk critical temperature as a function of nanoslit width or nanotube radius. The solid line is calculated from the van der Waals equation of state and for \( y = 0.001 \). The solid circles are the MD simulation data for confined water in a nanoslit pore and a nanotube [20].

Figure 2.4. The ratio of critical density of a nanoconfined van der Waals fluid in a nanotube and a nanoslit relative to the bulk critical density as a function of nanotube radius or nanoslit width, as calculated from the van der Waals equation of state and for \( y = 0.001 \) [20].

The agreement between the predictions obtained from the van der Waals equation of state and the results of the MD simulations for confined water is surprisingly good. The sensitivity of the coexistence curve of a nanoconfined fluid to the nature of the confining wall is in agreement with data in the literature [82].
II.B. The local pressure profile of a nanoconfined fluid

The local pressure profile in a nanoconfined fluid determines its mechanical stability. In a simple molecular fluid contained in a nanoslit with structureless walls the pressure tensor is diagonal. The normal component, $P_{zz}$, is different from the lateral (transverse) components of pressure, $P_{xx}, P_{yy}$, which are equal to each other. The pressure that is exerted on all parallel $zx$- and $zy$-planes is the same, but the pressure on each point of the $zx$- and $zy$-surfaces depends on the $z$-coordinate. There exist a number of methods with which to calculate the local pressure in a fluid [83]. For homogeneous fluids the standard Irving-Kirkwood method [84] is well suited, but it is not valid for strongly inhomogeneous fluids. The virial theorem is routinely used to compute the average, pressure over the entire volume of a closed box, but not the local pressure. The general approach discussed here is satisfactory for calculation of the local pressure and it’s normal and lateral components in an inhomogeneous fluid [18-20,85-87].

Consider a fluid confined in a nanoslit consisting of two parallel walls in the $xy$ planes $xy$ plane located at $z = 0$ and $z = H$, as shown in Figure 2.5.

![Figure 2.5](image)

Figure 2.5. Illustration of a nanoslit consisting of two structureless parallel walls located at $z = 0$ and $z = H$ and two confined particles, 1 and 2. [87].

We assume that the fluid in the nanoslit is in equilibrium with bulk fluid with density $\rho_b$ at the same temperature and chemical potential. Experimental observations and computer simulations have indicated that the fluid in such a nanoslit is inhomogeneous, hence its thermodynamic properties are functions of the local density. The local density is a function of $H$, $\rho_b$, $T$, and the interactions between fluid-fluid and fluid-wall molecules; we consider...
here only the case that the potential energy can be decomposed into two-body interactions. To calculate the different components of the local pressure tensor we need to know the local force vector. The force on the surface \( s_b \) in an arbitrary direction \( b \) is [88],

\[
\mathbf{F}_b = \oint_{s_b} \mathbf{\tau}_{ab} \cdot \mathbf{n}_b \, ds_b
\]

(2.4)

We adopt the convention that the subscript \( b \) refers to the force component and the subscript \( a \) refers to the direction normal to the surface \( s_b \). In (2.4), \( \mathbf{\tau}_{ab} \) is the shear stress tensor and \( \mathbf{n}_b \) is the unit vector perpendicular to the surface \( s_b \). The total force exerted on \( s_b \) in a confined simple molecular fluid has the following form [57]:

\[
\mathbf{F}_i = \oint_{s_i} \mathbf{\tau}_{ii} \cdot \mathbf{n}_i \, ds_i
\]

(2.5)

The calculation of \( \mathbf{F}_i \), and from it the lateral and normal components of the pressure tensor, is carried out by summing (i) a kinetic contribution, (ii) a fluid-fluid molecular interaction contribution, and (iii) a wall-fluid molecular interaction contribution. The kinetic contribution to the local pressure tensor arises from the momentum transferred by passage of molecules through a surface. It can be shown to be

\[
\mathbf{\tau}_{ii} = -k_B T \rho(\mathbf{r}_i)
\]

(2.6)

The fluid density in a nanoslit is nonuniform along the perpendicular to the slit walls, hence so will be the local normal and lateral components of the kinetic contribution to the pressure tensor, noting that the lateral pressure is the same for each \( zx \) plane, but varies in the \( z \)-direction. Thus [18,85,87],

\[
P_{ii}^K = \rho(z)k_B T.
\]

(2.7)

The intermolecular interaction contribution to the local pressure tensor can be shown to be

\[
P_{ii}^{FF} = -\frac{1}{2} \int_{V} \phi'(r_{12}) \rho^{(2)}(r_{12}, r_i) \frac{r_{12,i}}{r_{12}} d r_{12},
\]

(2.8)

Finally,

\[
P_{ii}^{FW} = \int \frac{\partial \phi_{ext}(r_{1z})}{\partial r_{1z}} \rho(r_{1z}) \, dr_{1z}
\]

(2.9)

is the molecule-wall contribution to the pressure tensor. Combining the three contributions we have

\[
P_{ii}(r_{1z}) = P_{ii}^K + P_{ii}^{FF} + P_{ii}^{FW}
\]

\[
= k_B T \rho(r_{1z}) - \frac{1}{2} \int_{V} \phi'(r_{12}) \rho^{(2)}(r_{12}, r_i) \frac{r_{12,i}}{r_{12}} d r_{12} + \int \rho(r_{1z}) \frac{\partial \phi_{ext}}{\partial r_{1z}} d r_{1z}
\]

(2.10)
and the lateral and normal components of the pressure are

\[ P_{xx} = P_{yy} = k_b T \rho(z) - \frac{1}{2} \int \varphi'(r_{12}) \rho^{(2)}(r_{12}, r_1) \frac{r_{12}^2}{|r_{12}|} dr_{12} \]  

(2.11)

\[ P_{zz} = k_b T \rho(z) - \frac{1}{2} \int \varphi'(r_{12}) \rho^{(2)}(r_{12}, r_1) \frac{r_{12}^2}{|r_{12}|} dr_{12} \]  

(2.12)

II.C. The hard sphere and perturbed hard sphere fluids

As a simple example, we analyze first the properties of \( N \) hard spheres with diameter \( d \) confined in a nanoslit with hard walls separated by \( H \). The kinetic contribution to the lateral pressure is given by Eq. (2.7). The intermolecular interaction contribution depends on the pair distribution function

\[ \rho^{(2)}(r_{12}, r) = \rho(z_1) \rho(z_2) g_{z,H}(r_{12}) \]  

(2.13)

with \( g_{z,H}(r_{12}) \) the pair correlation function. Then [87]

\[ P_{xx} = P_{yy} = k_b T \rho(z_1) \left[ 1 + \frac{\pi}{4} \int_{-d}^{d} \rho(z_2) g_{z,H}(d)(d^2 - z_2^2) dz_2 \right] \]  

(2.14)

\[ P_{zz} = k_b T \rho(z_1) + \pi k_b T \rho(z_1) \int_{-d}^{0} \rho(z_2) g_{z,H}(d)z_2^2 dz_2 \]  

(2.15)

In the limit \( H \to \infty \) (2.14) and (2.15) reduce to the 3D hard sphere equation of state

\[ P = \rho k_b T \left[ 1 + \frac{2\pi}{3} \rho d^3 g(d) \right]. \]  

(2.16)

Keshavarzi et al. [87] and Heidari et al. [18,85] used the local density profile of a hard-sphere nanoconfined fluid reported by Kamalvand et al [19] and the approximation \( \langle g_{z,H}(d) = 1 \rangle \) to calculate the normal and lateral pressure profiles shown in Figure 2.6.
Figure 2.6. Lateral pressure (solid lines) and normal pressure (dashed lines) profiles of a hard-sphere confined fluid in a nanoslit with widths $H^* = H/d = 4$ and 6 for two different reduced bulk densities, $\rho_b^* = \rho d^3 = 0.3$ and 0.6, and $T^* = 2$ [85, 87].

Note that the amplitude of the density variation is greater for the normal pressure than for the lateral pressure.

How are the preceding properties of the confined hard sphere fluid altered when there is an attractive interaction between pairs of molecules? Consider the properties of a fluid with $N$ molecules, enclosed by hard walls separated by $H$, that have a pair interaction consisting of a hard core (diameter $d$) and a Lennard-Jones potential for separations larger than $d$. For this system the lateral and normal components of the pressure are

$$ P_{yy} = k_b T \rho \left[ 1 + \frac{\pi}{4} \int_{-d}^{d} \rho(z_2) g_{2ff}(d^2 - z_2^2) dz_2 \right] $$

$$ -\frac{1}{2} \iiint \phi'(r_z) \rho(z_1) \rho(z_2) g_{2ff} \frac{y_2^2}{(x_2^2 + y_2^2 + z_2^2)^{3/2}} dx_2 dy_2 dz_2 \quad |r_z| > d $$

(2.17)
\[ P_{zz} = k_B T \rho(z_1) + \pi k_B T \rho(z_1) \int_{-d}^{0} \rho(z_2) g_{zH}(d) z_2^2 \, dz_2 \]

\[ -\frac{1}{2} \int \int \int \varphi'(r_2) \rho(z_1) \rho(z_2) g_{zH} \frac{z_2^2}{(r_2^2 + z_2^2)^{3/2}} r_2 \, dr_2 \, dz_2 \, d\Theta \quad |r_2| > d \]

(2.18)

As before, using the approximation \( g_{zH}(r_2) = 1 \), Heidari et al. [85] numerically calculated \( P_{yy} \) and \( P_{zz} \) for a confined Lennard-Jones fluid; the results are shown in Figure 2.7.

![Figure 2.7](image)

**Figure 2.7.** Lateral pressure \( P_{yy}^* = P_{zz}^* \sigma^3 / \varepsilon \) (solid lines) and normal pressure \( P_{zz}^* = P_{zz}^* \sigma^3 / \varepsilon \) (dashed lines) profiles of nanoconfined Lennard-Jones fluid in nanoslits with widths \( H^* = 4 \) and \( 6 \), as a function of \( z_1^* \) for two different bulk densities \( \rho_b^* = 0.6 \) and 0.8 at temperature \( T^* = k_B T / \varepsilon = 2 \) [85].

As for the confined hard sphere fluid, the amplitude of density variation is greater for the normal pressure than for the lateral pressure.
III. The Density Functional Theory description of confined fluids

III.A. General remarks

We start by restricting attention to the properties of a confined fluid that remains in one phase; phase transitions in the confined fluid will be discussed in a later section. Arguably the most obvious characteristic of a confined fluid is its inhomogeneous density distribution, which depends on the shape, separation and potential field of the confining walls. The majority of analytic treatments of that distribution are based on density functional theory, which represents the Helmholtz free energy of a fluid in an external potential $V_{\text{ext}}(r)$ as a functional of the local density $\rho(r)$

$$A[\rho(r)] = A_0[\rho(r)] + \int \rho(r)V_{\text{ext}}(r)\,dr. \quad (3.1)$$

Then the equilibrium density distribution determined by minimization of the grand potential, $\Omega = A - \mu N$, with $\mu = \left(\frac{\partial A_0[\rho(r)]}{\partial \rho(r)}\right)_{T, \mu_0} + V_{\text{ext}}(r) = \mu_0 + V_{\text{ext}}(r)$.

It is conventional to split the functional $A_0[\rho(r)]$ into ideal and excess contributions,

$$A_0[\rho(r)] = A_0^{\text{id}}[\rho(r)] + A_0^{\text{ex}}[\rho(r)], \quad (3.2)$$

where

$$A_0^{\text{id}}[\rho(r)] = k_B T \int \rho(r)(\ln \Lambda^3 \rho(r) - 1)\,dr \quad (3.3)$$

is the Helmholtz free energy of the ideal fluid in the absence of the external field, and $\Lambda = h / (2\pi mkT)^{1/2}$. Then the equilibrium density distribution satisfies

$$\rho(r) = \rho_b \exp \beta \left[ \mu^{\text{ex}} - \left(\frac{\partial A_0^{\text{ex}}[\rho(r)]}{\partial \rho(r)}\right)_{T, \mu_0} - V_{\text{ext}}(r) \right], \quad (3.4)$$

where $\mu^{\text{ex}}$ is the excess chemical potential with respect to the value in the bulk fluid. Eq. (3.4) is exact, and the principal approximation in all versions of density functional theory is made when an expression for the excess free energy is adopted. The accuracy of a density functional theory analysis depends on finding a form for $A_0^{\text{ex}}[\rho(r)]$ that appropriately describes the non-ideality of the fluid. We note that the force density associated with the non-uniform density distribution is

$$\rho(r)\nabla \left(\frac{\partial A_0^{\text{ex}}[\rho(r)]}{\partial \rho(r)}\right)_{T, \mu_0} + \rho(r)\nabla V_{\text{ext}}(r) = 0. \quad (3.5)$$

The first term on the left-hand side of Eq. 3.5 is the sum of the contributions arising from intermolecular interactions and the kinetic energy of the system, while the second term is the contribution arising from the external potential. At equilibrium the total force vanishes, so that integration of Eq. 3.5 with respect to $r$ yields the relation
\[
\int \rho(r) \nabla \left( \frac{\partial A^{\alpha \beta}}{\partial \rho(r)} \right) \bigg|_{\tau, \rho_0} \, dr + \int \rho(r) \nabla V_{\text{ext}}(r) \, dr = 0.
\]  \hspace{1cm} (3.6)

On the other hand, the component of the force on a closed surface \( s \) in the direction \( j \) is related to the stress tensor with elements \( \sigma_{ij} \) via

\[
F_j = \int_s \sigma_{ij} n_j \, ds = \int \nabla \cdot \sigma \, dr
\]  \hspace{1cm} (3.7)

where \( n_j \) is the \( j \)th component of the normal to the surface \( s \). Comparing Eq. 3.7 with Eq. (3.6) and using \( \sigma = -P \), \( \sigma_{ij} = -P_{ij} \) we find

\[
dP_{ji} = \rho(r) d\mu_0(r)
\]  \hspace{1cm} (3.8)

An integration-by-parts leads to

\[
P_{ji}(r) = \rho(r) \mu_0(r) - \int \mu_0(r) d\rho(r).
\]  \hspace{1cm} (3.9)

Since \( A_0[\rho(r)] = \int a_0(\rho(r), \nabla \rho(r), r) \, dr \),

Eq. (3.9) simplifies to

\[
P_{ji}(r) = \rho(r) \mu_0(r) - a_0(\rho(r)),
\]  \hspace{1cm} (3.10)

where \( a_0 \) is the intrinsic Helmholtz free energy density of the nanoconfined fluid. Eq. 3.10 is a general expression for the local pressure in a confined fluid; it properly yields the macroscopic pressure when the size of the system approaches infinity.

Consider the case of a nanoconfined hard sphere fluid. We choose for discussion, from the many density functional theory studies of this system, the work of Yu and Wu [89] who have formulated a version of Rosenfeld’s fundamental-measure theory, denoted mFM-DFT, that uses the excess Helmholtz free energy density from the work of Mansoori et al [90]:

\[
A^{\text{ex}}[\rho(r)] = k_b T \int \left( \Phi^{bs}_S[n_a(r)] + \Phi^{bs}_V[n_a(r)] \right) \, dr
\]  \hspace{1cm} (3.11)

In Eq. (3.11), \( \Phi^{bs}_S[n_a(r)] \) represent the so-called scalar and vector contributions to the excess Helmholtz free energy density of a hard-sphere fluid as a function of the weighted density distribution, \( n_a(r) \) [89,91,92]. These contributions are

\[
\Phi^{bs}_S[n_a(r)] = -n_0 \ln(1 - n_3) + \frac{n_a n_2}{1 - n_3} + \frac{1}{36 \pi n_3^2} \ln(1 - n_3) + \frac{1}{36 \pi n_3^2 (1 - n_3)^2} \left[ n_2^3 \right]
\]  \hspace{1cm} (3.12)

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\[
\Phi_h^{kr}[n_\alpha(r)] = -\frac{n_{\gamma_1} \cdot n_{\gamma_2}}{1-n_3} + \left[\frac{1}{12\pi n_3} \ln(1-n_3) + \frac{1}{12\pi n_3(1-n_3)^2}\right] n_{\gamma_1} n_{\gamma_2} \cdot n_{\eta_2},
\]

(3.13)

where the weighted density is defined as

\[
n_\alpha(r) = \int \rho(r') w^{(\alpha)}(r-r')dr', \quad \alpha = 1, 2, 3,
\]

(3.14)

and the weight functions that characterize the geometry of a hard-sphere fluid are given by

\[
\begin{align*}
w^{(0)}(r) &= \frac{1}{\pi \sigma^2} \delta(\sigma/2 - r), \\
w^{(1)}(r) &= \frac{\sigma}{2} w^{(0)}(r), \\
w^{(2)}(r) &= 2\pi \sigma w^{(1)}(r), \\
w^{(3)}(r) &= \Theta(\sigma/2 - r), \\
w^{(v)}(r) &= 2\pi \sigma w^{(v)}(r) = \frac{r}{H} \delta(\sigma/2 - r)
\end{align*}
\]

(3.15)

where \( \sigma \) is the hard sphere diameter and \( \Theta(r) \) is the Heaviside step-function.

### III.B. Density distribution and local pressure tensor in a nanoconfined hard sphere fluid

We consider a hard sphere fluid confined in nanoslit by two structure-less hard parallel walls located in the \( xy \)-planes at \( z = 0 \) and \( z = H \). The fluid in the slit is in equilibrium with the bulk fluid (see Figure I.1). Then the hard sphere-wall interaction has the form

\[
V_{ex}(z) = \begin{cases} 0; & (\sigma / 2) < z < H - \sigma / 2 \\ \infty; & H - (\sigma / 2) \leq z \leq \sigma / 2 \end{cases}
\]

(3.16)

(see Figure I.1). The hard sphere equilibrium density distribution in this geometry is given by [89],

\[
\rho(z) = \rho_b \exp\left\{ \beta \mu_{xs} - \int \left[ \sum_{\alpha} \frac{\partial \Phi_h^{kr}}{\partial n_\alpha(z)} w^{(\alpha)}(z-z') - \beta V_{ex}(z) \right] dz' \right\},
\]

(3.17)

and is obtained by minimizing the grand potential. The excess part of the hard-sphere chemical potential, \( \mu_{xs}^{kr} \), is obtained from the hard-sphere equation of state. For calculation of the normal component of the pressure tensor Eq. (3.10) can be written in the following form,
\[ P_z(z) = \rho(z) \mu_0(z) - a_0[\rho(z)] \]  

which is evaluated using the equilibrium density distribution in the nanoslit, as given by Eq. (3.17). The Helmholtz free energy derivative with respect to \( \rho(\mathbf{r}) \) yields the intrinsic chemical potential \( \mu_0(\mathbf{r}) = \left( \frac{\partial A_0[\rho(\mathbf{r})]}{\partial \rho(\mathbf{r})} \right)_{\rho, \rho_0} \). In this case, the weighted densities that appear in Eq. (3.11) are [93]

\[
\begin{align*}
  n_0 &= \frac{2 n_1(z)}{\sigma} \\
  n_1 &= \frac{n_2(z)}{2 \pi \sigma} = \frac{\mathbf{e}_z \cdot \int_{-\sigma/2}^{\sigma/2} \rho(z + z') z' \, dz'}{2} \\
  n_3(z) &= \pi \int_{-\sigma/2}^{\sigma/2} \rho(z + z') \left( \frac{\sigma^2}{4} - z'^2 \right) \, dz' 
\end{align*}
\]  

(3.19)

where \( \mathbf{e}_z \) is the unit vector in the \( z \) direction. The equilibrium density profile of the hard-sphere fluid is obtained by minimization of the grand canonical potential, or iterative solution of Eq. (3.4), with the excess chemical potential obtained from the Carnahan-Starling equation of state [94],

\[
\beta \mu^{*} = \eta \left( 8 - 9 \eta + 3 \eta^2 \right) / (1 - \eta)^3; \quad \eta = \frac{\pi \rho \sigma^3}{6}
\]  

(3.20)

Figure II.1 displays a comparison of the mFM-DFT prediction of the density profile of a hard sphere fluid with reduced bulk fluid density \( \rho^* = \rho \sigma^3 = 0.813 \) in contact with a hard wall with Monte Carlo simulation data.

**Figure 3.1.** Comparison of the hard-sphere reduced density profiles obtained by mFM-DFT and simulation results of Pospisil et al. [93] for \( \rho_0 \sigma^3 = 0.81303 \) [19].
Similar calculations, by Kamalvand et al. [19], of the density distribution in confined hard sphere fluids in slits of varying size and for varying bulk fluid densities, are displayed in Figure 3.2. The maximum error in these calculated densities occurs for the contact density at the hard wall when the bulk density is large and the slit width is small; the error for other conditions is very small. Noteworthy features of the results displayed are the layered structure of the confined fluid, and the convergence, as $H$ becomes large, of the density distribution to that characteristic of a bulk fluid in contact with a wall.

**Figure 3.2.** Density profile of a hard-sphere fluid confined within nano-slit pores with various widths. For clarity, the density profile for $\rho^*_b = 0.7$ is shifted upward by 0.5, for $\rho^*_b = 0.8$ by 1 and for $\rho^*_b = 0.9$ by 2 for slit widths $H = 2\sigma - 5\sigma$; the density profile for $\rho^*_b = 0.6$ is shifted upward by 0.1, for $\rho^*_b = 0.8$ by 1 and for $\rho^*_b = 0.9$ by 2 for slit widths $H = 8\sigma - 9\sigma$; the density profile for $\rho^*_b = 0.6$ shifted upward by 0.1, for $\rho^*_b = 0.8$ by 1 and for $\rho^*_b = 0.9$ by 3 for slit width $H = 10\sigma$ and the density profile for $\rho^*_b = 0.7$ it is shifted upward by 0.5 and for $\rho^*_b = 0.9$ by 2.5 for slit width $H = 11\sigma$ [19].

Heidari et al. [86] have used Eq. (3.18) to calculate the local normal component of the pressure tensor of a nanoconfined hard sphere fluid. Figure 3.3 displays the calculated...
local normal pressure at $\rho_b^* = 0.6$ and 0.8, and for three different reduced slit widths $H^* = 4, 6$ and 8. These data show that the local normal pressure of a confined hard sphere fluid displays symmetric oscillations, as a function of $z^*$, that decrease with distance from the walls, consistent with the fluid layering inferred from the density distribution. The highest normal pressure occurs at the walls. As is clear from the data in Figure 3.4 (left), as the slit width increases the accessible volume for molecules increases and, therefore, so does the number of layers whilst the layer resolution becomes less marked. In this situation, the repulsive intermolecular interactions play a significant role, leading to a larger pressure at the center of the slit when $H^* = 6$ than when $H^* = 4$.

![Figure 3.4](image)

**Figure 3.4.** The normal pressure for a hard-sphere fluid in a nanoslit pore with hard-walls. (Left): $\rho_b^* = 0.6$ and $T^* = 2.5$ for two different reduced pore widths $H^* = 4$ and 6. (Right): For $H^* = 6$ and $T^* = 2.5$ at two different bulk densities $\rho_b^* = 0.6$ and 0.8 [86].

Figure 3.4 (right), which displays the local normal pressure at $T^* = 2.5$ and $H^* = 6$ for two different bulk densities $\rho^* = 0.6$ and $\rho^* = 0.8$, shows that when the bulk density increases at constant temperature and slit width there is a strong tendency for hard spheres to accumulate at the walls, thereby increasing the amplitude of the normal pressure oscillations.

For some purposes it is convenient to define a solvation force, namely, the normal force exerted by the fluid on the confining walls, by [95-97]

$$f(H) = k_BT(\rho^*_H(0) - \rho^*(0)), \quad (3.21)$$

where $\rho^*_H(0)$ is the fluid density in contact with each wall in the confined system and $\rho^*(0)$ is the corresponding quantity for infinite wall separation. Figure 3.5 shows the solvation force of the hard sphere fluid, which is proportional to $\rho(z = H)$, at the reduced bulk density $\rho\sigma^3 = 0.9$ as a function of slit width. The layering of confined fluids and
solvation force oscillations are related; both are consequences of the confinement of the fluid [95].

Figure 3.5. The solvation force of the hard-sphere fluid confined in nanoslit pores at reduced bulk dimensionless density $\rho_h^* = 0.9$ [19].

III.C. Confined fluids with attractive and repulsive intermolecular interactions

The hard sphere fluid provides valuable information concerning the influence of excluded volume effects on the structure and thermodynamic properties that is vital to understanding real fluids in which there are both repulsive and attractive components of the intermolecular potential function. That information must be complemented by determination of the effect of attractive intermolecular potential energy contributions to the fluid structure and thermodynamic properties. One approach, developed for confined fluids, is the perturbative-density-functional theory [17,23,89,92,98,99], which divides the excess part of the intrinsic Helmholtz free energy into repulsive (hard core) and attractive contributions

$$ A_{xs}^{\text{ux}}[\rho(r)] = A_{xs}^{\text{rep}}[\rho(r)] + A_{xs}^{\text{att}}[\rho(r)]. \quad (3.22) $$

Then $A_{xs}^{\text{att}}[\rho(r)]$ is calculated using perturbation theory. Tang and Wu (100) use the Barker and Henderson effective-diameter prescription to split the Lennard-Jones potential energy function between terms representing repulsion and attraction. The effective hard sphere diameter so obtained is then used in the mFM-DFT representation for the functional $A_{xs}^{\text{rep}}[\rho(r)]$. The contribution to the excess Helmholtz free energy functional arising from intermolecular attraction is approximated using the analytical expression for the direct correlation function obtained from the first order mean spherical approximation [101].

$$ A_{xs}^{\text{att}}[\rho(r)] = -\frac{k_B T}{2} \int \int \rho(r_1)\rho(r_2) \exp\left(-\frac{|r_1 - r_2|}{\sigma}\right) d^{3}r_1 d^{3}r_2, \quad (3.23) $$

where $\exp\left(-\frac{|r_1 - r_2|}{\sigma}\right)$ is the attractive energy part of the direct correlation function,
in which \( z_1 = 2.9637/\sigma, z_2 = 14.0167/\sigma, T_1^* = T^*/k_1, T_2^* = T^*/k_2, k_1 = k_0 \exp(z_1(\sigma-d)), k_2 = k_0 \exp(z_2(\sigma-d)), k_0 = 2.1714\sigma \). The lengthy expression for the first order Yukawa direct correlation function, \( c_Y \), appearing in Eq. (2.26) can be found in the paper by Fu [17]. Using these approximations Tang and Wu calculated the equilibrium density distribution of the confined Lennard-Jones fluid; Figure 3.6 displays their results for the density profile in contact with a hard-wall compared with the density profiles obtained from several other theories at \( T^* = k_B T/\epsilon = 1.35 \) and for several bulk densities.
Figure 3.7 displays the calculated density profiles of the LJ fluid inside three different nanoslits with widths $H^* = 3.0, 4.0$ and $7.5$ at $T^* = 1.2$ and $\rho_b^* = 0.5925$, and the Monte Carlo simulation data for these systems.

![Density profiles for different slit widths](image)

**Figure 3.7.** Density profile of the LJ fluid inside a slit pore with $T^* = 1.2$, $\rho_b^* = 0.5925$, for three different slit widths ($H^* = 3.0, 4.0$ and $7.5$) versus distance $z^*$ from the hard-wall. The square symbols are the computer simulation data [103]. The solid and dashed lines are the predictions of the FMSA and MFT theories, respectively [100].

To calculate the normal pressure for a confined Lennard-Jones fluid in a nano-slit, Heidari et al. [86] used the mFM-DFT excess Helmholtz free energy functional for the effective hard core repulsion contribution and the DCF-FMSA of Tang and Wu [100] for the intermolecular attraction contribution. The results of these calculations of the local normal pressure of the nano-confined LJ fluid are displayed in Figure 3.8. Clearly, increased density and temperature lead to an increase in the normal pressure and more pronounced...
layering of the fluid. An increase in slit width contributes to an increase in number of layers.

Given the important role played by the excluded volume in determining the structure of a nanoconfined fluid it is of some interest to directly compare the properties and structures of a confined hard sphere fluid with those of a confined Lennard-Jones fluid. This can be done in several different ways. For example, for a given slit width two of the three variables density, temperature and pressure can be held the same for the two fluids and the third compared. This comparison is direct and unambiguous, but does not separate the relative contributions from softening of the repulsive interaction and addition of an attractive interaction on going from the hard sphere to Lennard-Jones potentials. The problem is that although both interactions have a repulsive component, the hard sphere potential has no attractive component, hence no parameter suitable for scaling the temperature. This problem has been addressed in the literature [18] by adoption of a scaling definition. The densities of the hard sphere and Lennard-Jones fluids are scaled in the same fashion, $\rho_b^* = \rho \sigma^3$, using convention that the Lennard-Jones size parameter is equal to the diameter of a hard sphere. Then, at the same reduced densities, the reduced pressure of the hard sphere fluid is defined to the actual pressure multiplied by the factor $\sigma^3 / \epsilon$, where $\epsilon$ is the Lennard-Jones potential well depth. An analogous definition is used to create a reduced temperature for the hard sphere fluid: The actual temperature of the hard sphere fluid is multiplied by $k_B T / \epsilon$. These definitions are the same as for the reduced pressure and temperature of the Lennard-Jones fluid, but are artificial constructs for the hard sphere fluid.

The normal pressure in the confined Lennard-Jones fluid is found to be much less than that in the corresponding hard sphere fluid. The tendency for molecules to accumulate at the walls increases with increasing temperature or decreasing intermolecular attraction.
Figure 3.8. The normal pressure in a LJ fluid confined in a nanoslit with hard-walls versus distance from the hard-wall. (1): $H^* = 6$ and $T^* = 2$ at bulk densities $\rho_b^* = 0.6$ and 0.8. (2): $\rho_b^* = 0.6$ and $T^* = 2.5$ for pore widths $H^* = 4$ and 6. (3): $\rho_b^* = 0.6$ and $H^* = 6$ for bulk temperatures $T^* = 2$ and 2.5. (4): $\rho_b^* = 0.6$, $T^* = 2.5$ for pore widths $H^* = 4$ and 6 [86].
Figure 3.9 shows the local density of the truncated Lennard-Jones confined fluid in a nanoslit pore with hard-walls at two reduced temperatures $T^* = 2$ and 2.5, two reduced bulk-densities $\rho_b^* = 0.6$ and 0.8, and two slit widths $H^* = 4$ and 6. Figure 3.9 also displays the density profiles of the nanoconfined hard sphere fluid for the same conditions. The similarity of the density profiles of the hard sphere and Lennard-Jones fluids is quite striking. Figure 3.9c shows the variation of the density profile with reduced temperature at constant $H^*$ and $\rho_b^*$. Increasing $T^*$ is equivalent to reducing the well depth of the potential. As the temperature is increased, or the interaction strength decreased, the average density in the slit increases.

Figure 3.9. (a) Comparison of the local density of LJ and HS confined fluids in nanoslit pores with hard-walls versus distance from the hard-wall at $\rho_b^* = 0.6$ and $T^* = 2.5$ for pore widths $H^* = 4$ and 6. (b) The same as (a) except for $H^* = 6$ for densities $\rho_b^* = 0.6$ and 0.8. (c) The same as (b) except at $\rho_b^* = 0.6$ for $T^* = 2$ and 2.5 [18].
IV. Structure and phase behavior in confined colloid suspensions

The preceding Section dealt with theoretical descriptions of the one phase domain of a confined simple fluid derived from Density Functional Theory, with the properties of the hard sphere fluid serving as the major discussion vehicle. Attention was focused on the spatial dependence of the one particle distribution function. We now turn to discussion of the two-particle distribution function and phase transitions in a confined fluid.

Although there are many studies from which the thermodynamic properties of a nanoconfined fluid are inferred, technical difficulties complicate the application of diffraction methods to the determination of the structure of the confined fluid, hence such data are rare. In contrast, because of advances in technology, such as digital video microscopy and stimulated emission depletion microscopy, there are many studies of particle distribution functions in a confined colloid suspension. These microscopic techniques have opened up for examination questions that cannot presently be addressed in a nanoconfined molecular system. Prominent amongst these questions are the dependence of structure on the conditions of confinement and the dependence of the nature of phase transitions on system dimensionality and interactions. The segue from nano-confinement to micro-confinement follows from application of by the McMillan-Mayer theory [10], which shows that the equilibrium properties of a confined colloid suspension of particles undergoing Brownian motion are isomorphous with those of a confined molecular system in which the potential of mean force between colloid particles in the suspension replaces the direct interaction between molecules. The density, temperature and composition dependences of the colloid-colloid potential of mean force play roles in defining particular equilibrium states of the system. And, by varying the single colloid properties the functional form of the colloid-colloid potential of mean force can be varied from short-ranged to long-ranged, from near-hard-sphere-like to dipolar.

We now examine the nature of the structure and phase transitions in confined colloidal suspensions, with attention paid to the roles of the colloid–colloid interaction and the extent of deviation from an idealized geometry of confinement. Our selective review will be restricted to one-component suspensions of spherical colloids, with attention paid to whether and/or how phase transitions in quasi-one-dimensional (q1D) and q2D systems differ from those in a two-dimensional (2D) system or a three-dimensional (3D) system. Although the experimental and simulation results reported are for micro-scale systems, as already noted the McMillan-Mayer theory implies that, in a dimensionless representation, the structural features, properties and phase transitions of these microconfined systems map one-to-one into the structural features, properties and phase transitions of nanoconfined systems, modulo similarity of the potential of mean force to the molecular interaction potential energy function.

IV.A. Quasi-one-dimensional systems

We consider a suspension of colloid spheres in some small molecule solvent. The packing structure supported in a one dimensional (1D) suspension is not very interesting since the close packed configuration is a linear array of spheres (rods) and there can be no transition from a disordered phase to a phase with long range order at nonzero temperature if the sphere-sphere interaction has finite range [104]. In a q1D planar ribbon channel with width less than two particle diameters, so hard spheres cannot pass one
another, a close packed array has zigzag geometry. Increasing the planar channel ribbon width to several sphere diameters generates a system with between q1D and q2D character. In such a system, at any nonzero temperature, fluctuations destroy all possible order not imposed by the explicit symmetry breaking associated with the boundary conditions. If the walls that define a q1D planar ribbon channel are smooth, they break continuous rotational symmetry but support rotations by $\pm \pi$, permit nonzero even order bond orientation order, and permit density modulation along the normal to the channel axis [105]. The length scale for the density modulation depends on the particle packing fraction, and the number of strata (lines of particles parallel to the channel walls) is dependent on the ribbon width. If the walls that define a q1D ribbon channel are regularly corrugated, or have some other defined structure, the confined system can be ordered [106].

We now examine the structures supported in planar q1D systems. The q1D structures found in the limiting cases of very short-range and very long-range sphere-sphere interaction have interesting similarities and differences. Consider, first, hard sphere systems confined by smooth walls. If the ribbon channel holds an integer number of close packed strata (a commensurate configuration), the system forms a perfect 2D triangular lattice [27]. Nevertheless, this solid cannot support a shear stress, and it can flow along the channel like a liquid. If the ribbon channel can hold somewhat more than an integer number of close packed strata, say $n + \delta$, $n = 1, 2, \ldots$; $0 < \delta < 1$, there is a linear buckling instability in the direction perpendicular to the channel axis, and the system breaks into many triangle shaped close packed hexagonal regions that are displaced in the direction parallel to the channel axis [27]; the scale length of the local ordered regions is the channel width. In general, long wavelength fluctuations in the particle positions destabilize long-range order. If the channel width and hard sphere diameter are commensurate, the amplitude of fluctuation is suppressed and only long-range order is destabilized. If the channel width and hard sphere diameter are incommensurate, the fluctuations destabilize local order. Viewed overall, as shown by both experiment [107] and computer simulation [27,108], a finite length q1D ribbon channel will support apparent crystalline order at high packing density and, for fixed density, many discontinuous transitions involving changes in the number of strata parallel to the confining walls as the wall separation increases. A “phase diagram” for ribbon widths from 8 – 10 sphere diameters, obtained from simulation data, is displayed in Figure 4.1, and sample experimental data are displayed in Figure 4.2.
Figure 4.1. From Ref. 27. Part of the phase diagram (for the region with 8-10 strata) of hard discs confined in a ribbon channel. In this figure the one-phase regions are clear, the two-phase coexistence regions are vertically striped and the forbidden regions are horizontally striped. The symbols ○, △ and △ represent data obtained from simulations. On the lines labeled $n_j = 9, 10, 11$ the width of the ribbon is commensurate with the hard disc diameter. Densities smaller than corresponding to any particular point marked ○ are modulated liquid, and densities greater than corresponding to any particular point marked □ are solid. The continuous curves are the phase boundaries predicted by a mean field theory analysis of the system.
Figure 4.2. From Ref. 108. Upper panel. The transverse density distributions of (left) 1.58 μm particles with packing fraction 0.697 in a 25 μm channel, and (right) 3.01 μm diameter particles with packing fraction 0.440 in a 14 μm channel. Lower panel. The pair correlation functions of the colloid particles along the individual strata in the 25 μm ribbon channel with packing fraction 0.697.

At a specified packing fraction, the structure supported in a confined system of hard spheres is determined by the commensurability of the wall spacing and sphere diameter. Colloids that interact via long-range screened Coulomb repulsion (Yukawa potential) [28] or long-range magnetic dipole-dipole repulsion [105,110] also form ordered structures in a ribbon channel. In these cases, the structures are determined by the strength of the long-range part of the repulsion and not the particle diameter. For example, Monte Carlo simulations of configurations with minimum energy at $T = 0$ show that a system with colloids that interact with a Yukawa potential ($V_0 \exp(-\kappa R) / R$, with screening length $1 / \kappa$) and are confined to a q1D channel by a harmonic potential perpendicular to the channel axis undergoes successive transformations from a configuration with one ordered chain to two ordered chains, then to three ordered chains, then to four ordered chains, etc, as the particle density increases [28] (see Figure 4.3). The one-to-two chain transition is continuous.

Figure 4.3. From Ref. 28. Phase diagram for colloid particles, confined to a ribbon channel, that interact with a Yukawa potential; $\kappa$ is the inverse shielding length and $\bar{n}_e$ the density.
and all other transitions involving more chains are first order. At nonzero temperature, the thermal excitation of the particles is anisotropic, with larger amplitude motion parallel to than perpendicular to the channel walls. At sufficiently high temperature, there occur transitions between the ordered chain structures. The simple Lindemann criterion for melting asserts that a solid melts when the average amplitude of displacement of a particle from its lattice site is of order 10% of the lattice spacing. Using that criterion to define melting at any specified particle density, when the screening length in the Yukawa interaction is very large, the ordered system melts to a liquid and the apparent melting temperature as a function of particle density has minima at those densities at which the $T = 0$ transitions between structures occur (Figure 4.4). The melting temperature decreases as the screening length in the Yukawa interaction decreases. When the screening length in the Yukawa interaction is small, the system melts first in the unconfined direction whilst it remains ordered in the confined direction, forming what is sometimes called a locked floating solid. The melting process occurs first in the chains adjacent to the confining wall. Both experimental studies and Brownian dynamics simulations of particles that interact via long-range magnetic dipole-dipole repulsion and are confined in ribbon channels have been reported [28,105,110]. The equilibrium packing structures exhibit layering parallel to the channel walls with periodic changes in widths of the strata in the interior of the channel as the channel width changes; the latter are associated with changes in the defect concentration (deviations from six-fold nearest neighbor packing) in the center of the channel as the channel width changes (Figure 4.5). In the large ribbon width limit, the bond orientation correlation function for the interior strata is indistinguishable from that in 2D, but as the channel width is decreased the q1D system becomes more disordered than the unbounded 2D system and supports oscillations in the defect concentration. The oscillatory changes in defect concentration are like order-to-disorder transitions.
Figure 4.4. From Ref. 28. The melting temperature of an assembly of colloid particles, confined to a ribbon channel that interact with a Yukawa potential, as a function of density.
Figure 4.5. From Ref. 105. Top: Density distribution of colloid particles that interact with magnetic dipole repulsion normal to the ribbon channel axis, for several dimensionless channel widths $w = L / (\sqrt[3]{3} \cdot \rho)^{1/2}$ and dimensionless field $\Gamma = \mu_0 M^2 / 4 \pi k_B T R^3$, with $\mu_0$ the magnetic permeability of free space, $M$ the magnetic dipole moment and $R = (\sqrt[3]{3} / 2 \rho)^{1/2}$ the average particle spacing. Bottom: Image of the particle distributions and associated Delaunay triangulations. Open triangles denote seven-coordinated particles and circles denote five-coordinated particles. The dimensionless field strength for these experiments was $\Gamma = 12$.

The modulation of the density distribution perpendicular to the axis of the ribbon channel in each of the colloid systems described is the common signature of repulsion between the particles. While commensurability of the channel width to particle diameter ratio plays an important role in determining the structures available to hard spheres, it is not well defined when the interaction has long-range.
A different class of q1D systems is generated when a colloid suspension is confined in a capillary with diameter comparable to the colloid diameter. Consider the case of hard spheres confined in a smooth hard linear capillary \[111,112\]. If the capillary diameter is less than 2 hard sphere diameters the system supports only a fluid phase. When the capillary diameter is increased to 2.2 hard sphere diameters there is a discontinuous transition to a structure that consists of triads of spheres arranged in stacked planes that are perpendicular to the capillary axis. When the capillary diameter is increased further there are transitions to defected two-dimensional triangular lattices wrapped circumferentially within the capillary, with the number of wrapped shells determined by the capillary diameter. The first four densest hard sphere structures in a cylinder as a function of cylinder diameter are displayed in Figure 4.6.

An even more complex set of q1D structures is exhibited by colloid particles that interact with the repulsive screened Debye-Huckel (or Yukawa) interaction \( V(r) = V_0 \exp(-\kappa r)/\kappa r \) when packed in a hard cylinder of radius \( a \) \[113a\] (see Figure 4.7).
Figure 4.7. From Ref. 113a. Top panel: Zero temperature phase diagram in the screening length-reduced density plane, for colloid particles that interact with a Yukawa potential when confined to a hard cylinder. Bottom panel: The structures identified in the upper panel.

If the capillary houses particles with both attractive and repulsive interactions, as will be the case for molecules, a different kind of phase transition can occur, the so-called capillary condensation. Panagiotopoulos [114] has reported the results of simulations of a Lennard-Jones fluid in a capillary with radius $D$, including, Lennard-Jones type molecule-wall interactions. The fluid in the pore is in equilibrium with bulk fluid outside the pore. The state of the fluid in the pore is represented by the adsorption

$$\Gamma = \left(2\pi\sigma^3 \right) \int_0^D r \rho(r) dr . \quad (3.1)$$

Figure 4.8 displays an example of the adsorption as a function of the density of the bulk fluid outside the capillary for the case that $D^* = D / \sigma = 3$, $T^* = k_B T / \varepsilon = 0.80$. Note the
discontinuous jump in adsorption, and the hysteresis of the adsorption isotherm. The spatial distribution of the liquid and vapor along the capillary axis is shown in Figure 4.9.

**Figure 4.8.** From Ref. 114. Adsorption of a Lennard-Jones fluid in a capillary with radius $D^* = 3$, in equilibrium with a bulk fluid, as a function of bulk liquid density $\rho^* = \rho \sigma^3$ when $T^* = 0.80$.

A density functional theory analysis of adsorption in a nano-cylinder has been reported by Evans, Marconi and Tarazona [115]; their results capture the features of behavior displayed by the simulation data.

**Figure 4.9.** From Ref. 114. Adsorption as a function of position along the axis of the capillary for the system described in the caption to Figure 4.7. The lower figure is a projection onto a plane of three instantaneous configurations.
IV.B. Two-dimensional systems: General remarks

Fluids confined to nano-slits are greatly influenced by interactions with the walls. Yet there is much to be learned from a study of q2D systems confined by smooth hard walls. The distinction between 2D and q2D systems has real physical content since all real world nominally 2D systems are necessarily q2D systems. Yet the analysis of the data from experimental studies of q2D systems relies heavily on the predicted properties of 2D systems, so we must start with an overview of the latter.

It has been known for many years that, because of large amplitude thermal motions, at nonzero temperature, a 2D system does not support long-range translation (crystalline) order. In the solid phase, the short-range translation order is very similar to crystalline order, but instead of having constant amplitude, the envelope of the position correlation function decays algebraically as a function of increasing particle separation, i.e. displays quasi-long-range order. However, a 2D system does support a different kind of true long-range order, bond orientation order. In the 2D ordered state, the envelope of the bond orientation correlation function does not decay with increasing particle separation.

The study of 2D phase transitions has been greatly enriched by examination of the hard square [116] and hard hexagon [117] lattice gases. In the former case, an occupied site in a square lattice prohibits occupation of the four nearest neighbor sites and in the latter case, an occupied site in a triangular lattice prohibits occupation of the six nearest neighbor sites. In both cases, there is a continuous transition from the disordered state to an ordered state at a critical packing fraction, specifically 0.74 for hard squares and 0.83 for hard hexagons. Similarly, hard squares that can move continuously but only parallel to the $x$ and $y$-axes exhibit a continuous freezing transition at a packing fraction of 0.79 [118]. Hu and Mak [119] have argued that the phase transitions in the hard square and hard hexagon lattice gases are also percolation transitions at which there suddenly appears a continuous path of contacts from one side of a system to the other. We will return to this interpretation below. Removing the parallel motion restriction, Wojciechowski and Frenkel have reported the results of simulations of the 2D hard square fluid with continuous particle translation and rotation. They find that the isotropic fluid does not freeze into a square lattice with quasi-long-range translational order. Rather, the isotropic fluid transforms into a tetratic phase with quasi-long range orientation order of coupled molecular axes and intermolecular bonds and translational order that decays faster than algebraically.
Figure 4.10. From Ref. 120. Snapshots of the equilibrium configurations in the hard square system at different densities: (a) starting configuration, $\rho > 0.8400$, (b) tetratic phase, $\rho = 0.8012$, (c) coexistence region, $\rho = 0.7444$, (d) isotropic phase $\rho = 0.6600$.

Figure 4.11. From Ref. 120. The orientation correlation function, $g_4(r) = \langle \cos[4\theta(r) - 4\theta(0)] \rangle$, corresponding to the three equilibrium densities shown in Figure 4.7.

An experimental study of a q2D colloid suspension of hard squares that undergo continuous translation and rotation has been reported by Zhao, Bruinsma and Mason [121]. In contrast with the simulation results they observe a transition from the isotropic liquid to a hexagonal rotator crystal followed by a transition from the hexagonal rotator crystal to a rhombic crystal (see Figure 4.12). They do not observe the existence of a phase
that has four-fold-symmetry at any packing fraction. The origin of the rhombic phase is attributed to the shape of the excluded volume of rotationally swept squares (squiroids, see Figure 4.12), implying that interplay between the rotational entropy of a particle and the excluded volume associated with its shape combine to stabilize the rhombic unit cell. It is not at present clear why this rhombic phase was not observed in the very careful simulations of Wojciechowski and Frenkel [120].

Figure 4.12. From Ref. 121. Particle configurations in a q2D suspension of Brownian squares. The packing fractions are (A) 0.52, (B) 0.62, (C) 0.65, and (D) 0.74. The corresponding diffraction patterns are displayed in the lower left corners of the figures. In (A) the system is an isotropic fluid (I), in (B) a hexagonal rotator crystal (RX), in (C) there is coexistence of rotator (circled domain) and rhombic crystal (square enclosed domain) phases, and in D the system is in a rhombic crystal phase (RB).

Figure 4.13. From Ref. 121. Squiroid packing model for the q2D suspension of Brownian squares. (A) Rotation of a square about its center by $\Delta \theta = \pm \pi / 2$ produces the squiroid perimeter shown. In (B) these squiroids are shown packed in a hexagonal RX array at a density just below the RX to RB transition.

Squares and hexagons match the fundamental symmetries of the square and triangular lattices, respectively; they can be packed so as to completely fill the 2D space. Pentagons and heptagons cannot be packed so as to completely fill the 2D space since they do not have symmetries that match any regular lattice. Simulation studies by Frenkel and coworkers [122] lead to the conclusion that in these cases there is a first order transition.
from a disordered phase to a rotator phase with the particle centers on a triangular lattice and random orientation of the pentagons (heptagons), and at higher density, a first order transition to a striped phase with oriented pentagons (heptagons).

Systems with strong magnetic dipole-dipole repulsion or only lightly screened Coulomb repulsion have properties that do not depend on the size of the particles. In a sense, they can be considered to completely fill the 2D space. On the one hand, this analogy hints that the phase transitions in such systems will have features that resemble those found in the hard square and hard hexagon systems more than those in the hard pentagon system. On the other hand, the range of the interactions in such systems couples many particles simultaneously, unlike the nearest neighbor interactions in hard particle systems, which hints that the analogy is flawed and the character of the phase transitions of such systems can be fundamentally different from that in hard particle systems.

The most widely accepted description of 2D phase transitions is that developed by Kosterlitz, Thouless, Halpern, Nelson and Young (KTHNY) [123]. This theory does not make direct reference to the structure in the system or the nature of the particle-particle interaction. Rather, it describes the 2D solid as a deformable elastic medium, with inclusion of the two classes of point topological defects with smallest excitation energy to mediate structural changes, and it relates the melting process to the mechanical instability of the 2D solid, not to equality of chemical potentials of the solid and liquid. The structure of the system and the nature of the particle-particle interaction are implicit in the calculation of the elastic constants and of the properties of the point topological defects. Because the amplitudes of the fluctuations in a 2D system are very large, the elastic constants are altered from the bare values characteristic of the non-fluctuating uniform solid; KTHNY compute the change in the elastic constants from a renormalization analysis. The onset of instability of the solid is determined by a ratio of renormalized elastic constants and the core energy of a dislocation. When, at some temperature and density,

\[ K = \frac{4a_0^2 \mu(\mu + \lambda)}{k_B T \ 2\mu + \lambda} = 16\pi, \]  

with \( \mu \) and \( \lambda \) elastic constants and \( a_0 \) the lattice constant, there is a continuous transition to a hexatic phase in which the envelope of the position correlation function decays exponentially, and the envelope of the bond orientation correlation function decays algebraically, provided that the dislocation core energy is greater than 2.84 \( k_B T \). The hexatic phase is, fundamentally, an anisotropic liquid. At a higher temperature (and/or lower density), the dislocations, which consist of bound pairs of disclinations, unbind, leading to a transition from the hexatic phase to a liquid phase, in which the envelopes of both the position and bond orientation correlation functions decay exponentially. Although the theory allows for other possibilities, it is commonly taken to predict that a 2D system that supports only one ordered solid phase melts via sequential continuous phase transitions: solid-to-hexatic followed by hexatic-to-liquid.

The prediction of the existence of a hexatic phase intermediate between the 2D liquid and ordered solid phases is the most important contribution of KTHNY theory; it defines a qualitative difference between phase equilibrium in 2D and 3D systems. The other theoretical predictions, namely of the nature of the liquid-to-hexatic and hexatic-to-ordered solid transitions, and of the rates of decay of the envelopes of the bond orientation and position correlation functions in the different phases, are less central to characterizing the differences between 2D and 3D matter.

As noted above, the KTHNY theory buries the role of the particle interactions in the values of the elastic constants. In 3D, although there is no theorem that establishes that it must be so, the
nature of the melting transition is found, via experiments, to be independent of the intermolecular potential; all known crystalline materials melt via a first order transition. The situation appears to be different in 2D, as illustrated by computer simulations reported by Bladon and Frenkel [124] and Mazars [125], a density functional analysis of 2D melting, reported by Pomirchi, Ryzhov and Tareyeva [126], and available experimental data. Bladon and Frenkel studied the properties of a 2D assembly of particles in which the particle-particle interaction has a hard core of diameter $\sigma$ and a very narrow attractive square well or repulsive shoulder with depth/height $\varepsilon$. This generic pair interaction supports an iso-structural solid I-to-solid II transition. In the vicinity of the critical temperature for this iso-structural transition, fluctuations both induce formation of a hexatic phase and influence the nature of the phase transitions at lower densities. When the range of the attractive square well (or the repulsive shoulder) is of order $0.01\sigma$ the domain of stability becomes vanishingly small; that domain of stability increases as the width of the square well (or the repulsive shoulder) increases. Mazars studied 2D melting in systems with the inverse power pair interaction $\varepsilon(\sigma/r)^n$. He finds that for $n \leq 3$ the melting process agrees with the KTHNY predictions, but for $n > 4$ melting does not follow the KTHNY description. Pomirchi, Ryzhov and Tareyeva also studied 2D melting in a system with square well interaction as a function of the width of the square well. They determine the density of the continuous transition of the solid-to-hexatic phase at a specified temperature using the KTHNY criterion for the instability of the 2D solid, with values of the elastic constants calculated from density functional theory and they find the density of the first order solid-to-liquid transition using a variational calculation of the free energy of the solid. This theory predicts that when the square well has zero width, i.e. in the hard disc limit, the melting transition is first order and that there is no hexatic phase between the solid and liquid phases. When the square well width is increased from zero, the first order solid-to-liquid transition is initially replaced by a continuous transition, presumably to a hexatic phase, then with growth of the square well width replaced again by a first order transition and, when the attractive well becomes large enough that it includes second neighbor particles the melting occurs via two continuous transitions. We will later describe a different version of density functional theory that predicts that in a hard disc system, the continuous transition from the liquid to the hexatic phase just preempts the first order liquid-to-solid transition. The available experimental data for q2D systems with long-range pair interactions, e.g. dipole-dipole interactions, support the KTHNY description of melting. The available experimental data for q2D systems with short-range pair interactions, specifically near hard core interactions, support the KTHNY prediction of the existence of the hexatic phase, but often do not support the predicted order of the phase transitions or the detailed behavior of the defect concentrations (see below).

A few further observations concerning the hard disc system are relevant to our discussion. Just as is the case for hard pentagons and heptagons, hard discs cannot be packed so as to completely fill the 2D space. Because of large amplitude fluctuations and very slow approach to equilibrium in 2D, the determination of the nature of the 2D freezing transition is very sensitive to the size of the simulation sample. After many years of uncertainty, several computer simulations have reached the same conclusion for the melting behavior of the 2D hard disc system. Large-scale simulations of a dense 2D hard disc system ($4 \times 10^6$ discs), reported by Mak [127], imply that the melting process consists of a continuous transition from the ordered 2D solid to the hexatic phase at a packing fraction close to 0.723, and either a very weak first order or a continuous transition from the hexatic to the fluid phase at a packing fraction close to 0.699. These results are consistent with the results of a study of the elastic moduli [128] that suggest that the KTHNY
continuous transition from the hard disc solid to a hexatic phase just barely preempts the solid-to-liquid first order transition. They are also consistent with the results of recent simulation studies by Bernard and Krauth [129] and by Anderson, Engel and Glotzer [130]. Werner and Krauth studied systems with $10^6$ particles and concluded that the liquid-to-hexatic transition is first order, with packing fractions of 0.700 and 0.716 of the liquid and hexatic phases, respectively, that the domain of stability of the hexatic phase is the packing fraction range 0.716 to 0.720, and that the hexatic-to-solid phase transition is continuous. Anderson, Engel and Glotzer exploited three different simulation methodologies and used samples with up to $10^6$ discs; they concluded that the liquid-to-hexatic transition is first order starting at a packing fraction of 0.702, and that the domain of stability of the hexatic phase spans the very small packing fraction range 0.716 to 0.720.

If the percolation transition can be identified with a geometric criterion for a phase transition, as has been suggested for the hard square and hard hexagon lattice gases [119], can one find a geometric criterion for the phase transitions in the hard disc system? Kozak, Brzezinski and Rice [131] have conjectured that in a 2D system of hard discs, the packing fraction at which the continuous transition from the ordered solid to the hexatic phase occurs, and that at which the very weak first order or continuous transition from the hexatic to the fluid phase occurs, can be correlated with the packing fractions of patterned networks (tessellations) of disc positions. They identify three tessellations that have less than close packed density, span 2D space, and have percolated continuity of disc-disc contact. One has a packing fraction of 0.729, very slightly larger than the estimated packing fraction at the continuous ordered solid-to-hexatic transition (0.720), and the other two have packing fractions of $\sim 0.680$, slightly smaller than that identified as the upper end of the stability range of the liquid phase (0.700-0.702). These packing fractions correspond to tessellations in which the defining unit structures are regular polygons. Intermediate between these packing fractions the tessellations have randomly dispersed clusters that need not be regular polygons. Kozak, Brzezinski and Rice suggest that the densities at which the percolated tessellations span the 2D space be regarded as special points along the density axis, since the symmetries and packing fractions of the tessellations at higher and lower density are different. They also suggest that the possibility of forming different symmetry tessellations with sensibly the same packing fraction is a geometric analogue of a bifurcation condition that divides the configuration space into qualitatively different domains. At the smaller of the special densities, the system chooses between changing from a disordered state to a partially ordered state or one of two ordered states. That is, viewing the space of possible disc configurations as a function of density, there is a density below which only disordered configurations are stable. Kozak, Brzezinski and Rice do not assert that such a correlation implies the actual occurrence of those tessellations, rather that each of the densities at which the solid-to-hexatic and hexatic-to-liquid transitions occur is a signature of the existence of a nearby tessellation that completely spans the 2D space. They do show that it is possible to construct a continuous many particle transformation from the dense fluid to the crystalline phase, and from the crystalline phase to the dense fluid, with both transformations mediated by the same intermediate configuration. The putative relationship between percolated tessellations of the plane and phase transitions and the ideas underlying the KTHNY theory is consistent with the calculated values of the bond orientation function.

IV.C. One layer quasi-two-dimensional systems: Some details
How accurately do the predictions concerning phase transitions in a 2D system describe those in a one-layer q2D system? The answer to this question draws on a mixture of results from real experiments and computer simulations.

There are several colloid systems that have pair interactions reasonably close to, but somewhat deviant from, the idealized hard-core repulsion. In a realizable suspension of uncharged colloid particles, one source of deviation of the interaction from the hard-core form arises from the nonzero dispersion of particle diameters. When the suspension is considered to be a one-component system of particles with an effective diameter, the averaging over the distribution of pair separations at contact generates an effective pair interaction with a repulsive part that is softer than the hard-core repulsion and an attractive well with a depth that depends on the width of the distribution of diameters [132]. In a suspension of uncharged colloids with stabilizing polymer brushes, and in a suspension of charged colloids with salt concentration large enough to shield the Coulomb interaction with a screening length that is small compared to the colloid diameter, the repulsion between particles is softer than the hard-core repulsion. The same characterization applies to a suspension of microgel colloid particles with temperature tunable diameter [133], noting that in this case the steepness of the repulsion is also temperature dependent. Finally, for all realizable q2D systems account must be taken of the small amplitude out-of-plane motion. The most trivial consequence of the out-of-plane motion is the need to describe the colloid-colloid interaction with an effective diameter; more consequential changes in the system description will be necessary if the motion generates qualitative changes in the system behavior.

With these caveats in mind, the available experimental data for tightly confined q2D systems with near hard sphere interactions fall short of providing an unambiguous test of the KTHNY theory predictions.

We consider first systems composed of particles with long-ranged pair interactions, such as a q2D suspension of colloids with embedded paramagnetic ions [134]. Application of an external magnetic field induces parallel magnetic dipoles in the colloids, the strengths of which are proportional to the applied field. It can be arranged that the dominant interaction between particles is the long-range magnetic dipole-dipole repulsion. This system is arguably the best real world realization of a 2D system for three reasons. First, in this case, the nonzero dispersion of the colloid diameters is unimportant. Second, the variation from particle to particle of the concentration of paramagnetic ions and, hence, of induced magnetic moments, appears to be small. Third, the colloids used are large and heavy, so out-of-plane motion is more limited than in other systems. For this q2D system the available experimental evidence [134-137] supports all of the KTHNY predictions concerning the order of the liquid-to-hexatic transition and the decays of the envelopes of the position and bond orientation correlation functions (Figure 4.14).
Figure 4.14. From Ref. 135. The translational (left) and bond orientation (right) correlation functions of the q2D suspension with magnetic dipole interactions. \( \Gamma = \left( \mu / 4\pi \chi_{\text{eff}} B \right)^2 (\pi n)^{3/2} / k_B T \) with \( \chi_{\text{eff}} B \) the effective magnetic susceptibility, B the magnetic field and \( n \) the packing fraction. The particle-particle separation is reduced by the lattice constant, \( a \), of the ordered solid. The KTHNY predictions of the asymptotic forms for the decays of these correlation functions are shown as the straight lines.

Lin and Chen [138,139] have studied another q2D system with long-range colloid-colloid interaction, an assembly of charged polystyrene particles trapped in the water-decane interface. Because the amplitude of thermal capillary wave motion of this interface is very small, the centers of the particles are very tightly constrained to a nearly 2D configuration. The interaction in this system, including the shielding by counterions, falls off as \( r^{-3} \). Consequently, phase transitions are observed at small densities, as shown in Figure 4.15. The data establish the existence of a hexatic phase, but unlike the case with magnetic dipole-dipole repulsion, the liquid-to-hexatic transition is first order rather than continuous. The solid-to-hexatic phase transition is induced by generation of equal numbers of five-fold and seven-fold defects, as predicted by KTHNY theory, but the hexatic-to-liquid transition is accompanied by dramatic increases in the numbers of four-fold and eight-fold defects, and a growing difference between the concentrations of five-fold and seven-fold defects, not accounted for by KTHNY theory.

Figure 4.15. From Ref. 139. Phase diagram of a q2D assembly of charged colloid particles constrained to lie in the water-decane interface.
Studies of phase transitions in q2D systems with short-ranges pair interactions have yielded results that agree with some but not all of the predictions of KTHNY theory. Marcus and Rice [140,141] used digital video microscopy to study the equilibrium structure of q2D suspensions of sterically stabilized uncharged poly-methyl-methacrylate colloidal spheres confined between the surfaces of a very thin glass cell with wall separation about 1.2 particle diameters. Their experiments revealed the existence of a hexatic phase and first-order fluid-to-hexatic and hexatic-to-solid phase transitions. They identified the several phases using the coincidence of four indicators: the local density, the local bond orientation correlation function, the shape of the calculated diffraction peak, and the local characteristic time required for a particle to diffuse a distance equal to its diameter (see Figs. 4.16 and 4.17).

Figure 4.16. From Ref. 141. Angular dependences of the line shapes of the first peaks of the two-dimensional structure functions displayed in Figure 16. The curves are displaced on the vertical scale for clarity. (A) isotropic liquid; (B) hexatic; (C) solid. The functional forms of the curves in (B) and (C) are square-root Lorentzian and simple Lorentzian, respectively.
Figure 4.17. From Ref. 141. Two-dimensional structure functions corresponding to (A) the liquid with packing fraction 0.58, (B) the hexatic phase with packing fraction 0.83 and (C) a compressed solid with packing fraction 0.93. Panels (D), (E) and (F) display the Voronoi constructions for (A), (B) and (C), respectively.

Marcus and Rice suggested that the colloid-colloid interaction in the system they studied has a functional form compatible with the generic pair interaction studied by Bladon and Frenkel, and that this pair interaction supports the observed first-order phase transitions between the fluid and hexatic phases and between the hexatic and solid phases. We call this interaction the MR potential.

A few words about the pair interaction suggested by Marcus and Rice are pertinent at this point. That interaction was constructed for uncharged colloids, the surfaces of which are covered with short non-polar polymer chains. If the colloids are suspended in water, incipient contact between the non-polar polymer brushes will be attractive; then as
the colloid-colloid separation decreases the loss of configurational entropy by the interpenetrating brushes leads to an effective soft repulsion. If the colloid-colloid separation is reduced still further, the interaction becomes strongly repulsive, nearly hard-core like. The attractive component (depth $\varepsilon$) has a range that is only a few percent of the particle diameter (see the insert in Figure 4.18). In the 2D limit, as shown by simulation studies reported by Bladon and Frenkel [124], a colloid system with interaction of this generic type supports an iso-structural solid I-to-solid II transition. In the vicinity of the critical temperature for this iso-structural transition, fluctuations both induce formation of a hexatic phase and influence the nature of the phase transitions at lower densities.

Frydel and Rice [142] have reported the results of simulations using the pair interaction suggested by Marcus and Rice. Figure 4.17 displays the equation of state for 2D and q2D assemblies of MR particles, and Figure 4.18 displays the results of the renormalization analysis of the influence of fluctuations on the values of the elastic constants. The simulation results reported by Frydel and Rice show that a 2D system with an MR interaction can exhibit first order liquid-to-hexatic, hexatic-to-solid I, and solid I-to-solid II transitions. It is worth noting that the KTHNY theory can be extended to the case when the 2D system supports two ordered solid phases by assuming that the elastic free energy of the system includes a term descriptive of the strain arising from the change in density associated with an iso-structural solid-to-solid transition [143]. With this assumption, the modified KTHNY theory can account for all of the essential results of the simulation studies of Bladon and Frenkel. However, the modified analysis does not provide a priori guidance as to when the elastic free energy should or should not contain such an extra contribution.

Figure 4.18. From Ref. 142. Phase boundaries for 2D and q2D suspensions of colloid particles that interact with an MR potential (see inset). $L$, $S_I$, $S_{II}$ and $S_{III}$ denote the stable liquid, solid I, solid II and solid III phases, respectively. The dotted line connects the density points for $T^* = 1.00, 0.60$ and $0.50$ where the square-root Lorentzian characteristic of a hexatic becomes a better fit than a Lorentzian to the structure function. For both the 2D and q2D systems at all temperatures the density at which it occurs is $\rho^* = 0.87$. 
Figure 4.19. From Ref. 142. Renormalization of $K/16\pi$ (bold lines) at $T^* = 1.00$, 0.60 and 0.50 as a function of density for 2D and 2qD suspensions of colloid particles that interact with an MR potential. The data points are values of $K/16\pi$ obtained from simulation data, and the vertical lines denote the first-order transition melting densities.

How, if at all, do phase transitions in a q2D system differ from those in a 2D system? The issue to be resolved is whether the small amplitude out-of-plane motion in a q2D system generates only quantitative corrections to the 2D phase diagram, or if it generates qualitative changes to that phase diagram. Frydel and Rice [142] have compared the phase diagrams of q2D and 2D systems composed of particles with an MR interaction (Figure 4.18). Both systems undergo a first order solid I-solid II and solid II-solid III isostructural transitions induced by the attractive and repulsive components of the interaction, respectively. In q2D, although solid II has a puckered structure, the symmetry of that structure projected on a plane is the same as that of solid I.

Introduction of the out-of-plane motion shifts the low-density portion of the phase boundaries involving the solid II phase. The liquid-solid I coexistence line is nearly the same for the two systems. The solid II-solid III transition is shifted to lower temperature and to higher density in the q2D system. Calculation of the renormalized elastic constants reveals that in the q2D system the first order melting transition preempts the KTHNY transition for the reduced temperatures $T^* = k_bT/\varepsilon = 1.00$, 0.60, and 0.50 (Figure 4.19). The findings are similar for the 2D system: when $T^* = 0.60$ the KTHNY transition barely preempts the first order melting transition, and when $T^* = 1.00$ and 0.50 the first order melting transition preempts the KTHNY transition. The shift in the coexistence line is that expected from a simple physical argument, namely, at any selected density at which the liquid is stable its entropy is increased by allowing out-of-plane motion. Similarly, allowing out-of-plane fluctuations of the solid I structure increases its entropy and thereby extends the density range over which it is stable. Eventually the density becomes so
large that the puckered structure of solid II becomes stable. Clearly, the change from 2D to 2qD confinement has nonnegligible influence on the nature of the phase transitions in the system studied.

The colloid-colloid pair interaction can be varied in a variety of fashions. To study q2D phase equilibrium in a system with pair interaction that better approaches the hard-core ideal, Karnchanaphanurach, Lin and Rice [144] used 12-carbon surfactant sterically stabilized uncharged 1.58 μm silica spheres; the short chain brush that stabilizes the colloid particle extends only to 1.002σ, which implies that the pair interaction is very close to hard-core-like. The results of their studies show a first-order liquid-to-solid transition with an estimated coexistence region \(0.684 < \rho^* < 0.704\), and without intervention of a hexatic phase. This conclusion is supported by fitting the shapes of the diffraction peaks computed from the observed positions of the particles and the rate of decay of the envelope of the pair correlation function. Because the spacing of the densities studied is rather coarse, the estimated locations of the end points of the coexistence region are likely uncertain by \(\pm(0.02 – 0.03)\). We note that the end points of this coexistence region are close to but slightly smaller than the densities of the liquid and solid phases estimated from simulations \(\rho^*_L = 0.700, \rho^*_S = 0.720\), but the uncertainties of the densities are as large as the difference in densities determined from the simulations. Also, the interpretation of the nature of the transitions is different. That said, residual polydispersity of the spheres and out-of-plane motion could hide a small density region where the hexatic phase is stable. Clearly, comparison of the Marcus-Rice and the Karnchanaphanurach-Lin-Rice experimental results confirms the sensitivity of the q2D melting transition to the form of the pair interaction.

Han et al. [133] have reported studies of suspensions of microgel spheres, with temperature tunable diameter, confined between glass plates with a hydrophobic coating and separated by approximately 1.25 particle diameters. Their data clearly show the existence of a hexatic phase interpolated between the fluid and solid phases. The liquid-to-hexatic and hexatic-to-solid transition densities are found to be, approximately, 0.69 and 0.70, but the data are insufficient to unambiguously determine the order of the transitions. It is important to note that in this system the shape of the repulsive interaction also changes with temperature (see Figure 1a of Ref. 133), which complicates the comparison with predictions for a hard sphere system.

IV.D. Multi-layer quasi-two-dimensional systems: Some details

We can generalize the class of q2D systems to include those confined to have a thickness of more than one but only a few sphere diameters. That kind of confinement will support new structures, different from both the 2D and 3D structures. Indeed, experimental studies of colloid suspensions confined between two plates [29-38], whether the interaction has short-range or long-range, show a cascade of ordered solid-to-ordered solid transitions.

For suspensions of particles with near hard sphere interaction, increasing the confining wall separation generates the following sequence of structures:

\[ 1\Delta \rightarrow 2\square \rightarrow 2\Delta \rightarrow 3\square \rightarrow \ldots \]

The symbol \(\Delta\) denotes a layer with hexagonal lattice symmetry and \(\square\) a layer with square lattice symmetry. The integers in front of these symbols denote the number of layers of particles.
between the confining walls. A phase diagram derived from Monte Carlo simulations is displayed in Figure 4.20. As written, the structural sequence \( \Delta \rightarrow 2\Delta \rightarrow 2\Delta \rightarrow 3\Delta \rightarrow \ldots \) is incomplete in that it includes only lattices with hexagonal and square symmetries, and it implies that increasing the wall separation leads only to integer numbers of layers in the available space. However, when the wall separation is greater than that needed for the \( n\Delta \) structure but smaller than that needed for the \( (n+1)\Delta \) structure, instability with respect to other structures can occur. Specifically, the layer of particles can buckle [39,145]. The buckling of a plane of particles is coupled to an in-plane order-

![Figure 4.20](image)

**Figure 4.20.** From Ref. 39. Phase diagram for hard spheres contained between smooth hard walls separated by \( H = \sigma(1 + h) \).

disorder transition in which the lateral positions of particles that are localized at the same height are ordered. This ordering can take the form of linear or zigzag rows of particles. The symmetry of the emerging up and down phases for a single layer makes the buckled phase, \( B \), an intermediate structure between the \( n\Delta \) and \( (n+1)\Delta \) lattices. The stability region of \( B \) increases with the gap between the confining walls until \( B \) becomes unstable with respect to the formation of a crystal with an additional layer. The two transitions, \( n\Delta \rightarrow nB \rightarrow (n+1)\Delta \), are found to be first order.

All of these qualitative considerations are also valid for confined particles with softer repulsive interactions [40], and for confined particles with MR-type interactions [40,145], and they follow from the Landau theory of phase transitions, in which the thermodynamic potential is expanded about that for the flat state [146], and from an analysis based on free-volume theory [39]. Finally, for a system with colloid-colloid interactions of the MR type, the two-layer packing of particles in the square array has large interlayer lattice spacing, with the particles located at the minima of the attractive well. In this case the hexagonal to square lattice transition is first order. On the other hand, for a two layer system with hard core colloid-colloid interactions, there are two degenerate stable intermediate states, linear and zigzag rhombic phases, that are separated from the square lattice by strong first order transitions, and from the hexagonal lattice by either weak first order or by second order transitions [40,145].
A simple interpretation of the phase diagram as a function of wall separation for suspensions of near hard spheres follows from the observation that, because the equilibrium state in the limit of high pressure corresponds to maximum volume density, the successive transitions are driven by the competition between the free volume available to \( n \) square packed layers with smaller overall thickness than \( n \) hexagonal packed layers, and the free volume associated with more efficient packing within a hexagonal packed layer than in a square packed layer. Computer simulations and cell model calculations for the hard sphere system each generate a phase diagram that replicates the alternation of hexagonal and square lattice symmetry found [39], noting that neither theoretical approach addresses whether, as a function of wall separation, a hexatic phase intervenes between the solid and liquid phases.

For suspensions of particles with Coulomb interaction, immersed in uniformly distributed counterions and neglecting the discrete structure of the counterions, increasing the confining plate separation at \( T = 0 \) generates the following sequence of structures [147,148]:

\[
1\Delta \to 2B \to 2\bar{\Delta} \to 2R \to 2\Delta \to \ldots
\]

The symbol \( R \) denotes a phase with rhombic symmetry. At small density the colloid particles tend to stay in the potential minima generated by the counterion background, but at larger density the particle-particle repulsion dominates the particle background attraction, and the system supports a complex sequence of multi-layer ordered structures.

A Yukawa interaction can, by varying the screening length \( 1/\kappa \), be thought of as intermediate between the hard sphere and Coulomb interactions. The zero temperature phase diagram is rather complex (Figure 4.21). For example, interpolating between the \( 2\Delta \) and \( 3\bar{\Delta} \) phases, Oguz, Messina and Lowen [148] find the following transitions:

\[
2\Delta \to 3\bar{\Delta}
\]
\[
2\Delta \to BWI \to 3\bar{\Delta}
\]
\[
2\Delta \to BWI \to 2P_\Delta \to 2P_\bar{\Delta} \to 3\bar{\Delta}
\]
\[
2\Delta \to BWI \to 2P_\Delta \to hcp(100) \to 2P_\Delta \to 2P_\bar{\Delta} \to 3\bar{\Delta}
\]
\[
2\Delta \to BWI \to 2P_\Delta \to hcplike \to hcp(100) \to 2P_\Delta \to 2P_\bar{\Delta} \to 3\bar{\Delta}
\]
The symbols $\text{BWI}$, $P_{\Delta}$ and $P_{\square}$ refer to a so-called Belgian waffle iron phase and prism phases with triangular and square bases, respectively. This cascade is qualitatively different from that separating the $2\Delta \rightarrow 3\square$ transition in the hard sphere system.

None of the studies sketched above looked for the interpolation of a hexatic phase between the liquid and ordered solid phases as the wall separation of the confined suspension is increased from the 2D limit of zero. There is only one reported analysis of the dependence on wall separation and density of the liquid-to-hexatic, liquid-to-$1\Delta$ and liquid-to-$2\Delta$ transitions in a q2D colloid system. Xu and Rice [24,149] locate these transitions by the bifurcation of solutions of the first and second equations of the Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy for the particle distribution functions in the system [150]. The theory, which makes no direct reference to either the elastic constants of the system or the concentrations and interactions between particular lattice imperfections, determines the wall separation dependence of the density at which the pair correlation function of a q2D hard sphere system changes analytic form.

Consider, first, the 2D limit of the q2D hard sphere system. There are three key elements in the Xu-Rice analysis. First, to predict the liquid-to-hexatic transition one needs a representation of the two-particle distribution function of the anisotropic liquid that describes long-range bond orientation order. The diffraction pattern, hence the structure function, of a hexatic phase has
peaks with a characteristic elongation into finite arcs. Xu and Rice use this property to represent the pair correlation function in the hexatic phase in the form

\[ g_2(\mathbf{r}_1, \mathbf{r}_2) = g(r_{12}) + \int \frac{d\mathbf{k}}{\mathcal{V}} \phi(k) \cos(6\theta) \exp(i\mathbf{k} \cdot \mathbf{r}_{12}), \]  

(3.2)
in which \( \phi(k) \) is a function centered at \( k_0 = 4\pi / r_0 \) that decays to 0 at about \( k_0 / 2 \), and \( r_0 \) is the separation between nearest neighbors. This choice for the representation of the pair correlation function is different from that proposed by Ryzhov and Tareyeva [151]. Second, to predict the liquid-to-ordered solid transition, they employ a representation of the non-uniform one-particle distribution function that reflects the particular lattice symmetry. Third, because the BBGKY hierarchy relates the \( n \)-particle distribution function to the \((n+1)\)-particle distribution function, a representation of the triplet correlation function is needed. Xu and Rice use a Pade approximant extension of the exact density expansion of the triplet correlation function truncated after the five-particle term [152]. This approximation has been shown to give a rather good but not perfect description of both the pair correlation function and the equation of state of simple liquids. With these approximations Xu and Rice find that the 2D hard disc system undergoes a continuous liquid-to-hexatic transition at lower density than the liquid-to-crystal transition (Figure 4.22), in agreement with the KTHNY theory prediction, and unlike the prediction by Ryzhov and Tareyeva [151]. The 2D liquid-to-hexatic transition is predicted to occur at a packing fraction of 0.708, slightly greater than determine from computer simulation data (0.700-0.702). This prediction is based on the assumption that the transition is continuous, which does not agree with the simulation data. The packing fraction difference between the liquid and hexatic phases determined from the simulation data is very small (0.014-0.016), which suggests that locating the

![Figure 4.22.](image)

*Figure 4.22.* From Ref. 149. Thickness dependences of the liquid-to-crystal phase transition (black line and red line) and the liquid-to-hexatic phase transition (blue line). Simulation results for the liquid-to-crystal phase transition, by Schmidt and Lowen [47], are shown as points. Note that the density used in this figure is \( N\pi\sigma^2 / 4A \), hence is larger than that used in the text by the factor \( 4 / \pi \).
limit of stability of the fluid with respect to the hexatic phase under the assumption that the transition is continuous leads to only a small quantitative error in the predicted transition density. For lack of an accurate real space correlation function for the hexatic phase, Xu and Rice do not predict the density at which the hexatic-to-solid transition occurs, but from a prediction of the liquid-to-solid transition they predict that the solid packing fraction is 0.712, slightly lower than the value 0.720 obtained from the simulation data.

In the approach adopted by Xu and Rice, analysis of the wall separation dependence of the confined liquid-to-hexatic and liquid-to-ordered solid transitions requires knowledge of the wall separation dependence of the pair correlation function of the liquid. That information is not available, so Xu and Rice used an approximation that maps the q2D system onto a 2D system via a scaled-particle ansatz. Specifically, for wall separation \( H = \sigma(1 + h) \) they assumed that the effective diameter for particles with separation \( r \) is \( \sigma_{\text{eff}}^2(r) = \sigma^2[1 - (\sigma^2h^2/6r^2)] \). This approximation is best when \( h \ll 1 \), and becomes increasingly unsatisfactory as the system thickness increases. Xu and Rice find that for wall separations less than about 1.4 \( \sigma \), the liquid-to-hexatic transition density occurs at lower density than the liquid-to-crystal transition, with the reverse order of transitions predicted for wall separations greater than 1.4 \( \sigma \). Turning now to the liquid-to-solid transition, Xu and Rice find the agreement between the predicted shape of the q2D thickness dependence of the coexistence line between the hard sphere liquid and the \( 1\Delta \) phase and that obtained from computer simulations to be rather good (see Figure 4.22), as is the identification of the thickness at which the liquid prefers to freeze to the \( 2\pi \) phase, but the predicted shape of the q2D thickness dependence of the coexistence line between the hard disc liquid and the \( 2\pi \) phase is poor.

The variation in crystal structure to which a q2D liquid freezes as the wall separation is increased can be used to examine whether structured fluctuations in the liquid serve as precursors to transitions to particular crystal lattices. The nucleation of crystallization has been studied for many years, but there remain ambiguities concerning the role of local ordered fluctuations in a liquid because of the lack of a direct connection between the definition of which structured fluctuations are important and a prescription for verifying such identifications. Sheu and Rice [153] have addressed this ambiguity for a q2D system by coupling an observable that can be used to identify local hetero-phase fluctuations in a liquid with an examination of the liquid \( \rightarrow 1\Delta \) and liquid \( \rightarrow 2\pi \) transitions. The observable they used is the aperture cross-correlation function of the liquid, \( C(k,q) \), which correlates the intensities of radiation, \( I(k) \) and \( I(q) \), scattered from a small volume measured at two distinct wave vectors \( k \) and \( q \), with two detectors positioned such that \( k \) is the difference between the incident radiation and scattered radiation wave vectors. \( C(k,q) \) is defined as the following grand canonical average over the particles contained in the illuminated volume:

\[
C(q,k,t) = \frac{\langle I(q,0)I(k,t) \rangle}{\langle I(q)\rangle\langle I(k)\rangle}_{GC} \tag{3.3}
\]
$C(\mathbf{k}, \mathbf{q})$ is a measure of fluctuations that generate local order in the illuminated volume, specifically those that create configurations that satisfy the conditions for Bragg diffraction. Different choices of angle between the detectors can be used to monitor different locally ordered fluctuations, and measurements of the correlation between the intensities of the scattered radiation at two angles can be carried out at a single time or as a function of time.

Sheu and Rice have used $C(\mathbf{k}, \mathbf{q})$, calculated from molecular dynamics simulation data, to monitor locally ordered fluctuations in a q2D hard sphere fluid with thickness less than two sphere diameters. They find (see Figs. 4.23 and 4.24) that for wall separation $H$ in the range $1\sigma \leq H \leq 1.57\sigma$ the liquid freezes into a single layer hexagonal solid and the locally ordered fluctuations exhibit only hexagonal symmetry that extends well into the liquid region. For $1.57\sigma \leq H \leq 1.75\sigma$ hexagonal fluctuations persist, and fluctuations with square ordered symmetry, that of the solid to which the liquid freezes, only emerge at densities $\sim 2\%$ below freezing. For $H = 1.8\sigma$ and $1.85\sigma$, hexagonal ordered fluctuations are no longer found, and the square ordered fluctuations dominate the dense liquid region as the system freezes into a two layer square solid. For $H = 1.9\sigma$ and $1.95\sigma$, where the liquid freezes into a two layer hexagonal solid, both square and hexagonal ordered fluctuations are observed. At lower densities, for these latter wall separations, the ordered fluctuations exhibit only square symmetry. Hexagonal symmetry ordered fluctuations appear at densities $\sim 7\%$ below freezing and become more dominant as the density is increased, but the square ordered fluctuations persist until the system is converted into the solid.

The results of these simulation studies show clearly that locally ordered fluctuations occur deep in the stable liquid domain of a q2D confined colloid system. The particular order exhibited by these fluctuations is a function of both density and wall separation. At a specified wall separation and density, there is a precursor ordered local fluctuation in the q2D liquid that anticipates the character of the solid to which the liquid freezes, and the transformation from hexagonal to square packing in the solid-solid transition has a precursor in the ordered fluctuations in the liquid.

IV.E. A 2D model molecular system

Aside from the special cases of squares, pentagons and hexagons, all of the preceding discussion has dealt with confined systems of particles with isotropic pair interactions. In the next Section we discuss the properties of nano-confined water. A transition to that discussion is provided by an examination of a 2D assembly of particles that have a pair interaction with both isotropic and anisotropic components of different strengths and ranges. A simulation study of such a system has been reported by Singh, Santra and Bagchi [154]. The isotropic component of the pair interaction has the form of a Lennard-Jones potential, and the anisotropic component has three-fold-symmetry and is designed to mimic hydrogen bonding. In this so-called Mercedes-Benz (MB) potential, which is a caricature of the water-water interaction, the ratio of the strengths of the two components of the interaction is $\lambda_{an} = \varepsilon_{LJ} / \varepsilon_{HB}$. The presence of two energy scales, two length scales and anisotropy greatly affects the phase diagram of the system. Figure 4.25A displays melting characteristics of this system obtained from the simulations, represented
as melting lines in the $T\lambda_{an}$ plane for two different pressures. The equilibrium packing structures are shown in Figure 4.25B.

When $\lambda_{an}$ is small, corresponding to large anisotropy in the pair interaction, there is a first order transition from the low-density honeycomb lattice to the high-density liquid phase, reminiscent of the melting of ice, without intervention of a hexatic phase (Figure 4.26).

![Figure 4.23. From Ref. 153. The zero time aperture cross correlation function as a function of angle for various densities with wall separation 1.50 particle diameters. The fluid $\rightarrow$ 1\Delta and 1\Delta $\rightarrow$ buckled phase transitions occur at $\rho^* = 0.62$ and 0.73.](image)
Figure 4.24. From Ref. 153. The zero time aperture cross correlation function as a function of angle for various densities with wall separation 1.80 particle diameters. The fluid → 2D phase transition occurs at $\rho^* = 0.75$. 

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**Figure 4.25.** From Ref. 154. (A) Solid-liquid and solid-solid transitions for a 2D system of MB particles. The red line and triangle symbols is for a system at a reduced pressure of 0.10, and the black line and circle symbols is for a system at a reduced pressure of 0.19. (B) Particle arrangements in the honeycomb and oblique lattices. Note the alignment of the components of the anisotropic interaction, modeling hydrogen bond formation. (C) Range of stability of the liquid and honeycomb phases, represented via the density dependences of the bond orientation correlation function in these phases for the case of weak anisotropy $\lambda_{an} = 0.1$ and reduced pressure 0.19. (D) Range of stability of the liquid, oblique and honeycomb phases, represented via the density dependences of the bond orientation correlation function in these phases for the case of strong anisotropy $\lambda_{an} = 0.4$ and reduced pressure 0.19.

**Figure 4.26.** From Ref. 154. (A) Temperature dependence of the density for the system with $\lambda_{an} = 0.1$. (B) Temperature dependences of the translational and bond orientation parameters for the system with $\lambda_{an} = 0.1$. (C) Temperature dependence of the density for the system with $\lambda_{an} = 0.4$. (D) Temperature dependences of the translational and bond orientation parameters for the system with $\lambda_{an} = 0.4$. In all cases the reduced pressure is 0.19.

We note that the density changes on melting are of opposite sign for $\lambda_{an} = 0.1$ and $\lambda_{an} = 0.4$. En $\lambda_{an}$ is increased the honeycomb lattice-liquid melting line bifurcates into two melting lines, one the melting line of the honeycomb-oblique lattice transition and the other the melting line of the oblique lattice-liquid transition. The structures of the honeycomb and oblique lattices are displayed in Figure 4.25B. The honeycomb phase is stabilized by the three strong hydrogen bond-like interactions, and the oblique phase by the central Lennard-Jones interaction and two hydrogen bond interactions. The ranges of stability of the several phases are displayed in Figs. 4.25C and 4.25D. In this system an
increase in pressure shifts the honeycomb lattice-liquid and honeycomb lattice-oblique lattice melting lines to lower temperature, while the oblique lattice-liquid melting line shifts to higher temperature, as expected from the density and entropy differences between the phases. The absence of any intermediate phase in the melting transition is inferred from the decay of the envelopes of the pair correlation function and the bond orientation correlation function, shown in Figure 4.27.

Figure 4.27. From Ref. 154. (A) Bond orientation correlation function, \( g_6(r) \), for several temperatures spanning the melting transition (\( \lambda_an = 0.1, P^* = 0.19 \)). These data reveal an absence of quasi-long-range bond order as the temperature is increased (lack of algebraic decay of the envelope of \( g_6(r) \)). (B) Translation correlation function, \( g_G(r) \), for several temperatures spanning the melting transition (\( \lambda_an = 0.1, P^* = 0.19 \)). (C) Bond orientation correlation function for several temperatures spanning the melting transition (\( \lambda_an = 0.4, P^* = 0.19 \)). These data reveal the existence of weak quasi-long-range bond order as the temperature is increased. (D) Translation correlation function for several temperatures spanning the melting transition (\( \lambda_an = 0.4, P^* = 0.19 \)). Note the existence of quasi-long-range order in the solid and short range order in the liquid.

Clearly, when the pair interaction in a system is anisotropic and has several components with different strengths and ranges its phase diagram can be complicated. We will find that to be the case for nano-confined water. We will also find that the specific forms adopted for the water-water and water-wall interactions profoundly affect the properties of confined water.

V. Nanoconfined water
In almost all of the preceding Section we focused attention on the structure of confined fluids composed of spherical particles with isotropic pair interactions and simple particle-wall interactions, using colloid fluids as the vehicle for the discussion. Such systems are at one end, the simple end, of the spectrum of possible complexity of confined fluids. We now examine some of the properties of confined water, which can arguably be considered at the other end of the spectrum of possible complexity of confined fluids. The behavior and properties of bulk water exhibit several peculiarities in the thermodynamically stable domain and in the supercooled domain that are not observed in most liquids, hence it is reasonable to expect that nanoconfined water will also exhibit properties not found in other nanoconfined liquids. These unusual properties are relevant to the several important roles played by nanoconfined water in biological, geophysical and industrial processes. In what follows we examine a selected set of experimental, computer simulation and theoretical studies of the structure, properties and phase behavior of nanoconfined water. Attention will be focused on two systems: water in carbon nanoslits and nanotubes and water in silica nanotubes.

The majority of all simulation studies of water, whether bulk or nanoconfined, are carried out using classical mechanics, and they start with a representation of the water-water interaction. Designing that interaction is complicated by the anisotropy of the intermolecular interactions, the anisotropy of the water molecule charge distribution, and the interplay between intermolecular and intramolecular degrees of freedom. In particular, the dipole moment of the free water molecule is different from the effective dipole moment of the water molecule in the liquid phase, in part because of the non-zero polarizability of water molecules, and the anisotropic electron density distribution implies that electrostatic interactions between water molecules will contribute to the hydrogen bonding that defines the local tetrahedral packing in the liquid. Also, the symmetric and antisymmetric OH stretching frequencies of the free water molecule are reduced by water-water hydrogen bonding, and the magnitude of the reduction depends on the deviation from linearity of the hydrogen bond. It has been inferred \([155,156]\) that the consequent change of zero-point energy of the OH stretching vibrations with deviation from linearity of the hydrogen bond is an important differential contribution to the energies of the many forms of ice. Attempts to capture these and other features of the interactions in a representation that can be used in simulation studies have led to a very large number of proposed water-water interactions. The majority of these model potentials assume the water molecule is rigid, and only a few account for intramolecular motion. A few of the model potentials incorporate more than two body interactions, e.g. three body interactions. And one model interaction, the mW interaction \([157]\), represents each water molecule as a single particle that interacts with other water molecules via a short-range anisotropic potential that mimics the hydrogen bond interaction. Almost all of the model potentials are parameterized by best fits to selected properties of bulk water, amongst which fitting the OO pair correlation function of bulk water is a favorite.

The most commonly used water-water interactions fall into a group, called TIPnP, with very similar characteristics \([158,159]\). All of these models assume that the triatomic water molecule is rigid, that there is a Lennard-Jones interaction between oxygen atoms of different molecules, and that there are electrostatic interactions between molecules arising from charges distributed on the rigid frame. The model water-water interactions differ, primarily, in the number, location and magnitudes of the distributed charges, designated by

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the integer n in the acronym TIPnP; the extant models have n = 3, 4 and 5. The model denoted TIP5P/E [160] exploits variation in the Lennard-Jones component of the interaction to better fit to experimental data. The water-water interactions labeled SPC [161] and SPC/E [162] also assume the molecular frame is rigid; they build the electrostatic component of the interaction from a distribution of three charges on each water molecule.

Given the empirical nature of the parameterization of the water-water interaction it is an extrapolation, albeit reasonable, to use the form developed for bulk water for nanoconfined water. This caveat should be kept in mind when examining the results of computer simulation studies, so as to distinguish robust predictions from those that are peculiar to a particular form of the assumed water-water interaction.

V.A. Nanoconfined water between smooth walls

We examine first the results of a set of studies that are representative of the numerous investigations of the influence of smooth, unstructured, confining walls on the properties of nanoconfined water, namely the studies reported by Brovchenko et al [14,82,163]. Amongst other matters addressed, Brovchenko’s studies show that nanoconfined water adjacent to hydrophilic or hydrophobic surfaces, respectively, behaves differently [45,164-166].

Brovchenko et al [163] report the results of molecular dynamics simulation studies, in the NPT ensemble, of TIP4P water in a cylindrical nanopore with radius 1.2 nm and periodic boundary conditions along the pore axis. The water-pore surface interaction was modeled with a Lennard-Jones (9-3) potential, obtained by integration over the pore surface; it depends only on the distance between the oxygen atom and the pore surface. The results of their simulations for the vapor-liquid coexistence curve are shown in Figures 5.1 and 5.2; they show a shift of the two-phase region to lower temperature with increasing depth of the water-wall interaction ($U$), and an accompanying dramatic change in the shape of the coexistence curve. Stronger water-wall interactions generate a splitting of the vapor-liquid coexistence curve into two regions (Figure 5.2(a), $U = -3.85$ kcal/mol, or three regions (Figure 5.2(b), $U = -4.62$ kcal/mol).
Figure 5.1. From Ref. 163. Vapor-liquid coexistence curves of bulk water (a), and water confined in cylindrical nano-pores (b). The results reported in (a) are in agreement with the experimental bulk water data. In (b) the circles represent data for a Lennard-Jones (9-3) water-wall interaction with well-depth $U = -0.39$ [kcal/mol] for and the squares data for a Lennard-Jones (9-3) well-depth $U = -3.08$ [kcal/mol]. The parameter $\sigma$ of the LJ potential was fixed at 0.25 nm. The lines represent best fits to the data using an scaling equation.
The data displayed in Figures 5.1 and 5.2 also reveal an appreciable decrease of the critical temperature of nanoconfined water relative to that of bulk water; the change in shape of the coexistence curve with increasing water-wall interaction is attributed to a crossover from three-dimensional to two-dimensional behavior in the surface layer.

In later publications Brovchenko et al. [14,82] reported the results of studies of the influence of hydrophobic and hydrophilic nanopore walls on the phase behavior of water. One interesting example of their results is shown in Figure 5.3.
Figure 5.3. From Ref. 82. The effect of hydrophilic and hydrophobic walls on the liquid-vapor transition of water in a 4 nm inner diameter nanopore, along with the arrangement of the water oxygens in the nanopore at 300K. The dashed lines represent the coexistence curve of bulk water. The two coexistence curves shown for the hydrophilic wall case were found to be due to layering transitions.

Giovambattista et al [167] have reported the results of systematic MD simulations of SPC/E water confined between two plates at \( T = 300 \) K. They investigated the effect of pressure in the range \(-150 \text{ MPa} \) to \( 200 \text{ MPa} \) and plate separation in the range 0.4 - 1.6 nm on the vapor-liquid phase behavior of water when the plates are either hydrophobic or hydrophilic. These investigators noticed that when water is confined between hydrophobic plates, capillary evaporation occurs at low pressure. The threshold plate separation at which this transition occurs decreases with increasing pressure (e.g., 1.6 nm at \( P = -50 \text{ MPa} \); 0.5 nm at \( P = 100 \text{ MPa} \)) until, at high pressure, no capillary evaporation occurs. For a plate separation of 0.6 nm and pressure of 100 MPa the system crystallizes into an ice bilayer. From these data Giovambattista et al constructed the pressure-plate separation phase diagram shown in Figure 5.4.
Figure 5.4. From Ref. 167. MD simulation results for phase behavior of nanoconfined water as a function of pressure and separation between nanoscale hydrophobic plates at $T = 300$ K. For $z = 0.6$ nm plate separation, a bilayer crystal is formed. The dashed line corresponds to the assumption that there is no ‘triple point’ between the liquid, the vapor, and the bilayer crystal.

MD simulations of water confined by hydrophilic plates [165,166] indicate that water remains in the liquid phase at all pressures and plate separations studied. A systematic study of the effect of pressure under conditions of confinement by both hydrophilic and hydrophobic plates showed that, for the range of conditions studied, when confined by hydrophobic plates the effect of pressure was to enhance water structure and to push water molecules toward the plates. The average orientation of water molecules next to the hydrophobic plates does not change as the pressure is increased. In contrast, when confined by hydrophilic plates, the water structure was found to be insensitive to pressure (Figure 5.5).
Figure 5.5. From Ref. 167. Nanoconfined water density profiles, $\rho_{\text{slab}}(z)$ as a function of distance from the nanoslit center at various pressures in a slab with plate separation $d = 1.6$ nm, width $0.0411$ nm and at $T = 300K$. Left: hydrophilic plates. Right: hydrophilic plates.

Koga et al [168] have reported the results of molecular dynamics simulations of TIP4P water confined to a nanoslit with smooth walls. Figure 5.6 shows the temperature dependence of the potential energy, excluding contributions from the water-wall interactions and after subtraction of $3RT$. As the system is cooled, the potential energy first gradually decreases at a slightly higher rate than in bulk water and then suddenly drops by about $5$ kJ/mol to a lower value. Upon heating, the potential energy jumps to a greater value at a temperature higher than the transition temperature in the cooling process. The discontinuities shown in the potential energy curves suggest a first-order phase transition. The hysteresis between heating and cooling curves is characteristic of phase transition in nanosystems. In the freezing transition the ice system contracts when the load is 50 and 150 MPa, whereas it expands when the load is 1 GPa (see Figure 5.7). Since bulk water expands when it freezes to ice this behavior is rather surprising.

Figure 5.6. From Ref. 168. Temperature dependence of the isobaric potential energy of confined water in a nanoslit pore with smooth walls for 3 different normal pressures of 50 MPa (diamonds), 150 MPa (circles), and 1 GPa (squares), excluding contributions from the water-wall interactions and subtraction of $3RT$. 
Figure 5.7. From Ref. 168. Temperature dependence of the distance between the walls (Z) of the nanoslit. The number of water molecules and the lateral dimensions are fixed, so the change of distance between the walls is proportional to the density change of the confined water. The symbols are the same as Figure 5.7. The inset is a magnification of the data for 1 GPa load.

The ice formed in these simulations has a bilayer crystal structure with a honeycomb lattice consisting of flat planes of distorted hexagons that do not resemble any found in the known ice crystals (Figure 5.8). Each water molecule in a layer is hydrogen bonded to three molecules in the same layer and to a fourth molecule in the adjacent layer. Because of extra constraints on the bonding, the residual entropy of this hydrogen bonded structure is $(R/4)\ln 2$, which is only 43% of the residual entropy of ice Ih. Koga has also reported [159] the formation of bilayer amorphous solid water (Figure 5.9) via a first order

Figure 5.8. From Ref. 159. Structure of bilayer ice between hydrophobic walls (From Koga)
transition from the liquid. It closely resembles but differs from the bilayer ice by having a broad distribution of OOO angles and rings of molecules other than hexagons (77% hexagons, 11% pentagons and heptagons and 1% other). The structures of bilayer ice and bilayer amorphous solid water appear have the same one-to-one relationship as do the structures of three-dimensional ice Ih and amorphous solid water. However, it has been determined that the melting points of the bilayer hexagonal ice and the bilayer amorphous solid water have the same melting point [74], hence it is possible that the bilayer amorphous solid water is merely a very defective form of the bilayer hexagonal ice that has not yet annealed to the lowest free energy lattice configuration.

Figure 5.9. From Ref. 159. Structure of bilayer amorphous solid water between hydrophobic walls (From Koga)

A very extensive study of a bilayer of water confined between smooth walls has been carried out by Johnston, Kastelowitz and Molinero [169]. In these NPT ensemble simulations the wall separation was fixed at 0.85 nm, the wall-water interaction was taken to have the Lennard-Jones form, and the water-water interaction was taken to have either the mW form or the TIP4P/ice form. The mW interaction represents each water molecule as a single particle that interacts with other water molecules via a short-range anisotropic potential that mimics the hydrogen bond interaction [157]. Although only a one-particle representation, simulations with the mW interaction reproduce the structure and phase equilibria of bulk water rather well. The results of the simulation reveal a rich phase diagram that includes the hexagonal bilayer ice (H) discussed above, a dodecagonal quasicrystal phase (W) and two other crystalline phases (C and T); see Figure 5.10. A comparison of the results of the simulations using the mW and TIP4P/ice water-water interactions reveals the same structures and relative stabilities of the phases (Table 5.1).
Figure 5.10. From Ref. 169. Top view of the phases of a confined bilayer of TIP4P/ice water and their associated diffraction patterns.

Table 5.1. From Ref. 169. Volume, enthalpy and entropy changes at the several phase transitions of confined bilayer mW water and TIP4P/ice water. The several phases are labeled as follows: L = liquid (column 5 of Figure 5.10), H = hexagonal crystal (column 1 of Figure 5.10), C = 4-fold (Coffin) crystal (column 2 of Figure 5.10), T = 4-fold (TicTac) crystal (column 3 of Figure 5.10), and W = quasicrystal (column 4 of Figure 5.10).

<table>
<thead>
<tr>
<th>Water model</th>
<th>$p_c$ (GPa)</th>
<th>$T_s$ (K)</th>
<th>Phase transition</th>
<th>$\Delta V$ (cm$^3$ mol$^{-1}$)</th>
<th>$\Delta H$ (kJ mol$^{-1}$)</th>
<th>$\Delta S$ (J K$^{-1}$ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>mW</td>
<td>0, 297.5</td>
<td></td>
<td>H $\rightarrow$ L</td>
<td>$-0.331$</td>
<td>3.38</td>
<td>11.4</td>
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<tr>
<td>mW</td>
<td>0.46, 237.5</td>
<td></td>
<td>H $\rightarrow$ L</td>
<td>$-1.39$</td>
<td>1.73</td>
<td>7.1</td>
</tr>
<tr>
<td>mW</td>
<td>0.41, 242.5</td>
<td></td>
<td>T $\rightarrow$ L</td>
<td>0.555</td>
<td>1.48</td>
<td>6.1</td>
</tr>
<tr>
<td>mW</td>
<td>0.51, 250</td>
<td></td>
<td>T $\rightarrow$ L</td>
<td>0.455</td>
<td>1.66</td>
<td>6.6</td>
</tr>
<tr>
<td>mW</td>
<td>0.41, 240</td>
<td></td>
<td>C $\rightarrow$ L</td>
<td>0.151</td>
<td>1.25</td>
<td>5.2</td>
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<tr>
<td>mW</td>
<td>0.51, 242.5</td>
<td></td>
<td>C $\rightarrow$ L</td>
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<td>1.43</td>
<td>4.7</td>
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<tr>
<td>mW</td>
<td>0.41, 235</td>
<td></td>
<td>W $\rightarrow$ L</td>
<td>$-0.063$</td>
<td>0.79</td>
<td>3.4</td>
</tr>
<tr>
<td>mW</td>
<td>0.51, 230</td>
<td></td>
<td>W $\rightarrow$ L</td>
<td>$-0.120$</td>
<td>0.49</td>
<td>2.1</td>
</tr>
<tr>
<td>TIP4P/ice</td>
<td>0.0, 317.5</td>
<td></td>
<td>H $\rightarrow$ L</td>
<td>$-1.303$</td>
<td>4.02</td>
<td>12.7</td>
</tr>
<tr>
<td>TIP4P/ice</td>
<td>0.2, 267.5</td>
<td></td>
<td>H $\rightarrow$ L</td>
<td>$-3.265$</td>
<td>2.22</td>
<td>8.3</td>
</tr>
<tr>
<td>TIP4P/ice</td>
<td>0.51, 300$^a$</td>
<td></td>
<td>$\theta_T$ $\rightarrow$ L$^b$</td>
<td>$-0$</td>
<td>2.1</td>
<td>7.0</td>
</tr>
<tr>
<td>TIP4P/ice</td>
<td>0.51, 282.5$^a$</td>
<td></td>
<td>C $\rightarrow$ L</td>
<td>0.5</td>
<td>3.0</td>
<td>10.8</td>
</tr>
<tr>
<td>TIP4P/ice</td>
<td>0.3, 265$^a$</td>
<td></td>
<td>C $\rightarrow$ L</td>
<td>1.2</td>
<td>2.7</td>
<td>10.1</td>
</tr>
<tr>
<td>TIP4P/ice</td>
<td>0.3, 270$^a$</td>
<td></td>
<td>W $\rightarrow$ L</td>
<td>$-0$</td>
<td>1.7</td>
<td>6.2</td>
</tr>
<tr>
<td>TIP4P/ice</td>
<td>0.5, 270$^a$</td>
<td></td>
<td>W $\rightarrow$ L</td>
<td>$-0.2$</td>
<td>1.6</td>
<td>5.3</td>
</tr>
</tbody>
</table>

$^a$One phase decomposition temperature.

$^b$T indicates defective T crystal.

The unique quasicrystal phase and the pentagonal ice polymorph phases are stabilized by compression of the water bilayer. These phases are intrinsic to the confined bilayer water system, since the smooth bounding walls can impose no symmetry on the assembly of water molecules. Phases H and T are stable, whilst phases C and W are metastable. The phase diagram of TIP4P/ice bilayer water is shown in Figure 5.11.
Johnston, Kastelowitz and Molinero [169] discuss some analogies between the phase diagram of bilayer water and that of bulk water. They note that in both cases an increase of pressure does not increase the number of neighbors of a water molecule; all of the water bilayer phases are 4-coordinated and satisfy the ice rules. They further note that the structure of bilayer ice H resembles a 2D projection of the structure of bulk ice Ih, and the structure of metastable bilayer ice C resembles a 2D projection of metastable bulk ice XII.

![Figure 5.11](image)

**Figure 5.11.** From Ref. 169. Phase diagram of TIP4P/ice bilayer water. Filled circles define the equilibrium melting lines for the transitions L ⇔ H (black) and L ⇔ C (red). Empty circles indicate one-phase transformation temperatures for L ⇔ T (blue) and L ⇔ W (green). The filled diamond denotes the melting temperature of bulk ice Ih at 0.1 MPa.

**V.B. Nanoconfined water between structured walls**

We expect that the properties of nanoconfined water will be influenced by the atomic structure of the containing walls. The majority of this Section will discuss water contained in a slit between graphene walls, as a complement to the discussion in the next Section of water confined in carbon nanotubes, but it is pertinent to also examine the influence of other ordered walls on the properties of confined water.

We start with an examination of the work of Wu *et al* [45], who have reported the results of a set of molecular dynamics simulations designed to investigate the behavior of water molecules confined between two crystalline Au plates. Three different choices were made for the surfaces of the Au plates that enclose the water, namely the crystal planes with Miller indices (100), (110) and (111). The gap between the plates was taken to be 1.02 nm, the water density to be 0.973 g/cm³ and the temperature to be 300 K. Wu *et al.* included in the model the interactions between the Au atoms, interactions between the water molecules, O–H bonding and H–O–H bending intra-molecular interactions within individual water molecules, and interactions between the Au atoms and the water molecules. Their simulation results indicate that three layers of water molecules are
formed in the nanoslit and the arrangements of the water molecules are dependent on the particular Au plate surface structures (Figure 5.12). They conclude that adsorption of water on the Au plates creates flat layers of water on the (100) surface and the (111) surface, and wave-like water layers on the Au (110) surface. The water layer adsorbed on the (110) surface has the shortest water-Au separation. In the central area of the gap between the two (100) surfaces, or between the two (111) surfaces, most of the water molecules lie flat, but they are randomly oriented in the central area of the gap between the (110) surfaces. The average number of hydrogen bonds per water molecule, as a function of increasing distance from the Au plates, is very different for the different crystal planes (Figure 5.12).

![Figure 5.12](image)

**Figure 5.12.** From Ref. 45. Left: Distributions of oxygen densities for water molecules confined in a nanoscale gap of 1.02 nm with different lattice structures of Au plates. Right: Average hydrogen bond number per water molecule, nHB, for water molecules confined in a nanoscale gap of 1.02 nm with different lattice structures of Au plates.

A detailed study of water confined between grapheen surfaces has been reported by Mosaddeghi, Alavi, Koswari and Najafi [170]. These investigators used the SPC/E water-water interaction, a Lennard-Jones interaction between the oxygens of a water molecule and the carbon atoms in the graphene walls. Each wall had two graphene sheets separated by 0.335 nm, as in graphite; NVT simulations were carried out with wall-to-wall separations of 0.7, 1.0, 1.5 and 2.0 nm. The first result obtained from these simulations that we examine is the density distribution perpendicular to the walls, shown in Figure 5.13. These data show that in the layer of water adjacent to the wall the Hydrogen atom is closer to the wall than is the oxygen atom, whereas
Figure 5.13. From Ref. 170. Density distributions of SPC/E water molecules in nanoslits between graphene sheets. The solid lines show the hydrogen distribution and the dashed lines the oxygen distribution. The asterisks show the locations of hydrogen atoms in inner layers.

In the central layers the Hydrogen atoms point away from the wall. The structure of the water layer adjacent to a graphene wall in a system with 0.7 nm between walls is shown in Figure 5.14. This layer is ordered, but the layers of water adjacent to the graphene walls in

Figure 5.14. From Ref. 170. (a) A view perpendicular to the plane of the graphene wall of the adjacent water layer for the system with 0.7 nm wall separation; this view shows both the Carbon atoms of the graphene wall and the water molecules. (b) The same view as (a) without the Carbon atoms of the graphene wall. (c) A view from above and laterally of 12 selected water molecules.
slits with wall separations of 1 nm and 1.5 nm have liquid-like disorder, as shown by their pair correlation functions. Of course, the structure of the confined water is dependent on the density of packing, as shown in Figure 5.15.

![Figure 5.15](image)

**Figure 5.15.** From Ref. 170. Density distributions of H and O of SPC/E water molecules in a 0.7 nm slit between graphene walls as a function of the molecular number density.

### V.C. Water confined in carbon nanotubes

A vast effort has gone into studies of water confined in carbon nanotubes. A schematic representation of an \((m,m)\) single wall carbon nanotube (SWCNT) and of the related graphene sheet is shown in Figure 5.16. A graphene sheet, which is one layer of a graphite crystal, can be commensurately wrapped in many different ways to form SWCNTs. The structures of these different SWCNTs are indexed by integers \((n,m)\) that denote the number of unit vectors \(\langle a_1, a_2\rangle\) along two directions in the honeycomb lattice of graphene. Distinguishing between the SWCNT structures is important because many of the properties of SWCNTs change significantly with changes in \(n\) and \(m\). So-called zigzag nanotubes are characterized by \(m = 0\), and so-called armchair nanotubes by \(n = m\). Other combinations of \(m\) and \(n\) generate chiral structures. We note that a typical SWCNT can have an enormous ratio of length to diameter and that the diameter of an ideal nanotube is related to the indices \(n\) and \(m\) by \(d = (a/\pi)(n^2 + nm + m^2)^{1/2}\) with \(a = 0.246\) nm. Multi-walled nanotubes (MWCNT) can be constructed either from sheets of graphene arranged in concentric...
cylinders or from a single sheet of graphene rolled around itself. The interlayer distance in multi-walled nanotubes is close to the distance between graphene layers in graphite.

A SWCNT is not a uniform hydrophobic cylinder. As shown by studies of water between graphene walls, and of water between Au crystal planes, the hexagonal arrangement of the carbon atoms in the wall, and the associated π-electron density distribution, can be expected to affect the structure and properties of the enclosed water in a fashion that is different from that expected when the wall is smooth. Nevertheless, comparisons of simulation studies have shown that the structures of the ices formed in SWCNTs are in large part independent of the choice of smooth wall or structured wall, but do depend on the choice of water-water interaction. To illustrate the first point, Figure 5.17 shows a comparison of the phase diagrams in the temperature SWCNT diameter-plane proposed by (a) Takaiwa, Hatano, Koga and Tanaka [171], computed using TIP4P water confined to smooth-wall SWCNTs, and (b) proposed by Kyakuno et al using TIP3P water and explicit water-carbon atom interactions. Phase diagram (b) also incorporates data obtained from x-ray diffraction measurements. The similarity between these phase diagrams is immediately apparent. Indeed, many of the data points in Figure 5.17a are taken from Figure 5.17b. To illustrate the second point, Figure 5.18 shows the density of water inside SWCNTs of different diameters as calculated with four water-water interactions, and Figure 5.19 shows the ice structures in (8, 8) and (9, 9) SWCNTs as calculated with four water-water interactions. All of the water-water interaction models studied to date lead to similar trends in behavior of averaged physical quantities, e.g. the overall density as a function of SWCNT diameter (Figure 5.19a), with the major differences occurring for small diameter SWCNTs. However, the structures of the ordered water molecules predicted using different water-water interactions show significant differences (Figure 5.19b). Thus, of the water-water interactions studied by Nakamura and Ohno [173], the TIP3P interaction leads to a less ordered structure than do the SPC/E, TIP4P and TIP5P/E interactions, the SPC/E and TIP4P interactions favor the formation of stacked

**Figure 5.16.** From Ref. 159. Schematic representation of an \((m,m)\) single wall carbon nanotube and a graphene sheet.
water layers inside the SWCNT, and only the TIP5P/E interaction generates a ferroelectric form of confined ice.

**Figure 5.17.** (a) Top. From Ref. 171. Phase diagram of TIP4P water in smooth-walled SWCNTs in the temperature-diameter plane at atmospheric pressure. Filled circles identify the freezing points in the absence of hysteresis, and open circles identify the highest temperature at which an ice does not melt when hysteresis occurs. Triangles indicate continuous freezing and melting at the inflection point of the temperature dependence of the enthalpy, squares denote the temperature above which an ice phase becomes unstable and the dashed vertical lines are estimates of the ice-ice phase boundaries. (b) Bottom. From Ref. 172. Phase diagram of TIP3P water in structured wall SWCNTs. Open squares and filled triangles denote data obtained from the simulations, while filled squares and circles denote data obtained from x-ray diffraction measurements. The dotted line is an extrapolation of bulk melting point data. The right hand side of this figure shows the hollow and filled ice structures obtained from simulations with SWCNT diameters shown as a and b.
Figure 5.18. From Ref. 173. Density of water inside (8, 8) SWCNTs at 280 K.

![Diagram showing density of water inside (8, 8) SWCNTs at 280 K.]

Figure 5.19 From Ref. 173. (a) Local water density perpendicular to the axis of a 2.1 nm long (9, 9) SWCNT as calculated from different water-water interactions, at 280 K. (b) Local water density perpendicular to the axis of a 2.1 nm long (8, 8) SWCNT as calculated from different water-water interactions, at 280 K.

![Diagram showing local water density calculations for different SWCNTs.]

Other systems of particular interest are water inside a (6, 6) SWCNT and inside large SWCNTs. All of the simulations published to date, no matter what model water-water interaction is used, predict that the water molecules inside a (6, 6) SWCNT are in a single file with dipole moments oriented along the SWCNT axis; see Figure 4.20 [174,175]. At the other end of the spectrum, Bai, Wang and Zeng [176] have found six distinct ice phases of
TIP5P water at high pressure in larger SWCNTs. In the (17, 0), (20, 0) and (22, 0) SWCNTs the water molecules form double walled helices. In the (17, 0) SWCNT the outer wall consists of four double stranded helices and the inner wall is a four-stranded helix. The ices in the (20, 0) and (22, 0) SWCNTs have a tubular structure and the ice in the (24, 0) SWCNT has a triple helix structure with an outer wall that is an 18-stranded helix and inner walls are 6-stranded helices (Figure 4.22).

Figure 5.20. From Ref. 174. The structure of TIP3P water inside a (6, 6) SWCNT.

Figure 5.21. From Ref. 176. Snapshots of the triple-walled ice formed in the (24, 0) SWCNT at 800 MPa. (a) Top view. (b) Projected top view. (c) Top view of the outer and middle walls. (d) Top view of the middle and inner walls.
V.D. Does water confined in a SWCNT exhibit a solid-liquid critical point?

Keeping in mind the sensitivity to the water-water interaction of the ice structures of water confined in SWCNTs, amongst the most interesting conjectures to arise from simulation studies is the suggestion that, under some conditions of confinement, there is a solid-liquid critical point. In a bulk system a critical point cannot terminate the coexistence line between phases with different symmetries, but studies reported by Koga et al. [174], of the results of MD simulations of the behavior of water confined in carbon nanotubes at constant temperature and normal (axial) pressure ($P_{zz}$), suggest one exists in those systems. Specifically, Koga et al. simulated water in (m, m) SWCNTs with various diameters (1.11, 1.19, 1.26, 1.34 and 1.42 nm) using the TIP4P water-water interaction and for the water-wall interaction a Lennard–Jones potential integrated over the cylindrical area of the SWCNT using the area density of the carbon atoms and the potential parameters for graphite. The properties of the confined water were examined, for each value of the diameter, along an isobaric path or an isothermal path in the

![Image](Figure 5.22. From Ref. 177. The temperature dependence of the isobaric potential energy of water confined in SWCNTS with diameters 1.11, 1.19, 1.26 and 1.34 nm. The potential energy is due to the water–water interactions; the water–SWCNT interaction energy is excluded. The applied axial pressure is 50 MPa (circles), 200 MPa (squares), and 500 MPa (triangles). Filled and unfilled symbols indicate the cooling and heating processes, respectively.)
$P_{zz} - T$ plane. The results of these calculations are shown in Figure 5.22. The well-defined hysteresis loops in the data imply that a first-order phase transition occurs. The low-$T$ phase is found to be a quasi-one-dimensional ice-nanotube composed of orderly stacked $n$-membered water rings, where $n = 6$ (hexagonal) in the 1.26 nm diameter SWCNT and $n = 7$ (heptagonal) in the 1.35 nm SWCNT. These simulation results are consistent with the experimental x-ray diffraction data of Manawa et al [178], whose measurements were carried out at ambient pressure for SWCNTs with an average diameter of 1.35 nm. The results obtained by Koga et al [177] also suggest the existence of crystalline ice phases not observed in bulk ice. For SWCNTs with diameters from 1.1 to 1.4 nm and applied axial pressures from 50 to 500 MPa, they find that water undergoes first-order freezing transitions to hexagonal and heptagonal ice-nanotubes that are hollow, and a continuous phase transformation into solid-like square or pentagonal ice-nanotubes that are hollow (Figure 4.23).

**Figure 5.23.** From Ref. 177. Snapshots of quenched molecular coordinates. (a) Square; (b) pentagonal; (c) hexagonal ice-nanotubes in 11.1 nm, 11.9 nm, and 12.6 nm inner diameter SWCNTs, respectively. Figures (d), (e) and (f) are the corresponding liquid phases. The ice-nanotubes were formed on cooling under an axial pressure of 50 MPa in MD simulations. The nearest-neighbor distances in both ice-nanotubes and encapsulated liquid water are about 0.27 to 0.28 nm in all of these structures, and this is in part responsible for the novel phase behavior.

An examination of the water potential energy as a function of axial pressure obtained from the results of the simulations for the SWCNT with diameter 1.11 nm (Figure 5.24), and the conversion of those data into an axial pressure-volume diagram (Figure 5.25), led Koga et al. to suggest the existence of a solid–liquid critical point.
Figure 5.24. From Ref. 177. Axial pressure dependence of the water potential energy in a SWCNT with diameter 1.11 nm. Filled and open circles indicate compression and expansion, respectively.

Figure 5.25. From Ref. 177. $P_{zz}-V$ phase diagram derived from the results of the MD simulations and free-energy calculations by Koga et al [177]. The temperatures along these isotherms are the same as shown in Figure 4.33.

The argument made by Koga et al for the existence of a critical point is based on the observation that isothermal compression of nanoconfined water stepwise from 50 to 900 MPa shows a marked sudden decline in potential energy and volume at 170 MPa on decompression; that is, a hysteresis loop appears. Their structural analysis showed that the low-density phase had a liquid-like disordered structure, whereas the high-density phase was a solid-like pentagonal nanotube phase. The sudden changes in potential energy and volume imply there is a first-order phase transition between the two distinct phases. On
the 300 K isotherm, however, the transformation seems to be continuous as no abrupt jumps in potential energy and volume are found. On the 330 K isotherm, the changes in potential energy and volume become much less abrupt, and finally on the 360 K isotherm the changes are essentially smooth. These data, when used with free energy calculations to generate the isotherms in the axial pressure-volume plane, lead to the display in Figure 4.25, which appears to be the same type as for bulk liquid-vapor equilibrium. Still, the conclusion that a critical point exists violates the constraint that the coexistence line between phases with different symmetries cannot end in a critical point. However, if increase in the axial pressure generates an amorphous phase of the confined water, whose symmetry is the same as the liquid, the conflict is removed. The spacing of the axial pressure isobars and of the isotherms in the simulation studies is such as to permit an unobserved transition to an amorphous state to precede the putative critical point. Whether or not that is the case remains to be learned.

V.E. Water confined by hydrophilic walls

In the preceding Section we displayed evidence, from both experimental and theoretical studies, that the hexagonal arrangement of the carbon atoms in the wall of a SWCNT, and the associated π-electron density distribution, affect the structure and properties of the enclosed water. Broadly speaking, the SWCNT presents a structured hydrophobic surface to the enclosed water. Water can also be confined in materials that present a hydrophilic surface. These surfaces typically offer opportunities for hydrogen bonding and/or electrostatic interaction with the enclosed water; they may be ordered or disordered. The hydrogen bonding interactions between and water and active groups attached to a hydrophilic surface exhibit a considerable range of strength; they can be weaker or stronger than in the liquid, noting that variation of the spacing between any interaction sites on the hydrophilic walls also influences the binding and the distribution and organization of water molecules in several layers adjacent to the wall. In general, we must expect the structure of the liquid near the wall to vary with layer distance from the wall because of alteration of the hydrogen bonding and molecular orientation constraints as the distance from the wall increases. An example of this behavior is provided by condensation of water from the gas phase on silica. The hydrogen bonding between hydroxyl groups of the silica walls and the water molecules in the immediately adjacent layer control the distortion of the hydrogen bond network. The structure of the second layer of water is also affected. Both cubic and amorphous ices can form at strongly binding silica surfaces at low temperatures [179].

The properties of water confined in a hydrophilic nanopore with crystalline walls, AlPO₄-54, have been studied by Alabarse et al [180]. Using data obtained from x-ray diffraction and vibrational (Raman) spectroscopy they infer that in a 1.2 nm pore the surface induces orientational order in the contact layer of water, but not freezing; the water does not crystallize even when the temperature is reduced to 173 K. Crystallization in the contact layer is suppressed because of the inability of the water in that layer to form a sufficient number of hydrogen bonds and, simultaneously, crystallization of the interior water is suppressed by the distortion of ice tetrahedral hydrogen-bonding network that is
forced by the curvature imposed by the nanopore walls. The cylindrical core is asserted to be glass or amorphous solid water. The results of their x-ray diffraction studies, and complementary simulation studies, are displayed in Figure 5.26.

The nanoporous silica matrix, MCM-41-S is another hydrophilic host for water, but in this case the nanopore walls are not crystalline. Zhang et al [181] used neutron scattering to measure the density of heavy water confined in MCM-41-S in the temperature range from 300 to 130 K and the pressure range from $10^2 - 2.9 \times 10^5$ kPa. The motivation for their study was the search for a first-order liquid–liquid phase transition in water that would exist in the bulk system if crystallization could be avoided. They observed a prominent hysteresis loop in the warming and cooling scans at and above $10^5$ kPa (see Figure 5.27), which they interpret as support for, although not a proof of, such a transition. A very recent, detailed, study by Limmer and Chandler [182,183] of supercooled water in a hydrophilic nanopore, reaches a different conclusion.

Before describing the Limmer-Chandler results it is worthwhile commenting on the suggestion that at low temperature supercooled bulk water is a mixture of structurally distinct low-density (LDL) and high-density (HDL) liquids separated by a first order transition. This proposal, first advanced by Poole, Sciortino, Essmann and Stanley [184], was introduced to account for the so-called anomalous properties of bulk water. These anomalous properties include, amongst others, a density maximum at 4°C, an increase of compressibility between 0.1 MPa and 190 MPa and, at atmospheric pressure, an increase in constant pressure heat capacity with decreasing temperature. The two coexisting liquid phases are postulated to be stable in the temperature domain below the temperature at which homogeneous nucleation of ice occurs. There is, at present, no microscopic description of the postulated low and high density liquid structures, although these species are, respectively, commonly assumed to be the thermodynamic continuations of low-density amorphous ice (LDA) and high-density amorphous ice (HDA) into the liquid state. To date, there is no direct evidence for a first-order liquid–liquid phase transition between LDL and HDL, as a thermodynamic extension of the established first-order transition between the amorphous solid waters [181], arguably because the hypothesized first-order liquid–liquid phase transition is located in a region of the phase diagram where bulk water is unstable. Nevertheless, two recent detailed analyses conclude that inclusion of the proposed liquid-liquid transition and critical point provides a more accurate account of the thermodynamic and transport properties of bulk water than any other representation available [185-187]. The Zhang et al experiment attempts to take advantage of confinement of water in a nanopore to suppress homogeneous nucleation. It is important to note that utilizing this approach requires the strong assumption that the properties of the nanoconfined water are the same as those of bulk water. This assumption appears dubious in view of the data available.
Figure 5.26. From Ref. 180. Experimental (top) and simulated (bottom) structures of water in AlPO₄-54 at several temperatures: 293 K (left), 235 K (center), and 173 K (right). Blue = O atoms of water molecules, grey = AlO₄ and AlO₆ units, red = PO₄ units. The inserts show the radial density and the dashed line the bulk density, of the confined water.

Figure 5.27. From Ref. 181. The density of confined D₂O in a hydrophilic substrate MCM-41-S along warming and cooling scans. The data are shifted by 0.05 g/cm³ between adjacent pressures for clarity. A hysteresis phenomenon becomes quite prominent at and above 10⁵ kPa. Error bars, due to counting statistics are smaller than the thickness of the curves. The two horizontal arrows indicate the locations of the sudden change of slope in the density profiles at 10² kPa and 10⁵ kPa.
Limmer and Chandler [190,191] have reported a detailed analysis of the phase diagram of water in a hydrophilic nanopore, based on both experimental data and simulations. The experimental data are drawn from a variety of studies of water in the porous silica MCM-41. The simulations use a model of the nanopore that treats the distribution of atoms in the silica walls as in a liquid, but frozen in position; the pore radius $R$ range explored was from 0.5 nm to 1.75 nm. The water is modeled using the mW interaction. The disorder in the atomic positions in the pore wall destabilizes ordered water structures, leading to an amorphous water monolayer with thickness $\lambda \approx 0.25$ nm in contact with the wall. This contact layer remains disordered under all conditions studied in the simulations. The interior water can be, depending on the temperature, pressure and pore diameter, either ordered or disordered. The role of pore diameter is of particular importance, in that for small diameter the influence of the amorphous contact water layer destabilizes all ordered arrangements of the interior water for all temperatures and pressures studied in the simulations. Even when the pore diameter is large enough to support ordered structures of the interior water that water may remain an amorphous solid (glass) on the time scale of

![Figure 5.28](image)

**Figure 5.28.** From Ref. 190. Phase diagram of mW water in MCM-41. (a) Melting ($T_m$) and glass transition ($T_g$) temperatures as a function of pore radius and pressure. (b) Phase diagram in the constant pressure plane $P = 1$ atm. $\square = T_m(\text{exp})$; $\bigcirc = T_m(\text{sim'}n)$; $\blacksquare = T_g(\text{exp})$. (c) Phase diagrams for pore radii $R = 0.5$ nm and 0.95 nm. $\bigcirc = \text{onset of hysteresis in experimental measurements using pores with } R \approx 0.5 \text{ nm}$. $\square = \text{calorimetric glass transition temperature for a pore with } R \approx 0.5 \text{ nm}$. 

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the simulations. A phase diagram delineating the liquid, crystal and glass domains found by Limmer and Chandler is displayed in Figure 5.28.

Lemmer and Chandler provide an incisive analysis of the interplay between the three length scales defined by the pore radius, the length at which bulk energetics favoring order is equal to the interfacial energetics favoring disorder,

\[ l_m = \frac{2\gamma}{\Delta h}, \]

and the length at which fluctuations that destabilize order become important,

\[ l_s = \frac{l_m}{1 - \left(\frac{T_S}{T_m}\right)}. \]

In Eq. (5.1), \( \gamma \) is the interfacial tension between liquid and ordered solid and \( \Delta h \) is the heat of fusion per unit volume. In Eq. (5.2), \( T_S \) is the temperature below which bulk amorphous solid water is unstable and \( T_m \) is the ordered solid melting temperature. For nanoconfined water \( T_S \) and \( T_m \) depend on the pore radius and the pressure. For water, \( l_m \approx 0.21 \text{ nm}, l_s \approx 0.91 \text{ nm}, \) and \( T_S = 210 \text{ K}. \) Limmer and Chandler show that

\[ T_m(p, R) \approx T_m(p) \left( 1 - \frac{l_m}{R} - \frac{l_m^2}{8\pi(R-l_s)R} \right) \]

for \( R > R_c \), where \( R_c \) is the positive square root of the right hand side of (5.3). For \( R < R_c \), \( T_m(p, R) = 0 \). Figure 5.28b displays Eq. (5.3) and the available experimental data. The experimental data fit well to the theoretical prediction for large pore radius, where \( l_m / R << 1 \). The fluctuation contribution drives the precipitous drop in \( T_m \) as \( R \) decreases, leading to termination of the melting line near \( R \approx 1 \text{ nm} \). Figure 5.28 also displays the pressure and pore radius dependences of the glass transition temperature, \( T_g \) along with the few experimental determinations of that temperature that are available. Limmer and Chandler note that the pressure dependence of \( T_g(p, R) \) is small and negative for large \( R \) and positive when \( R \) is small. That observation leads them to reinterpret the data of Zhang; they attribute the observed hysteresis in the experimental data as evidence for a transition from liquid water to amorphous solid water, and not as evidence for an unobserved liquid-liquid critical point at lower temperature.

VI. Epilogue

In the preceding text we have examined a subset of the equilibrium properties of strongly confined fluids, focusing attention on two limiting cases. These limiting cases are (i) a simple fluid bounded by unstructured walls that weakly interact with the enclosed molecules whilst geometrically constraining the configurations available to them, and (ii) water, a complex strongly structured fluid, bounded by structured or unstructured walls that strongly interact with the molecules in the liquid and also geometrically constrain the configurations available to them. The two important general inferences that can be drawn from studies of these limiting cases are, first, that when the smallest dimension of the confining enclosure is only a few molecular diameters the fluid has an inhomogeneous density distribution and, second, that the properties of the enclosed fluid and of the enclosed ordered solid phases can be very different from those of the bulk fluid.
and solid phases. Indeed, in a real sense it is more appropriate to consider a confined fluid and its enclosure walls together to be a system that is distinctly different from the corresponding bulk fluid.

In case (i), confined colloid suspensions served as the vehicle for the discussion. As noted in Section IV, by virtue of the McMillan-Mayer theory the equilibrium properties of a confined colloid suspension of particles undergoing Brownian motion are isomorphous with those of a confined molecular system in which the potential of mean force between colloid particles in the suspension replaces the direct interaction between molecules in the simple fluid. The confined colloid suspensions we have discussed contain spherical particles, are bounded by unstructured walls, and have weak and nonspecific wall-colloid particle interaction. These surrogate systems permit evaluation of the generic effects of confinement and excluded volume on the structure of a simple fluid, and of the effect of confinement, excluded volume and variation of the colloid-colloid interaction on the freezing transition of a simple fluid. Some experimental and theoretical studies have examined the influence of wall decoration, such as patterning with hydrophobic and/or hydrophilic stripes, on the properties of a confined colloid suspension. When the detail of that patterning has the same scale length as the particle diameter the surrogate system mimics the influence of atomic ordering of the walls on the properties of a nanoconfined molecular fluid. In the absence of such patterning the surrogate colloid suspensions cannot capture the effects of specific wall-molecule interactions. And, insofar as only suspensions of spherical colloids with isotropic pair interaction are considered, the influence of the walls on the properties of a structured fluid, such as water, cannot be captured.

From the results obtained from experimental and theoretical studies of confined colloid suspensions we can draw the following general conclusions:

1. The density profile of a liquid in a cylinder or in a one molecule thick flat ribbon that has confining walls only a few molecular diameters apart is stratified. For a given separation of the confining walls the density amplitude is greatest adjacent to the wall and decays to the bulk density on the scale of a few molecular diameters. The density distribution perpendicular to the wall of a q2D slit displays the same qualitative behaviour.

2. At sufficiently high density the fluid in a confined domain freezes into an ordered solid, the structure of which depends on the interplay between the particle-particle excluded volume and the particle-wall interaction. A confined system can support a phase that does not exist in 3D, e.g. the hexatic phase in 2D. The packing structures of the confined ordered phases can change dramatically as the small dimension of the confining environment changes, e.g. from hexagonal to square packing in a q2D slit as the slit width changes from 1 to 1.6 particle diameters.

3. The character of the melting transition in q2D confinement depends on the particle-particle interaction, unlike the universal first order character of the melting transition in 3D, which is independent of the particle-particle interaction. When the particle-particle interaction is long-ranged, such as dipole-dipole repulsion, the q2D melting process is well described by the KTHNY theory. In particular, the transitions between the solid and the hexatic phase and the hexatic and the liquid phase are continuous. When the particle-particle interaction is short-ranged, such as hard-core repulsion, the character of the
melting process is not yet resolved. Overall, for the case of 2D melting, the current evidence supports the existence of a hexatic phase intermediate between the liquid and ordered solid phases, but whether the liquid-to-hexatic phase transition is continuous or weakly first order is not fully resolved.

We have, at present, limited theoretical understanding of phase equilibrium in 2D and q2D systems. Simulations reproduce many of the experimental findings, and theoretical approaches that are variants of mean field theory provide clues with which to interpret the observations, but there is not yet a convincing physical picture that systematically captures and interprets all the observations. To improve our understanding of 2D and q2D phase transitions, we need to replace the instability representation of the phase transitions with an analysis that explicitly incorporates, without being externally imposed, the thermodynamic condition of equality of chemical potentials at the phase transitions, and which has an explicit dependence on the particle-particle interaction. This analysis must also incorporate the boundary conditions that define the system confinement in the representation of the various particle correlation functions.

Confined colloid suspensions can be used to examine multi-particle correlations that cannot yet be measured in molecular systems, such as the triplet correlation function and its dependence on density, particle interaction and liquid composition. The two reported studies of the triplet correlation function in a q2D liquid [58-59] show that our ideas concerning order in q2D liquids will likely require modification. Extensions of those studies to higher order correlation functions, and to changes associated with q2D \( \rightarrow \) 3D should be carried out.

We have discussed only the properties of one-component suspensions of spherical colloid particles confined to spaces with very simple geometries. When the colloid particles have more complex shapes, when mixtures are examined, and when the geometry of the confining domain has curvature with scale length comparable to a particle diameter, the range of system properties is greatly expanded. And, because of the subtle interplay between boundary conditions, the particle-particle interaction and the structures of ordered solids that a system supports, there is opportunity to control the structure of the system and to create completely new structures, such as designed self-assembling structures stabilized by designed particle-particle interaction [60-64].

Our discussion of case (ii) dealt only with nanoconfined water. From the experimental data and a variety of computer simulations we can draw the following general conclusions:

1. The properties of nanoconfined water are very strongly dependent on both the nanotube diameter and the structure of the confining wall. It is not possible to consider the confined water as a system independent of the character of the confining walls.

2. In the (6,6) SWCNT, which can hold only one line of water molecules, all of the simulations published to date, no matter what model water-water
interaction is used, predict that the water molecules are in a single file with dipole moments oriented along the SWCNT axis; see Figure 4.20.

(3) In SWCNTs with large diameters, say of order five or more water molecule diameters, and in materials such as MCM-41 with similar diameters, the density distribution of the enclosed water along the perpendicular to the wall is exhibits layering analogous to that found in confined colloid suspensions.

(4) At low temperature and/or high pressure the water enclosed in SWCNTs forms a variety of ordered structures; these ices have structures that play off hydrogen bonding, wall curvature and molecule wall interactions. Simulations using different water-water interactions agree broadly on the occurrence of ordered water structures inside SWCNTs, but differ in the specific details that characterize the predicted structures.

We close with the observation that definitive studies of how the properties of a system change as the dimensionality changes from 1D $\rightarrow$ q1D $\rightarrow$ 2D $\rightarrow$ q2D $\rightarrow$ 3D have yet to be reported. The issue to be addressed is whether change in dimensionality induces a qualitative change in the system response to variation of thermodynamic variables, or only a quantitative change in the parameters that describe those responses. For example, does out-of-plane motion of particles with the average position of the particle center restricted to lie in a 2D domain change the qualitative character of the 2D melting transition? Although not rigorously proven, for the 2D hard disc system the numerical evidence from studies of convergence of the virial series, simulation data, and bifurcation theory imply that there is a continuous liquid-to-hexatic phase transition. The bifurcation theory analysis predicts a crossover from a continuous to a first order liquid-to-hexatic transition as the system thickness is increased from zero up to about 1.4 particle diameters. Testing that prediction against experimental will provide a clue concerning the influence of dimensionality on the melting transition.

VII. References


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