

Theories of molecular fluids confined in disordered porous materials

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2008 J. Phys.: Condens. Matter 20 333101

(<http://iopscience.iop.org/0953-8984/20/33/333101>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 29/05/2010 at 13:54

Please note that [terms and conditions apply](#).

TOPICAL REVIEW

Theories of molecular fluids confined in disordered porous materials

Lev Sarkisov¹ and Paul R Van Tassel²¹ Institute for Materials and Processes, University of Edinburgh, Edinburgh EH9 3JL, UK² Department of Chemical Engineering, Yale University, New Haven, CT 06520-8286, USAE-mail: Lev.Sarkisov@ed.ac.uk

Received 28 May 2008, in final form 9 June 2008

Published 21 July 2008

Online at stacks.iop.org/JPhysCM/20/333101**Abstract**

A fundamental description of fluids under confinement is important to our efforts to design next-generation porous materials with specified characteristics. Computer simulation has been a great aid in this process, particularly for crystalline materials and materials with regular porous morphology. The situation is more complex for disordered porous materials, where a molecular model must capture the essential features of structural disorder on the appropriate length scales. This presents a serious challenge even with modern computer power. Theoretical methods can offer a more efficient alternative while providing broad, general insight to systems of interest. In this article, we review recent advances in theoretical integral equation approaches to molecular fluids under confinement in disordered media. We focus on replica Ornstein–Zernike-based approaches, and emphasize interaction site fluid and associating fluid applications. We also speculate on possible further directions in this rapidly developing field.

Contents

1. Introduction	1
2. Fluids in disordered porous structures	3
3. Interaction site fluids in disordered porous structures	5
4. Associating fluids in disordered porous structures	7
5. Perspectives	9
Acknowledgments	10
References	10

1. Introduction

Porous materials are widely used in chemical, biochemical, pharmaceutical, oil, gas and other industries as catalysts, supports, membranes and sensors. Broadly speaking, porous materials can be classified into crystalline materials, such as zeolites, and amorphous materials, such as silica gels, activated carbon materials, controlled porous glasses and clays. Recently, new families of materials have begun to emerge. For example, mesoporous molecular sieves are silicon (or other metal) oxide materials with amorphous solid

structure, but regular, well organized porous morphology. Metal organic frameworks are crystalline materials formed by metal complexes and organic linkers and characterized by very high porosity. Another example is provided by molecularly imprinted polymers. These materials form in the presence of templates which, upon extraction, leave cavities in the structure with molecular complementarity to the template. These imprinted polymers are therefore capable of molecular recognition, and can be employed in separation, sensing, drug delivery and other applications. It has been recognized that technological progress in a number of key areas will crucially depend on our ability to design and create porous materials with tailored, controlled functionalities [1].

The properties and overall function of a porous material depend sensitively on its structure. A fluid under confinement exhibits different physical properties from those in the bulk phase. The presence of solid–fluid interactions in addition to fluid–fluid interactions may lead to new phenomena and phase transitions, such as layering, wetting and shifts of freezing and vapour–liquid transitions. The development of new materials with specific characteristics requires fundamental understanding of fluid properties under confinement and, in

particular, the influence of the solid structure and surface heterogeneity on these properties. Naturally, there has been a strong interest in fundamental studies of fluids under confinement in porous morphologies. An excellent review of recent experimental and theoretical efforts in this field has been provided by Gelb and co-workers [2].

Computer simulation and theoretical approaches have contributed to substantial progress in the areas of crystalline porous materials and materials with regular pore geometries. Indeed, the structure of crystalline materials is determined from x-ray or neutron scattering experiments and thus is well defined. This structure can then be employed in computer simulations to study adsorption and transport phenomena. Studies of various zeolites have been particularly prolific and successful [3]. Other structures, such as mesoporous molecular sieves and carbons, are not crystalline yet possess a regular pore morphology that may be approximated, with varying degree of accuracy, as cylinders or slits with a distribution of diameters/widths. In this case, again, the structure of the solid suggests a fairly straightforward model to be employed via simulation. Furthermore, density functional theory (DFT) can be applied to study adsorption phenomena in cylinder and slit pores as in the series of works by, for example, Evans and co-workers [4–6] and by Neimark and co-workers [7–10].

The situation is much more complex in the case of disordered materials, such as controlled porous glass, silica (and other oxide) gels, activated carbon fibres and foams, and various types of clays and polymers. In these cases, the structure of the porous material cannot be unambiguously identified by x-ray or neutron scattering experiments. Thus, in order to construct a realistic model of a disordered porous material to be used in theoretical or computer simulation studies, one has to rely on other strategies. For example, it has been shown in a number of experimental studies that many silica xerogels produced in sol–gel processes are composed of roughly spherical silica beads with sizes from tens of nanometres to micrometres [11]. A simple model of this material would be a system of spherical particles quenched in space with a density corresponding to that of the silica material. This is the idea behind the model of Kaminsky and Monson [12–15]. In fact, their model was inspired by the more detailed model of MacElroy and Raghavan, where each silica bead was treated as a collection of oxygen atoms [16]. Positions of these oxygen atoms were determined from an additional annealing simulation based on accurate silica potential. Kaminsky and Monson derived an analytical potential that treats each silica bead as a sphere with uniformly distributed Lennard-Jones interaction sites (provided by oxygen atoms), thus significantly improving the efficiency of the model. Another example is provided by a series of studies on amorphous carbon materials. In these studies, the information about the structure of the material of interest was limited to carbon–carbon radial distribution functions from small-angle x-ray and neutron scattering (SAXS and SANS) and void–void correlations from TEM micrographs. A Reverse Monte Carlo scheme was then implemented to generate model structures of porous materials with characteristics converging towards the target

ones from the experiments [17–20]. This approach has been extensively applied to reconstruction of disordered carbon materials [21–23].

Another strategy to generate realistic structures of disordered porous materials is to imitate the actual process of their formation. An example of this strategy is provided by adsorption studies in controlled porous glasses, where the model structure was generated by mimicking the process of spinodal decomposition involved in glass formation. An early study of MacFarland *et al* used lattice model to imitate spinodal decomposition of liquid–liquid mixture at subcritical temperatures [24]. Similar in spirit, a more realistic, large scale off-lattice model was later proposed and investigated in a series of works by Gelb and Gubbins [25, 26]. Templated polymer structures provide another example [27]. As has been already mentioned, these structures form in the presence of molecular templates. Van Tassel and co-workers developed a model of these templated polymers based on a simple protocol that qualitatively repeats the steps of polymer formation [28–32]. Obviously validation of such models of disordered structures is a challenging task and the majority of studies are limited to qualitative insights.

The direct computer simulation of fluids confined in disordered porous structures represents an enormous challenge. The strategies described above can be used to generate a sample of a model porous material, but only of limited size. Thus, adsorption, transport and other properties of the confined fluid are specific to a given realization of the structure, and correlations over longer length scales are necessarily absent. In order to understand behaviour of fluids under confinement, properties of the fluids must be averaged over a representative sample of disorder. In computer simulation, this problem is resolved by averaging observed properties of the fluid over many realizations of the porous structure. This is a computationally daunting task, especially if each realization requires a separate simulation. In addition, some fundamental issues such as sufficient size of the realization and sufficient number of realizations still remain a subject of an ongoing debate.

An alternative approach is offered within the framework of integral equation theories of quenched–annealed models, where a disordered porous structure is treated as a system of quenched particles. An Ornstein–Zernike-like theory of a fluid confined in a quenched matrix was first proposed by Madden and Glandt [33–35] and further refined by Given and Stell [36, 37] and Rosinberg *et al* [38]. This theory is at the heart of the approaches described in this article and we review it in more detail in the next section.

Most of the theoretical studies in this area so far have been limited to simple fluids. However, a number of important problems focus on the behaviour of molecular species, and progress in this area has been much more modest. The objective of this article is to review recent developments in the integral equation theories of confined complex fluids with a focus on site interaction fluids and associating fluids. We will also offer some perspectives with a hope to outline the most interesting current problems in the field and to stimulate further research in this important area.

2. Fluids in disordered porous structures

A collection of quenched (i.e. fixed in space) particles often serves as a simple model of a disordered porous medium. Such a description captures in a qualitative way the size, randomness, connectivity, and tortuosity of the pore space found in real porous materials. As discussed above, it is also a reasonably realistic model of oxide xerogels. As noted by Madden and Glandt, a system of fluid molecules adsorbed within a collection of quenched ‘matrix’ molecules/particles bears some similarity to a fully equilibrated mixture consisting of the fluid and the matrix [33]. Employing a diagrammatic approach, they identified a class of diagrams present in the equilibrium mixture but absent from the fluid plus quenched matrix system. Additionally, they proposed a set of Ornstein–Zernike equations describing the relation between total and direct correlation functions.

Given and Stell [36, 37, 39] and Rosinberg *et al* [38] have noted that a fluid in a quenched matrix system is an example of a quenched–annealed system, in which certain degrees of freedom are quenched and others equilibrate with respect to the quenched ones. To properly apply statistical mechanics, the annealed partition function must be averaged over quenched degrees of freedom. For a fluid in a quenched matrix, with all interaction potentials spherically symmetric, the average excess Helmholtz free energy of the fluid (f) is

$$\begin{aligned} -\beta \bar{A}_f^{\text{ex}} &= \overline{\ln [Z_f(\vec{q}^{N_m})]} \\ &= \frac{1}{Z_m} \int e^{-\beta U_m(\vec{q}^{N_m})} \ln [Z_f(\vec{q}^{N_m})] d^{N_m} \vec{q}, \end{aligned} \quad (1)$$

where $\vec{q}^{N_m} = \vec{q}_1, \dots, \vec{q}_{N_m}$ is the shorthand for the position vectors of the N_m matrix (m) molecules, U_m is the total potential energy of the matrix species (due to matrix–matrix interactions and any external potential), β is $1/kT$, k is the Boltzmann constant, T is the absolute temperature, and the overbar indicates an average over matrix configurations. The partition function for the fluid within a given matrix configuration is

$$Z_f(\vec{q}^{N_m}) = \int e^{-\beta U_f(\vec{q}^{N_m}, \vec{r}^{N_f})} d^{N_f} \vec{r}, \quad (2)$$

where U_f is the total potential energy of fluid molecules (including fluid–fluid, matrix–fluid, and any external potential interactions), and $\vec{r}^{N_f} = \vec{r}_1, \dots, \vec{r}_{N_f}$ is shorthand for the position vectors of the N_f fluid particles. The partition function for the matrix species is simply

$$Z_m = \int e^{-\beta U_m(\vec{q}^{N_m})} d^{N_m} \vec{q}. \quad (3)$$

Equation (1) may be simplified through the replica method [40, 41]. Inserting the identity $\ln x = \lim_{s \rightarrow 0} \frac{x^s - 1}{s} = \lim_{s \rightarrow 0} \frac{dx^s}{ds}$ into equation (1), one obtains

$$\begin{aligned} \beta \bar{A}_f^{\text{ex}} &= -\frac{1}{Z_m} \lim_{s \rightarrow 0} \int e^{-\beta U_m(\vec{q}^{N_m})} [Z_f(\vec{q}^{N_m})]^s d^{N_m} \vec{q} \\ &= -\lim_{s \rightarrow 0} \frac{d}{ds} \ln Z^{\text{rep}}(s) = \lim_{s \rightarrow 0} \frac{d}{ds} \beta A^{\text{ex,rep}}(s), \end{aligned} \quad (4)$$

where Z^{rep} is the configuration integral of a special $s + 1$ component equilibrated mixture of matrix and s replicas of the fluid component, defined such that fluid molecules belonging to different replicas do not interact. $A^{\text{ex,rep}}$ is the excess Helmholtz free energy of this replica mixture.

Equation (4) offers a route toward determining the thermodynamic and structural properties of the quenched–annealed systems in terms of those of the fully annealed replica system. For example, various two-body densities may be determined via functional differentiation. Assuming pair potentials such that $U_f = \sum_{i=1}^{N_m} \sum_{j=1}^{N_f} v_{mf}(\vec{q}_i, \vec{r}_j) + \frac{1}{2} \sum_{i=1}^{N_f} \sum_{j=1}^{N_f} v_{ff}(\vec{r}_i, \vec{r}_j)$, we have

$$\begin{aligned} \rho_{ff}^{(2)}(\vec{r}_1, \vec{r}_2) &= \overline{\rho_{ff}^{(2)}(\vec{r}_1, \vec{r}_2, \vec{q}^{N_m})} = \frac{N_f(N_f - 1)}{Z_m} \\ &\times \int e^{-\beta U_m} \frac{1}{Z_f(\vec{q}^{N_m})} \int e^{-\beta U_f} d\vec{r}_3 \dots d\vec{r}_{N_f} d\vec{q}_1 \dots d\vec{q}_{N_m} \\ &= 2 \frac{\delta \beta \bar{A}_f^{\text{ex}}}{\delta \beta v_{ff}(\vec{r}_1, \vec{r}_2)} = 2 \lim_{s \rightarrow 0} \frac{d}{ds} \left[\frac{\delta \beta A^{\text{ex,rep}}(s)}{\delta \beta v_{ff}(\vec{r}_1, \vec{r}_2)} \right] \\ &= \lim_{s \rightarrow 0} \frac{d}{ds} \left[s \rho_{ff}^{(2)\text{rep}}(\vec{r}_1, \vec{r}_2; s) \right] = \rho_{ff}^{(2)\text{rep}}(\vec{r}_1, \vec{r}_2; s = 0) \end{aligned} \quad (5)$$

$$\begin{aligned} \rho_{mf}^{(2)}(\vec{q}_1, \vec{r}_1) &= \frac{N_m N_f}{Z_m} \int e^{-\beta U_m} \frac{1}{Z_f(\vec{q}^{N_m})} \\ &\times \int e^{-\beta U_f} d\vec{r}_2 \dots d\vec{r}_{N_f} d\vec{q}_2 \dots d\vec{q}_{N_m} \\ &= \frac{\delta \beta \bar{A}_f^{\text{ex}}}{\delta \beta v_{mf}(\vec{q}_1, \vec{r}_1)} = \lim_{s \rightarrow 0} \frac{d}{ds} \left[\frac{\delta \beta A^{\text{ex,rep}}(s)}{\delta \beta v_{mf}(\vec{q}_1, \vec{r}_1)} \right] \\ &= \lim_{s \rightarrow 0} \frac{d}{ds} \left[s \rho_{mf}^{(2)\text{rep}}(\vec{q}_1, \vec{r}_1; s) \right] = \rho_{mf}^{(2)\text{rep}}(\vec{q}_1, \vec{r}_1; s = 0). \end{aligned} \quad (6)$$

It is also useful to consider a second order functional derivative with respect to the external potential for the fluid component $u_f(\vec{r})$:

$$\begin{aligned} \frac{\delta^2 \beta \bar{A}_f^{\text{ex}}}{\delta \beta u_f(\vec{r}_1) \delta \beta u_f(\vec{r}_2)} &= -\rho_{ff}^{(2)}(\vec{r}_1, \vec{r}_2) - \rho_f(\vec{r}_1) \delta(\vec{r}_1 - \vec{r}_2) \\ &+ \overline{\rho_f(\vec{r}_1, \vec{q}^{N_m}) \rho_f(\vec{r}_2, \vec{q}^{N_m})} \\ &= \lim_{s \rightarrow 0} \frac{d}{ds} \left[\frac{\delta^2 \beta A^{\text{ex,rep}}(s)}{\delta \beta u_f(\vec{r}_1) \delta \beta u_f(\vec{r}_2)} \right] \\ &= \lim_{s \rightarrow 0} \frac{d}{ds} \left[-s \rho_{ff}^{(2)\text{rep}}(\vec{r}_1, \vec{r}_2; s) - s \rho_f^{\text{rep}}(\vec{r}_1; s) \delta(\vec{r}_1 - \vec{r}_2) \right. \\ &\quad \left. - s(s - 1) \rho_{ff_2}^{(2)\text{rep}}(\vec{r}_1, \vec{r}_2; s) - s^2 \rho_f^{\text{rep}}(\vec{r}_1; s) \rho_f^{\text{rep}}(\vec{r}_2; s) \right] \\ &= -\rho_{ff}^{(2)\text{rep}}(\vec{r}_1, \vec{r}_2; s = 0) - \rho_f^{\text{rep}}(\vec{r}_1; s = 0) \delta(\vec{r}_1 - \vec{r}_2) \\ &\quad + \rho_{ff_2}^{(2)\text{rep}}(\vec{r}_1, \vec{r}_2; s = 0). \end{aligned} \quad (7)$$

Through equation (7), we identify the $s = 0$ limit of the two-body density among distinct replica species (i.e. species f and f_2) with the two-body density of the quenched–annealed system $\overline{\rho_f(\vec{r}_1, \vec{q}^{N_m}) \rho_f(\vec{r}_2, \vec{q}^{N_m})}$; although distinct fluid species have no interaction with one another, this two-body density generally deviates from the product $\rho_f(\vec{r}_1) \rho_f(\vec{r}_2)$ due to correlations with matrix molecules.

A set of Ornstein–Zernike (OZ) equations for the $s + 1$ component replica system is given by

$$h_{mm}^{\text{rep}} = c_{mm}^{\text{rep}} + \rho_m^{\text{rep}} c_{mm}^{\text{rep}} \otimes h_{mm}^{\text{rep}} + s \rho_f^{\text{rep}} c_{mf}^{\text{rep}} \otimes h_{mf}^{\text{rep}} \quad (8)$$

$$h_{mf}^{\text{rep}} = c_{mf}^{\text{rep}} + \rho_m^{\text{rep}} c_{mm}^{\text{rep}} \otimes h_{mf}^{\text{rep}} + \rho_f^{\text{rep}} c_{mf}^{\text{rep}} \otimes h_{ff}^{\text{rep}} + (s - 1) \rho_f^{\text{rep}} c_{mf}^{\text{rep}} \otimes h_{ff_2}^{\text{rep}} \quad (9)$$

$$h_{ff}^{\text{rep}} = c_{ff}^{\text{rep}} + \rho_m^{\text{rep}} c_{mf}^{\text{rep}} \otimes h_{mf}^{\text{rep}} + \rho_f^{\text{rep}} c_{ff}^{\text{rep}} \otimes h_{ff}^{\text{rep}} + (s - 1) \rho_f^{\text{rep}} c_{ff_2}^{\text{rep}} \otimes h_{ff_2}^{\text{rep}} \quad (10)$$

$$h_{ff_2}^{\text{rep}} = c_{ff_2}^{\text{rep}} + \rho_m^{\text{rep}} c_{mf}^{\text{rep}} \otimes h_{mf}^{\text{rep}} + \rho_f^{\text{rep}} c_{ff}^{\text{rep}} \otimes h_{ff_2}^{\text{rep}} + \rho_f^{\text{rep}} c_{ff_2}^{\text{rep}} \otimes h_{ff}^{\text{rep}} + (s - 2) \rho_f^{\text{rep}} c_{ff_2}^{\text{rep}} \otimes h_{ff_2}^{\text{rep}}, \quad (11)$$

where $h_{ij}^{\text{rep}} = \rho_{ij}^{(2)\text{rep}} / \rho_i^{\text{rep}} \rho_j^{\text{rep}} - 1$ is the two-body total correlation function between species i and j , c_{ij}^{rep} is the two body direct correlation function between species i and j , and \otimes denotes a convolution integral. Note the simplified form engendered by the identicalness of the s replica species. Taking the $s = 0$ limit, and using the relations established in equations (5)–(7), we obtain the OZ equations for the quenched–annealed system

$$h_{mm} = c_{mm} + \rho_m c_{mm} \otimes h_{mm} \quad (12)$$

$$h_{mf} = c_{mf} + \rho_m c_{mm} \otimes h_{mf} + \rho_f c_{mf} \otimes h_C \quad (13)$$

$$h_{ff} = c_{ff} + \rho_m c_{mf} \otimes h_{mf} + \rho_f c_C \otimes h_{ff} + \rho_f c_B \otimes h_C \quad (14)$$

$$h_C = c_C + \rho_f c_C \otimes h_C, \quad (15)$$

where h_{ij} and c_{ij} are the total and direct correlation functions, and the fluid–fluid correlations are expressed as $h_{ff} = h_C + h_B$, $c_{ff} = c_C + c_B$, with $h_B = h_{ff_2}^{\text{rep}}(s = 0)$ and $c_B = c_{ff_2}^{\text{rep}}(s = 0)$ being the ‘blocking’ portion, so called due to a diagrammatic structure in which all paths connecting fluid root points pass through at least one matrix field point. In the special case of a vanishing external potential, the correlation functions of equations (12)–(15) become dependent only on the scalar separation distance between molecular centres.

As is typical of OZ approaches, equations (12)–(15) require additional closure relations in order to yield a full solution. The Percus–Yevick (PY) approximation is one such option

$$c_{ij}(r) = f_{ij}(r) y_{ij}(r), \quad (16)$$

where f_{ij} is the Mayer function defined as $f_{ij}(r) = e^{-\beta v_{ij}(r)} - 1$, with v_{ij} being the pair potential, and $y_{ij}(r) = e^{\beta v_{ij}(r)} [h_{ij}(r) + 1]$. Another common closure is the hypernetted chain (HNC) approximation,

$$c_{ij}(r) = -\beta v_{ij} + h_{ij}(r) - \ln [1 + h_{ij}(r)]. \quad (17)$$

In order to determine blocking contributions to fluid–fluid correlation function, equations (16), and (17) are applied to correlations between different replica species f and f_2 , where the pair potential v_{ff_2} is identically zero.

Thermodynamic properties may be determined by the usual routes, keeping in mind the special properties of the quenched–annealed system and its relation to the fully annealed replica system. For example, the chemical potential

may be determined by the compressibility route, starting with the relation

$$\left(\frac{\partial \rho_f}{\partial \beta \mu_f} \right)_T = \frac{1}{V Z_m} \int e^{-\beta U_m} [\rho_{ff}^{(2)}(\vec{r}_1, \vec{r}_2, \vec{q}^{N_m}) - \rho_f(\vec{r}_1, \vec{q}^{N_m}) \rho_f(\vec{r}_2, \vec{q}^{N_m}) + \rho_f(\vec{r}_1, \vec{q}^{N_m}) \delta(\vec{r}_1 - \vec{r}_2)] \times d\vec{r}_1 d\vec{r}_2 d^{N_m} \vec{q} = \rho_f^2 \hat{h}_C(k = 0) + \rho_f, \quad (18)$$

where V is the system volume and $\hat{h}_C(k)$ is the 3D Fourier transform of $h_C(r)$. Combining with equation (15), one obtains an expression for the excess chemical potential:

$$\beta \mu_f^{\text{ex}}(\rho_f) - \beta \mu_f^{\text{ex}}(\rho_f = 0) = - \int_0^{\rho_f} \hat{c}_C(k = 0, \rho'_f) d\rho'_f. \quad (19)$$

Another route toward the chemical potential involves introducing a coupling factor ξ into the intermolecular potential, such that for $\xi = 1$, an additional fluid molecule is fully coupled to the original molecules, for $0 < \xi < 1$, the additional molecule is only partially coupled, and for $\xi = 0$, no additional molecule is present. These ideas lead to

$$\begin{aligned} \beta \mu_f^{\text{ex,rep}} &= - \frac{\partial \ln Z^{\text{rep}}}{\partial N_f} = - \int_0^1 \frac{\partial \ln Z^{\text{rep}}}{\partial \xi} d\xi \\ &= - \int_0^1 \left[\rho_m \int g_{mf}^{\text{rep}} \frac{\partial \beta v_{mf}}{\partial \xi} d\vec{r} + \rho_f \int g_{ff}^{\text{rep}} \frac{\partial \beta v_{ff}}{\partial \xi} d\vec{r} + (s - 1) \rho_f \int g_{ff_2}^{\text{rep}} \frac{\partial \beta v_{ff_2}}{\partial \xi} d\vec{r} \right] d\xi. \end{aligned} \quad (20)$$

Employing the identity $\beta v_{ij} = h_{ij} - c_{ij} - \ln(h_{ij} + 1) + B_{ij}$ (where B_{ij} is the bridge function, defined in terms of its diagrammatic structure and approximated by various closure relations [42]), taking the $s = 0$ limit, and assuming (in two, but not all, integration steps) correlation functions to vary linearly with the parameter ξ allows one to write equation (20) as [43]

$$\begin{aligned} \beta \mu_f^{\text{ex}} &= \rho_m \int \left[\frac{h_{mf}^2}{2} - c_{mf} + \frac{h_{mf} c_{mf}}{2} + B_{mf} + h_{mf} B_{mf} - \frac{h_{mf}}{\gamma_{mf}} \int_0^{\gamma_{mf}} B_{mf}(\gamma) d\gamma \right] d\vec{r} \\ &+ \rho_f \int \left[\frac{h_{ff}^2}{2} - c_{ff} + \frac{h_{ff} c_{ff}}{2} + B_{ff} + h_{ff} B_{ff} - \frac{h_{ff}}{\gamma_{ff}} \int_0^{\gamma_{ff}} B_{ff}(\gamma) d\gamma \right] d\vec{r}, \end{aligned} \quad (21)$$

where the Bridge function B_{ij} is assumed to depend on $\gamma_{ij} = h_{ij} - c_{ij}$. Thus, this approach provides a direct method for the excess chemical potential of a fluid. As seen from equation (21) sufficient information about the excess chemical potential of a fluid in a particular state is provided solely by the pair correlation functions for the fluid at that state; therefore this approach alleviates the need for computationally intensive integration protocols as needed e.g. in the compressibility route. In principle, equation (21) is a general formula independent of the method used for calculation of the required pair correlation functions. One interesting avenue of research would be to adapt this method to calculate the excess chemical potential via computer simulation. The

idea is to generate the required total correlation function in a computer simulation, and then apply the OZ equations to generate the direct correlation function. Calculation of the bridge function is a more difficult task in computer simulation. Instead, a particular approximate closure can be employed to achieve this. Equation (21) is then used to calculate the excess chemical potential. Thus, this approach mixes data obtained from a computer simulation with an approximate integral equation theory, which is an obvious weakness. However, it may provide a relatively quick, yet possibly still quite accurate, route to the chemical potential. Accuracy and efficiency of this approach compared to other routes, such as particle insertion methods, are yet to be established.

3. Interaction site fluids in disordered porous structures

The standard Ornstein–Zernike (OZ) approach describes equilibrium systems consisting of spherically symmetric molecules. The OZ method may also be generalized to non-spherical molecules, but the equations become much more complicated and advanced methods, such as spherical harmonic expansions, are often required [44]. Alternatively, when the non-spherical molecules consist of a collection of linked sites (e.g. the atoms of a molecule), then the reference interaction site model (RISM), also known as the site–site OZ approach (SSOZ) may be employed [45–48]. Within RISM, molecules are modelled as collections of linked, spherically symmetric sites. Total and direct correlation functions between sites on different molecules are considered, in analogy to the standard OZ approach. In addition, intra-molecular correlation functions are employed. The RISM equations for a single component system read

$$h^{\alpha\beta} = \sum_{\lambda} \sum_{\mu} w^{\alpha\lambda} \otimes c^{\lambda\mu} \otimes w^{\mu\beta} + \rho \sum_{\lambda} \sum_{\mu} w^{\alpha\lambda} \otimes c^{\lambda\mu} \otimes h^{\mu\beta}, \quad (22)$$

where $h^{\alpha\beta}$, $c^{\alpha\beta}$, and $w^{\alpha\beta}$ are (respectively) the total, direct, and intra-molecular correlation functions between sites α and β , ρ is the number density of the molecular species, and \otimes is a convolution integral. Equation (22) may be simplified through Fourier transform and written in matrix form as

$$H = WCW + \rho WCH, \quad (23)$$

where H , C , and W are square matrices whose $\alpha\beta$ element is $\hat{h}^{\alpha\beta}$, $\hat{c}^{\alpha\beta}$, and $\hat{w}^{\alpha\beta}$ respectively, with $\hat{a}(k) = \int a(r) e^{-i\vec{k}\cdot\vec{r}} d\vec{r}$.

In the case of rigid molecular species (i.e. sites fixed in terms of relative positions), the intra-molecular correlations are known via

$$w^{\alpha\beta}(r) = \frac{\delta(r - L_{\alpha\beta})}{4\pi L_{\alpha\beta}^2}, \quad (24)$$

where δ is the one-dimensional delta function and $L_{\alpha\beta}$ is the centre to centre distance between sites α and β on a given molecule. The Fourier transform is simply $\hat{w}^{\alpha\beta}(k) = \frac{\sin(kL_{\alpha\beta})}{kL_{\alpha\beta}}$.

Schweizer and Curro have proposed a special case of RISM when the molecular species in question is composed of many nearly identical sites, such as a long homopolymer [49].

In this case, the site–site total and direct correlation functions become essentially independent of site index, so equation (22) simplifies to

$$\hat{h} = \hat{w}\hat{c}\hat{w} + \rho N\hat{w}\hat{c}\hat{h}, \quad (25)$$

where $h = h^{\alpha\beta}$, $c = c^{\alpha\beta}$, and $\hat{w} = \sum_{\lambda=1}^N \hat{w}_{\alpha\lambda} = \sum_{\mu=1}^N \hat{w}_{\mu\beta}$ are assumed independent of α and β , and N is the number of sites along the polymer chain. This polymer RISM approach is often referred to as PRISM.

As is typical in integral equation approaches, closure relations are needed to solve sets of equations as in equation (23). Some examples parallel those given in equations (16), and (17). In addition, various thermodynamic routes are available. For example, integration of the compressibility

$$\frac{\partial\mu}{\partial\rho} = -kT\hat{c}^{\alpha\beta}(k=0) \quad (26)$$

yields the chemical potential μ , where any pair of indices may be inserted for α and β . Another such route is by integration of the internal energy,

$$\frac{\partial}{\partial} \left(\frac{F}{VT} \right) = \frac{U}{V} = 2\pi\rho \sum_{\alpha} \sum_{\beta} \int_0^{\infty} v^{\alpha\beta}(r) [h^{\alpha\beta}(r) + 1] dr, \quad (27)$$

where F is the Helmholtz energy and U is the total internal energy.

Kovalenko and Hirata have combined the replica OZ approach with the RISM method to obtain a set of integral equations for modelling a molecular fluid adsorbed within a quenched matrix [50]:

$$H_{mm} = W_m C_{mm} W_m + \rho_m W_m C_{mm} H_{mm} \quad (28)$$

$$H_{mf} = W_m C_{mf} W_f + \rho_m W_m C_{mm} H_{mf} + \rho_f W_m C_{mf} H_C \quad (29)$$

$$H_{ff} = W_f C_{ff} W_f + \rho_m W_f C_{mf} H_{mf} + \rho_f W_f C_C H_B + \rho_f W_f C_{ff} H_C \quad (30)$$

$$H_C = W_f C_C W_f + \rho_f W_f C_C H_C. \quad (31)$$

In equations (28)–(31), again the subscripts m and f stand for matrix and fluid components as before, respectively, and the matrices therein contain elements $\hat{a}_{ij}^{\alpha\beta}(k)$, where a is a total, direct, or intermolecular correlation function, i and j correspond to matrix and/or fluid species, and α and β correspond to sites on species i and j . The subscripts C and B refer to ‘connected’ and ‘blocking’ correlation functions, which can be defined in the manner discussed in section 2. Specifically, the diagrams contributing to $h_C^{\alpha\beta}$ and $c_C^{\alpha\beta}$ contain at least one path connecting the fluid root points that does not pass through any matrix field points, and $h_B^{\alpha\beta} = h_{ff}^{\alpha\beta} - h_C^{\alpha\beta}$ and $c_B^{\alpha\beta} = c_{ff}^{\alpha\beta} - c_C^{\alpha\beta}$.

Kovalenko and Hirata used a combination of the standard HNC closure and the partially linearized HNC closure to solve equations (28)–(31) for a model of water adsorbed within a matrix of bare carbon and carboxylic acid activated carbon [50]. Specifically, they applied equation (17) for the blocking portion of the site–site fluid–fluid correlations,

and the below equation for the site–site matrix–matrix (mm), matrix–fluid (mf), and fluid–fluid (ff) correlations:

$$\begin{cases} c_{ij}^{\alpha\beta} = h_{ij}^{\alpha\beta} - \frac{v_{ij}^{\alpha\beta}}{kT} - \ln(1 + h_{ij}^{\alpha\beta}) & h_{ij}^{\alpha\beta} < 0 \\ c_{ij}^{\alpha\beta} = -\frac{v_{ij}^{\alpha\beta}}{kT} & h_{ij}^{\alpha\beta} > 0. \end{cases} \quad (32)$$

The idea here is to linearize the logarithm of the standard HNC approximation for positive values of the total correlation function, in order to keep its value from being too large at separations where the potential energy is large and negative [51].

Tanimura *et al* extended this model to investigate the electric double layer within a nanoporous carbon supercapacitor [52, 53]. The partially linearized HNC closure was again employed for mm , mf , and ff correlations, but a modified Verlet approximation to the bridge function was used to determine the blocking correlations. Matrix properties were chosen to be those of activated carbon and carbonized poly(vinylidene chloride), and it was determined that the mechanism behind the large experimentally determined capacitance involves the solvation structure and chemical potential of the electrolyte solution within the entire electrode—and not simply within the Helmholtz layer at the electrode surface. A particular interesting observation was that nanoporous confinement tends to increase the degree of hydration for cations, while decreasing that for anions (the latter tend to adsorb directly to the carbon surface).

By combining the Madden–Glandt OZ equations [33] with the PRISM method (equation (25)), Chandler [54] and Thompson and Glandt [55, 56] have developed a theoretical framework to treat long chain molecules adsorbed within a quenched matrix. Employing an ideal freely jointed chain approximation for $w(r)$ and a Percus–Yevick closure, Thompson and Glandt calculated the correlation functions for hard sphere polymers of various length and density within a quenched hard sphere matrix [55]. These results revealed enhanced correlation holes, i.e. regions of low probability of finding neighbouring segments from different chains, for low density or high length polymers. In further work, these authors employed the more accurate Koyama hard sphere chain intra-molecular correlation function, together with a coupling parameter approach toward the polymer chemical potential, to calculate the partition coefficient for a polymer between a quenched matrix and a bulk solution [56]. An interesting observation was that the concentration effect on partitioning is driven by deviations from ideality—in the bulk solution at lower concentration and in the pore solution at higher concentration.

Yethiraj and co-workers have combined the replica OZ equations (equations (12)–(15)) with the PRISM approach to investigate polymer adsorption within a quenched disordered medium [57, 58]. Using a Percus–Yevick closure and a variational approach toward a self-consistent intra-molecular correlation function, they were able to capture many of the interesting physical features of hard sphere chains in disordered media observed in computer simulation, such as the

non-monotonic relation between chain extension and matrix density.

Motivated by experimental efforts to engineer pore spaces using sacrificial template species, Sarkisov and Van Tassel have developed a RISM-based approach to model molecular adsorption in a templated porous material [59, 60]. The idea is to consider a binary matrix system with one component (the template) removed. Replica OZ equations may be written, and in the $s = 0$ limit become

$$H_{mm} = W_m C_{mm} W_m + \rho_m W_m C_{mm} H_{mm} + \rho_t W_m C_{mt} H_{mt} \quad (33)$$

$$H_{mt} = W_m C_{mt} W_t + \rho_m W_m C_{mm} H_{mt} + \rho_t W_m C_{mt} H_{tt} \quad (34)$$

$$H_{tt} = W_t C_{tt} W_t + \rho_m W_t C_{mt} H_{mt} + \rho_t W_t C_{tt} H_{tt} \quad (35)$$

$$H_{mf} = W_m C_{mf} W_f + \rho_m W_m C_{mm} H_{mf} + \rho_t W_m C_{mt} H_{tf} + \rho_f W_m C_{mf} H_C \quad (36)$$

$$H_{tf} = W_t C_{tf} W_f + \rho_m W_t C_{tm} H_{mf} + \rho_t W_t C_{tt} H_{tf} + \rho_f W_t C_{tf} H_C \quad (37)$$

$$H_{ff} = W_f C_{ff} W_f + \rho_m W_f C_{mf} H_{mf} + \rho_t W_f C_{tf} H_{tf} + \rho_f W_f C_C H_B + \rho_f W_f C_{ff} H_C \quad (38)$$

$$H_C = W_f C_C W_f + \rho_f W_f C_C H_C, \quad (39)$$

where the subscripts m , t and f represent matrix, template, and fluid components. It is important to note the necessity to account for template–fluid (tf) correlations. Although the template is removed from the system prior to entry of the fluid, these species are nonetheless spatially correlated owing to the presence of the matrix component. These authors have employed equations (33)–(39) along with various closures and thermodynamic routes to study adsorption of clusters of hard spheres as well as hard sphere plus attractive tail systems. (We note that Tanimura *et al* also employ a template species. However, their approach involves the original replica RISM equations, equations (28)–(31) [52, 53].) This integral equation approach was able to predict modestly selective adsorption due to differences in molecular shape, such as linear versus compact clusters of interaction sites. However, strongly selective adsorption was only observed for interaction site systems with attractive tail potentials.

Sarkisov has developed a RISM-based approach to determine the pair connectedness of a templated porous material [61]. In general, the objective of a pair connectedness analysis is, given a system of objects or particles, to determine the distribution of clusters formed by these particles. The particles may also form an infinite cluster spanning the entire system, and this effect is usually studied within a broader context of percolation analysis. This analysis is important in a number of physical phenomena and systems, including condensation and gelation processes, dispersed conductive materials, chemical association processes and properties of disordered media. An Ornstein–Zernike-like integral approach for the pair connectedness function has been put forward by Coniglio and co-workers [62, 63]. The solution to this equation can be obtained with the connectedness version of the Percus–Yevick closure. In a close analogy to the isothermal compressibility equation, it is possible to derive a similar expression for the average cluster size in the system. The divergence of this property signifies the onset of the percolation

effect. This approach has been applied to a number of systems including randomly placed spheres, adhesive spheres and extended sphere model of DeSimone *et al* [64–68]. Later, Lupkowski and Monson [69] and Leung and Chandler [70] extended this approach to molecular systems by combining the pair connectedness formalism with site–site interaction theories such as the RISM and Chandler–Silbey–Ladanyi theory [71]. This analysis extended to the templated quenched–annealed system provides insights on the connectivity of the matrix, template and adsorbed fluid components. The first property characterizes the integrity of the matrix, whereas the two remaining characteristics can be related to the accessibility of the porous space [61].

4. Associating fluids in disordered porous structures

In this section we focus on theories of associating fluids under confinement in disordered porous structures. The term ‘associating fluids’ generally encompasses both fluids undergoing a chemical reaction to form more complex molecular species and fluids interacting with strong, short range intermolecular potentials. An example of the latter one is a hydrogen bond, which in addition to being strong and relatively short ranged, is also directional. Clearly, the fundamental understanding of the behaviour of these fluids in porous structures is important for a number of problems, such as chemical reaction equilibria in porous media, behaviour of polar liquids under confinement and many other phenomena. Several theoretical treatments of associating fluids have been proposed over the years including Pratt and Chandler [72–74] and Cummings and Stell [75, 76] theories. An early study of associative fluids in disordered porous networks attempted to capture the process of fluid–fluid association via a strong square-like potential, with the rest of the ROZ formalism remaining intact [77]. However, the theory of Wertheim [78–83] seems to be particularly well adapted to studies of associating fluids under confinement. Following closely the original work of Trokhymchuk *et al* [84], here we use an example of a dimerizing fluid in a matrix of quenched particles to outline the basic elements of the theory.

Consider species where a spherical particle bears an additional binding site. When two such sites of two particles come in close proximity with each other they associate via a strong attractive potential. The interaction site is small compared to the main particle and thus steric hindrance prevents more than two particles associating with each other. This association can be treated as a chemical bond formation or a hydrogen bond depending on the system. For two such particles the intermolecular potential can be formulated in the following way:

$$v_{ff}^{(12)} = v_{ff}^R(r_{12}) + v_{ff}^A(x_{12}), \quad (40)$$

where $v_{ff}^A(x_{12})$ is the associative potential between attractive sites on two molecules, this potential depends on the distance x_{12} between two sites; $v_{ff}^R(r_{12})$ is the non-associative term. For example, it can be simply a hard sphere potential:

$$v_{ff}^R(r_{12}) = \begin{cases} \infty & r_{12} \leq \sigma \\ 0 & r_{12} > \sigma, \end{cases} \quad (41)$$

where r_{12} is the distance between fluid particles and σ is the collision diameter. The non-associative and associative terms combined form a total intermolecular potential $v_{ff}(12)$ which depends on the distance and mutual orientation of two particles. Splitting of the interaction potential into two contributions also allows one to decompose the Mayer function into two contributions:

$$\begin{aligned} f_{ff}(12) &= e_{ff}(12) - 1 = f_{ff}^R(r_{12}) + e_{ff}^R(r_{12})f_{ff}^A(12) \\ &= f_{ff}^R(r_{12}) + F_{ff}^A(12), \end{aligned} \quad (42)$$

where $e(12) = e^{-v_{ff}(12)/kT}$; $f_{ff}^R(r_{12})$ is the Mayer function for the non-associative term of the potential; $e_{ff}^R(r_{12}) = e^{-v_{ff}^R(r_{12})/kT}$; these last two terms depend on the distance between fluid particles only. $f_{ff}^A(12)$ is the Mayer function for the associative term and depends on the mutual orientation of two molecules.

Thus, any diagram expansion involving f -bonds can be reformulated by replacing each f -bond with either $f_{ff}^R(r_{12})$ bond or $F_{ff}^A(12)$. As a result, the graphical expansion in $\rho(1)$ will contain two classes of diagrams: one class where the labelled point 1 has no incident $F_{ff}^A(12)$ bond and the second class where the labelled point 1 is involved in the associating bond. Each class of diagrams can be viewed as a separate expansion with the first one corresponding to the monomer density and the second one to the density of particles that have associations (not exceeding dimers in our example). In essence we now consider a system of two species, one being monomer particles and the other being particles that participate in dimers. This two densities formalism is at the heart of the Wertheim approach. The standard tools of statistical mechanics allow us then to formulate a set of equations, analogous to the Ornstein–Zernike, to describe two particle correlation functions for this system.

A replica procedure described in section 2 can now be extended to associating fluids. Again, one starts with an equilibrium mixture of matrix (m) and s replicas of fluid (f) components. For this system a set of associative Ornstein–Zernike equations is formulated. Taking the limit of $s = 0$ we obtain the Associative Replica Ornstein Zernike (ARZO) equations:

$$h_{mm} = c_{mm} + \rho_m c_{mm} \otimes h_{mm} \quad (43)$$

$$h_{fm}^\alpha = c_{fm}^\alpha + \rho_m c_{fm}^\alpha \otimes h_{mm} + \sum_{\mu\nu} \rho_f^{\mu\nu} c_C^{\alpha\mu} \otimes h_{fm}^\nu \quad (44)$$

$$h_{ff}^{\alpha\beta} = c_{ff}^{\alpha\beta} + \rho_m c_{fm}^\alpha \otimes h_{mf}^\beta + \sum_{\mu\nu} \rho_f^{\mu\nu} \left[c_C^{\alpha\mu} \otimes h_{ff}^{\nu\beta} + c_B^{\alpha\mu} \otimes h_C^{\nu\beta} \right] \quad (45)$$

$$h_C^{\alpha\beta} = c_{ff,C}^{\alpha\beta} + \rho_m c_{fm}^\alpha \otimes h_{mf}^\beta + \sum_{\mu\nu} \rho_f^{\mu\nu} c_C^{\alpha\mu} \otimes h_C^{\nu\beta}, \quad (46)$$

where the first equation describes two particle correlation functions for the matrix component m ; the second equation describes matrix–fluid correlations; and the last two equations deal with the two particle correlations in the fluid component f in complete analogy with the equations (12)–(15). The Greek indices in equations (43)–(46) take value 0 if a particle is a monomer and 1 if a particle forms a bond. In a complete analogy with the ROZ formalism of section 2 the blocked and

connected parts in equations (43)–(46) are defined and related as:

$$h_{ff}^{\alpha\beta} = h_C^{\alpha\beta} + h_B^{\alpha\beta} \quad (47)$$

$$c_{ff}^{\alpha\beta} = c_C^{\alpha\beta} + c_B^{\alpha\beta} \quad (48)$$

and their physical meaning is the same as for the ROZ equations as discussed elsewhere. The matrix of density terms in equations (43)–(46) is:

$$\rho_f^{\alpha\beta} = \begin{pmatrix} \rho_f^{00} & \rho_f^{01} \\ \rho_f^{10} & \rho_f^{11} \end{pmatrix} = \begin{pmatrix} \rho_f & \rho_f^0 \\ \rho_f^0 & 0 \end{pmatrix}, \quad (49)$$

where ρ_f^0 is the number density of monomers. Following the original Wertheim prescription, there must be a self-consistent relationship for the densities:

$$\rho_f = \rho_f^0 + (\rho_f^0)^2 \int dr F_{ff}^A y_{ff}^{11}, \quad (50)$$

where y_{ff}^{11} is the cavity distribution function for the confined fluid species.

Similarly to the standard OZ approach, solution of equations (43)–(46) must be accompanied by the corresponding closures. Associative, or polymer, Percus–Yevick has been proposed following the original Wertheim development [83]; however, for studies of confined fluids the associative version of the hypernetted chain closure (AHNC) is more adequate. For fluid–matrix correlations this closure reads:

$$c_{fm}^0 = (1 + f_{fm}) \exp(\gamma_{fm}^0) - 1 - \gamma_{fm}^0 \quad (51)$$

$$c_{fm}^1 = (1 + f_{fm}) \exp(\gamma_{fm}^0) \gamma_{fm}^0 - \gamma_{fm}^0, \quad (52)$$

where, $\gamma = h - c$, following the notation adopted throughout the article. Again, in the spirit of the Wertheim theory these two equations represent two variations of the closure, one written for the fluid particles in the form of monomers and the other for the fluid particles that have bonds associated with them. Similarly, for fluid–fluid correlations:

$$c_{ff}^{00} = (1 + f_{ff}^R) \exp(\gamma_{ff}^{00}) - 1 - \gamma_{ff}^{00} \quad (53)$$

$$c_{ff}^{10} = (1 + f_{ff}^R) \exp(\gamma_{ff}^{00}) \gamma_{ff}^{10} - \gamma_{ff}^{10} \quad (54)$$

$$c_{ff}^{11} = (1 + f_{ff}^R) \exp(\gamma_{ff}^{00}) \left((\gamma_{ff}^{10})^2 + \gamma_{ff}^{11} \right) - \gamma_{ff}^{11} + \exp(\gamma_{ff}^{11}) F_{ff}^A. \quad (55)$$

For the blocking direct correlation functions these equations simplify to:

$$c_B^{00} = \exp(\gamma_B^{00}) - 1 - \gamma_B^{00} \quad (56)$$

$$c_B^{10} = \exp(\gamma_B^{00}) \gamma_B^{10} - \gamma_B^{10} \quad (57)$$

$$c_B^{11} = \exp(\gamma_B^{00}) \left((\gamma_B^{10})^2 + \gamma_B^{11} \right) - \gamma_B^{11}. \quad (58)$$

Partial matrix–fluid and fluid–fluid correlations calculated from equations (43)–(46) can be combined to produce the complete correlation functions, for example:

$$h_{fm} = h_{fm}^0 + x_f h_{fm}^1 \quad (59)$$

$$h_{ff} = h_{ff}^{00} + 2x_f h_{ff}^{10} + x_f^2 h_{ff}^{11}, \quad (60)$$

where

$$x_f = \frac{\rho_f^0}{\rho_f} \quad (61)$$

is the fraction of monomer fluid particles.

Again the correlation functions obtained in this fashion have to be linked to the thermodynamic properties of the system with the compressibility route being one of the possible options:

$$\beta \left(\frac{\partial P}{\partial \rho_f} \right)_T = 1 - \rho_f \int dr c_C. \quad (62)$$

These are the basic elements of the theory of associating fluids confined in a matrix formed by quenched particles. In the original article of Trokhymchuk *et al* [84], the theory was applied to Kaminsky and Monson (KM) model, proposed for studies of methane adsorption in xerogels [12–15]. It has been demonstrated that dimerization of fluid particles in KM matrix increases with the adsorbed fluid density and that this effect is more pronounced in matrices with higher densities and at lower temperatures of the system. The structure of dimerizing fluid in hard sphere matrices has been also explored and compared with Monte Carlo simulation. In particular, an assessment of the associative PY and HNC closure was made and it was concluded that the associative HNC closure performs better in the prediction of the structure of dimerizing fluids. Structure, adsorption and vapour–liquid phase behaviour of dimerizing hard disks in a hard disk matrix has also been investigated [85]. The issue of dimerizing fluid has been revisited by Padilla *et al* for the case of hard sphere particles dimerizing in disordered hard sphere matrices [86].

This approach also opened a possibility of studying a range of associating models and systems. One particularly interesting model is a model of water proposed by Nezbeda and co-workers [87–89]. In this model a hard sphere particle is decorated with four interaction sites of two different types in tetrahedral arrangement. As a result, the model is capable of imitating the network of hydrogen bonds in water. Orozco and co-workers and Kovalenko and Pizio adopted this model to study its properties under confinement within the AROZ formalism [90, 91]. Other models constructed in the same spirit ensued. Polymerization of two binding site model in bulk has been investigated by Chang and Sandler [92, 93], whereas Pizio and co-workers investigated properties of this model under confinement [94]. In the work of Pizio and co-workers, matrix particles were either impermeable to the fluid species or permeable so that the surface of a matrix particle behaves as a permeable membrane of a finite width. A particularly interesting analysis in that work is related to the behaviour of the partitioning coefficient as a function of the adsorbed fluid chemical potential. The partition coefficient is simply a ratio of adsorbed fluid density and the corresponding bulk density at the same chemical potential. In the absence of polymerization this is a monotonously increasing function of the chemical potential. Polymerization, however, leads to formation of bulky chains. Formation of these chains is also promoted by higher fluid density. As a result, the partition coefficient for polymerizing species exhibit a characteristic minimum at a certain value of chemical potential. This minimum is lower

and shifted to lower value of chemical potential as the strength of association is increased.

In general, all these models of associating fluids in a disordered quenched matrices exhibit several common features that are summarized here. Stronger association leads to higher adsorbed densities at a given chemical potential. The critical temperature of the vapour–liquid transition also increases with the stronger association. At the same time confinement, in general, suppresses the transition leading to a lower critical temperature. Thus, the two factors (association and confinement) work in opposite directions and a number of interesting effects are induced by this competition.

Recently, more studies of water under confinement emerged. This is important for a number of technological applications such as adsorption, drying and polyelectrolyte membranes. On the other hand, the interior space of a living cell is a very crowded environment and properties of water in this environment are also affected by confinement. Thus, studies of water confined in disordered morphologies are important in understanding cell functions. One example of theoretical studies of confined water, provided by Kovalenko and Hirata [50], has already been discussed in the previous section. Recently, Urbic *et al* applied the AROZ formalism to study properties of two dimensional water particles in a system of quenched Lennard-Jones disks [95]. Their model of water is a Lennard-Jones disk with three radial arms in Mercedes-Benz logo arrangement to form hydrogen bonds (hence the name Mercedes-Benz model). The model, originally proposed by Ben-Naim [96], is able to predict density anomaly, minimum in isothermal compressibility as a function of temperature and other qualitative features of water. Having a relatively small number of quenched Lennard-Jones obstacles in the system induces more order in the structure of the system and increased compressibility, in agreement with simulation studies and experiments. However, in a high density matrix the trends reverse, leading to a reduction of order in the structure of the fluid and a reduction of compressibility. This effect is associated with the disruption of the hydrogen bond network at higher densities of quenched obstacles.

The AROZ approach is general and flexible in considering a range of other systems and scenarios. For example, an effect of matrix polymerization (as oppose to fluid species) has been investigated by Labik *et al* [94]. Apparently, matrix polymerization leads to a more compact solid material and more open porous space. As a result adsorption is enhanced for highly polymerized structures. A recent article by Malo *et al* [97] can be considered as a variation of this study, where adsorption of a hard sphere fluid is considered in a disordered quenched matrix of short chain molecules. Furthermore, one can consider a strong association between matrix and fluid species [98]. On one hand this is an interesting case that models behaviour of adlayers in the case of strong matrix–fluid interactions. On the other hand, models such as KM, where there is a strong interaction between matrix and fluid and at the same time significant size differences between fluid and matrix particles, pose a significant challenge for the conventional ROZ methods, with the solutions available only in high temperature, low density regions. The AROZ treatment of this system may

alleviate this problem. Indeed, Trokhymchuk and co-workers analyzed matrix–fluid and fluid–fluid two particle correlation functions and found them in a reasonable agreement with the Monte Carlo simulation results even for relatively high fluid densities [98].

5. Perspectives

The adsorption of molecular species within disordered porous materials is of great importance to a number of natural and industrial processes. Modelling approaches tend to be significantly more complex than those of bulk molecular fluids or even molecular fluids within crystalline materials, owing to the need to accurately account for pore structure. The pore space generally forms in the absence of the fluid phase, and so a challenge in terms of traditional molecular simulation is to average over a sufficient number of material configurations. It is in this respect that approaches based on the replica Ornstein–Zernike (OZ) method are so valuable. Since properties of the quenched–annealed system are expressed in terms of those of a related fully annealed replica system, the resulting integral equations are no more complicated than those of a mixture. Thus, while enhanced computational resources during the last few decades have resulted in the use of theoretical methods, especially those based on OZ equations, declining somewhat in the face of burgeoning molecular computer simulation studies, OZ-based approaches may find their most important modern application to be molecular adsorption in disordered materials.

That said, key challenges remain in adapting replica OZ methods to realistically structured molecular systems. All of the challenges addressed earlier in the study of the liquid state—e.g. choice of closure and thermodynamic route, handling/avoiding thermodynamic inconsistency—must be addressed for these new systems. To date, most efforts along these lines have been in the context of atomic (i.e. spherically symmetric) systems. Especially challenging may be developing closures for the fluid–fluid ‘blocking’ or template–fluid correlation functions, where the intermolecular potential is identically zero. These highly asymmetric mixtures differ considerably from those upon which bulk system closures have been historically developed. In addition, classical closures such as PY neglect these correlations, an obvious oversimplification. Adding to the challenge is the frequent need to employ non-equilibrium material structures. Ultimately, one would like clear guidelines towards accurate closure relations and, in the presence of thermodynamic inconsistencies, appropriate thermodynamic routes, for a given set of system specifics. While significant, it would appear this task is roughly on the same scale as developing transferable intermolecular potentials capable of describing thermodynamic and structural properties of a variety of chemical species—an effort that is ongoing in several groups with many promising results.

Some of the most interesting developments in material science are anticipated to occur in the field of porous materials with tailored characteristics and functionalities. Quite often, a particular functionality of a porous material is a result of strong and specific interactions between the material and adsorbate

molecules. For example, the aforementioned imprinted polymers are capable of molecular recognition based on structural complementarity and strong interactions between the guest molecule and the substrate. In order to develop integral equation descriptions of these phenomena, it is important to include in the theory both an appropriate treatment of the molecular species and the possibility of strong associations between matrix and adsorbate species. Naturally, this suggests some combination of the site–site methods for quenched–annealed systems and theories of association covered in this review. Again, the development of these approaches will be accompanied by a number of difficulties characteristic of all integral equation methods, including availability of appropriate closures and thermodynamic consistency, convergence issues and the approximate nature of site–site theories. However, because of the limitations inherent to simulation, we believe that such theories are worth the effort and offer great promise towards the development of novel, molecularly tailored porous structures.

Acknowledgments

The authors thankfully acknowledge the financial support of the Engineering and Physical Sciences Research Council through grant no. EP/D074762/01 and the US National Science Foundation through grant no. CTS-0337829.

References

- [1] Barton T J, Bull L M, Klemperer W G, Loy D A, McEnaney B, Misono M, Monson P A, Pez G, Scherer G W, Vartuli J C and Yaghi O M 1999 *Chem. Mater.* **11** 2633–56
- [2] Gelb L D, Gubbins K E, Radhakrishnan R and Sliwinski-Bartkowiak M 1999 *Rep. Prog. Phys.* **62** 1573–659
- [3] Fuchs A H and Cheetham A K 2001 *J. Phys. Chem. B* **105** 7375–83
- [4] Tarazona P, Marconi U M B and Evans R 1987 *Mol. Phys.* **60** 573–95
- [5] Ball P C and Evans R 1988 *Mol. Phys.* **63** 159–63
- [6] Evans R 1990 *J. Phys.: Condens. Matter* **2** 8989–9007
- [7] Neimark A V, Ravikovitch P I, Grun M, Schuth F and Unger K K 1998 *J. Colloid Interface Sci.* **207** 159–69
- [8] Ravikovitch P I, Haller G L and Neimark A V 1998 *Adv. Colloid Interface Sci.* **77** 203–26
- [9] Ravikovitch P I and Neimark A V 2001 *J. Phys. Chem. B* **105** 6817–23
- [10] Ravikovitch P I and Neimark A V 2002 *Langmuir* **18** 1550–60
- [11] Brinker C J and Scherer G W 1990 *Sol–Gel Science: The Physics and Chemistry of Sol–Gel Processing* (New York: Academic)
- [12] Kaminsky R D and Monson P A 1991 *J. Chem. Phys.* **95** 2936–48
- [13] Vega C, Kaminsky R D and Monson P A 1993 *J. Chem. Phys.* **99** 3003–13
- [14] Kaminsky R D and Monson P A 1994 *Langmuir* **10** 530–7
- [15] Kaminsky R D and Monson P A 1994 *Chem. Eng. Sci.* **49** 2967–77
- [16] Macelroy J M D and Raghavan K 1990 *J. Chem. Phys.* **93** 2068–79
- [17] McGreevy R L and Pusztai L 1988 *Mol. Simul.* **1** 359–67
- [18] McGreevy R L, Howe M A, Keen D A and Clausen K N 1990 *Inst. Phys. Conf. Ser.* 165–84
- [19] McGreevy R L and Howe M A 1992 *Annu. Rev. Mater. Sci.* **22** 217–42
- [20] Walters J K, Rigden J S and Newport R J 1995 *Phys. Scr. T* **57** 137–41
- [21] O'Malley B, Snook I and McCulloch D 1998 *Phys. Rev. B* **57** 14148–57
- [22] Thomson K T and Gubbins K E 2000 *Langmuir* **16** 5761–73
- [23] Pikunic J, Clinard C, Cohaut N, Gubbins K E, Guet J M, Pellenq R J M, Rannou I and Rouzaud J N 2003 *Langmuir* **19** 8565–82
- [24] MacFarland T, Barkema G T and Marko J F 1996 *Phys. Rev. B* **53** 148–58
- [25] Gelb L D and Gubbins K E 1998 *Langmuir* **14** 2097–111
- [26] Gelb L D and Gubbins K E 1999 *Langmuir* **15** 305–8
- [27] Alexander C, Andersson H S, Andersson L I, Ansell R J, Kirsch N, Nicholls I A, O'Mahony J and Whitcombe M J 2006 *J. Mol. Recognit.* **19** 106–80
- [28] Van Tassel P R 1999 *Phys. Rev. E* **60** R25–8
- [29] Zhang L H and Van Tassel P R 2000 *Mol. Phys.* **98** 1521–7
- [30] Zhang L H and Van Tassel P R 2000 *J. Chem. Phys.* **112** 3006–13
- [31] Cheng S and Van Tassel P R 2001 *J. Chem. Phys.* **114** 4974–81
- [32] Zhang L H, Cheng S Y and Van Tassel P R 2001 *Phys. Rev. E* **64** 044004
- [33] Madden W G and Glandt E D 1988 *J. Stat. Phys.* **51** 537–58
- [34] Fanti L A, Glandt E D and Madden W G 1990 *J. Chem. Phys.* **93** 5945–53
- [35] Madden W G 1992 *J. Chem. Phys.* **96** 5422–32
- [36] Given J A and Stell G 1992 *J. Chem. Phys.* **97** 4573–4
- [37] Given J A and Stell G R 1994 *Physica A* **209** 495–510
- [38] Rosinberg M L, Tarjus G and Stell G 1994 *J. Chem. Phys.* **100** 5172–7
- [39] Given J A 1995 *J. Chem. Phys.* **102** 2934–45
- [40] Edwards S F and Anderson P W 1975 *J. Phys. F: Met. Phys.* **5** 965–74
- [41] Edwards S F and Anderson P W 1976 *J. Phys. F: Met. Phys.* **6** 1927–37
- [42] Hansen J-P and McDonald I R 1986 *Theory of Simple Liquids* (New York: Academic)
- [43] Feraud M J, Lomba E and Lee L L 1999 *J. Chem. Phys.* **111** 10275–86
- [44] Feraud M J, Lomba E and Weis J J 2001 *Phys. Rev. E* **64** 054005
- [45] Chandler D and Andersen H C 1972 *J. Chem. Phys.* **57** 1930
- [46] Chandler D 1973 *J. Chem. Phys.* **59** 2742–6
- [47] Cummings P T and Stell G 1982 *Mol. Phys.* **46** 383–426
- [48] Monson P A and Morriss G P 1990 *Adv. Chem. Phys.* **77** 451–550
- [49] Schweizer K S and Curro J G 1987 *Phys. Rev. Lett.* **58** 246–9
- [50] Kovalenko A and Hirata F 2001 *J. Chem. Phys.* **115** 8620–33
- [51] Kovalenko A and Hirata F 1999 *J. Chem. Phys.* **110** 10095–112
- [52] Tanimura A, Kovalenko A and Hirata F 2003 *Chem. Phys. Lett.* **378** 638–46
- [53] Tanimura A, Kovalenko A and Hirata F 2007 *Langmuir* **23** 1507–17
- [54] Chandler D 1991 *J. Phys.: Condens. Matter* **3** F1–8
- [55] Thompson A P and Glandt E D 1993 *J. Chem. Phys.* **99** 8325–9
- [56] Thompson A P and Glandt E D 1996 *Macromolecules* **29** 4314–23
- [57] Yethiraj A 2002 *J. Chem. Phys.* **116** 5910–1
- [58] Sung B J and Yethiraj A 2005 *J. Chem. Phys.* **123** 074909
- [59] Sarkisov L and Van Tassel P R 2005 *J. Chem. Phys.* **123** 164706
- [60] Sarkisov L and Van Tassel P R 2007 *J. Phys. Chem. C* **111** 15726–35
- [61] Sarkisov L 2008 *J. Chem. Phys.* **128** 044707
- [62] Coniglio A, Deangelis U and Forlani A 1977 *J. Phys. A: Math. Gen.* **10** 1123–39
- [63] Coniglio A, Deangelis U, Forlani A and Lauro G 1977 *J. Phys. A: Math. Gen.* **10** 219–28

- [64] Chiew Y C and Glandt E D 1983 *J. Phys. A: Math. Gen.* **16** 2599–608
- [65] Stell G 1984 *J. Phys. A: Math. Gen.* **17** L855–8
- [66] Bug A L R, Safran S A, Grest G S and Webman I 1985 *Phys. Rev. Lett.* **55** 1896–9
- [67] Chiew Y C, Stell G and Glandt E D 1985 *J. Chem. Phys.* **83** 761–7
- [68] Desimone T, Demoulini S and Stratt R M 1986 *J. Chem. Phys.* **85** 391–400
- [69] Lupkowski M and Monson P A 1988 *J. Chem. Phys.* **89** 3300–7
- [70] Leung K and Chandler D 1991 *J. Stat. Phys.* **63** 837–56
- [71] Chandler D, Silbey R and Ladanyi B M 1982 *Mol. Phys.* **46** 1335–45
- [72] Pratt L R and Chandler D 1977 *J. Chem. Phys.* **66** 147–51
- [73] Pratt L R and Chandler D 1977 *J. Chem. Phys.* **67** 3683–704
- [74] Chandler D and Pratt L R 1976 *J. Chem. Phys.* **65** 2925–40
- [75] Cummings P T and Stell G 1985 *Mol. Phys.* **55** 33–48
- [76] Cummings P T and Stell G 1984 *Mol. Phys.* **51** 253–87
- [77] Henderson D, Patrykiewicz A, Pizio O and Sokolowski S 1996 *Physica A* **233** 67–76
- [78] Wertheim M S 1986 *J. Chem. Phys.* **85** 2929–36
- [79] Wertheim M S 1987 *J. Chem. Phys.* **87** 7323–31
- [80] Wertheim M S 1986 *J. Stat. Phys.* **42** 459–76
- [81] Wertheim M S 1986 *J. Stat. Phys.* **42** 477–92
- [82] Wertheim M S 1984 *J. Stat. Phys.* **35** 19–34
- [83] Wertheim M S 1984 *J. Stat. Phys.* **35** 35–47
- [84] Trokhymchuk A, Pizio O, Holovko M and Sokolowski S 1997 *J. Chem. Phys.* **106** 200–9
- [85] Pizio O, Duda Y, Trokhymchuk A and Sokolowski S 1998 *J. Mol. Liq.* **76** 183–94
- [86] Padilla P, Pizio O, Trokhymchuk A and Vega C 1998 *J. Phys. Chem. B* **102** 3012–7
- [87] Smith W R and Nezbeda I 1984 *J. Chem. Phys.* **81** 3694–9
- [88] Nezbeda I, Kolafa J and Kalyuzhnyi Y V 1989 *Mol. Phys.* **68** 143–60
- [89] Kolafa J and Nezbeda I 1987 *Mol. Phys.* **61** 161–75
- [90] Orozco G A, Pizio O, Sokolowski S and Trokhymchuk A 1997 *Mol. Phys.* **91** 625–34
- [91] Kovalenko A and Pizio O 1998 *J. Chem. Phys.* **108** 8651–61
- [92] Chang J E and Sandler S I 1995 *J. Chem. Phys.* **102** 437–49
- [93] Chang J and Sandler S I 1995 *J. Chem. Phys.* **103** 3196–211
- [94] Pizio O, Trokhymchuk A, Henderson D and Labik S 1997 *J. Colloid Interface Sci.* **191** 86–94
- [95] Urbic T, Vlachy V, Pizio O and Dill K A 2004 *J. Mol. Liq.* **112** 71–80
- [96] Bennaïm A 1971 *J. Chem. Phys.* **54** 3682
- [97] Malo B M, Pizio O, Trokhymchuk A and Duda Y 1999 *J. Colloid Interface Sci.* **211** 387–94
- [98] Trokhymchuk A, Pizio O, Holovko M and Sokolowski S 1996 *J. Phys. Chem.* **100** 17004–10