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Abstract. The reference interaction site method (RISM) may be applied to polyatomic fluids sorbed by quenched materials. Formal aspects of such applications are discussed. Connections with and generalizations of the theory of Madden and Glandt are made.

1. Introduction

It is a pleasure to participate both in this Collection as well as in the Symposium honouring Peter Egelstaff. His enthusiasm and experimentation played a large role in motivating me and my generation to study the liquid state. For this collection of papers commemorating that Symposium, I wish to propose here a new use of the RISM equations [3]. Early applications of the RISM theory [4] were devoted to explaining the first neutron scattering experiments on molecular fluids, experiments that Peter Egelstaff had performed [5]. Calculations have not yet been done with what I now propose, but the structural predictions that will follow may be a stimulus for future neutron scattering experiments.

Madden and Glandt have derived and applied a theory for the equilibrium properties of simple atomic fluids sorbed by quenched amorphous materials [6, 7]. As we shall see, their theory may be viewed heuristically from the RISM perspective. From this view there is an apparent generalization to the case of polyatomic fluids in equilibrium with amorphous solids. This generalization is the subject of this article.

The development begins in section 2 where the general reduction of $N \times N$ RISM equations is discussed. This reduction is used profitably in RISM theories of polymers and electrons [9–11]. In the current context, it facilitates an approach in which a quenched material is treated as a single macroscopic molecule. This approach is put forth in section 3. The treatment of flexible polyatomic sorbates is discussed in section 4. A variational principle for solving the associated RISM equations is presented in section 5. A final discussion is presented in section 6.

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† Editor's note: the talk given by Chandler at the Egelstaff Symposium was on the structure and dynamics of electron transfer in aqueous solutions. However, since this work had already been published and reviewed in the Proceedings of the Lyon Liquid Matter Conference [1, 2], the following original paper was accepted in lieu of a conference paper, as it represents the profound influence that interaction with Peter Egelstaff has had on the career of the author.

2. Reduced RISM equations

The Ornstein–Zernike-like equation of Chandler and Andersen [3],

$$h = \omega c \omega + \omega c \rho h = \omega c [1 - \rho \omega c]^{-1} \omega = \omega c \omega + \omega c \rho \omega c \omega + \omega c \rho \omega c \rho \omega c \omega + \cdots \quad (2.1)$$

expresses the intermolecular site–site pair correlation function, $h_{\alpha M \gamma M'}(|r - r'|)$, in terms of the molecular densities, ρ_M, the intra-molecular pair correlation function,

$$\omega_{\alpha \gamma, M}(|r - r'|) = \langle \delta(r_{1M}^{(\alpha)} - r_{1M}^{(\gamma)} - r + r') \rangle \quad (2.2)$$

where $r_{iM}^{(\alpha)}$ is the position of the αth site in the ith molecule of type M, and the site-site direct correlation function $c_{\alpha M \gamma M'}(|r - r|)$. The abbreviated matrix notation was used in (2.1) [8]. Multiplication refers to convolutions in real space (or products in Fourier space), sums over site labels (the Greek subscripts) and sums over species labels (the capital Roman subscripts). The ω matrix is diagonal in M with elements (2.2), and the ρ matrix is diagonal in M and r with element ρ_M. The pointed brackets in (2.2) indicate ensemble average.

In terms of diagrams, (2.1) is the sum of all simple connected chains with c-bonds denoting the c-functions and ω-hypervertices denoting the ω-functions [8, 12]. In what follows, we will refer to this representation, and often partition the sum of all chains into subsets catalogued by the respective numbers of specific ω-functions.

The Chandler–Andersen equation is closed by specifying an additional connection between h and c. The mean spherical approximation (MSA) is one specific class of closures:

$$h_{\alpha M \gamma M'}(r) = -1 \qquad r < d_{\alpha M \gamma M'} \quad (2.3a)$$

and

$$c_{\alpha M \gamma M'}(r) = \phi_{\alpha M \gamma M'}(r) \qquad r > d_{\alpha M \gamma M'} \quad (2.3b)$$

where $d_{\alpha M \gamma M'}$ are distances of closest approach and $\phi_{\alpha M \gamma M'}(r)$ is a specified interaction (in units of $-k_B T$). Relations (2.1)–(2.3) are examples of RISM equations.

Consider their implementation for a one-component fluid, each molecule of which contains N sites. The equations involve $N \times N$ matrices. With N very large, the equations are generally intractable. If, however, there are only a few non-equivalent types among this large number, the RISM equations simplify considerably. For example, consider a melt of linear polymers with N identical monomer units. With N large enough, the vast majority of sites are far from chain ends. As a result,

$$h_{\alpha \gamma}(r) = h(r) \qquad \text{for nearly all } \alpha \gamma \quad (2.4)$$

where

$$h(r) = \frac{1}{N^2} \sum_{\alpha, \gamma} h_{\alpha \gamma}(r) \quad (2.5)$$

and we have dropped the species label M for convenience. Similarly,

$$c_{\alpha \gamma}(r) = c(r) \qquad \text{for nearly all } \alpha \gamma. \quad (2.6)$$

By employing the simplifications (2.4) and (2.6) in (2.1), we arrive at

$$h(r) = \frac{1}{N^2} \sum_{\alpha,\gamma,\eta,\lambda} [\omega_{\alpha\eta} * c * \omega_{\lambda\gamma}(r) + \rho_M \omega_{\alpha\eta} * c * h_{\lambda\gamma}(r)]$$

$$= \omega * c * \omega(r) + \rho\omega * c * h(r) = \rho^{-1}\omega * c * \chi(r) \tag{2.7}$$

which is a valid reduction in the limit of large N. In this equation we have introduced $\rho = N\rho_M$ which is the average density of monomer units, $\chi(r)$ which is the monomer density–density correlation function, and

$$\omega(r) = \frac{1}{N} \sum_{\alpha,\gamma=1}^{N} \omega_{\alpha\gamma}(r). \tag{2.8}$$

Equation (2.7) does not involve a matrix of functions, but only the scalars $h(r)$, $c(r)$ and $\omega(r)$. The reduced RISM equation is therefore tractable. It depends upon N only implicitly through $\omega(r)$.

Generalizations of (2.7) to block copolymers and/or to melts of a few components are straightforward and equally tractable. These equations form the basis of the RISM theories of polymers [9, 10]. Equation (2.7) is also a basic part of the RISM-polaron theory of solvated electrons [11]. In the next section, reduced RISM equations will be derived in yet another context.

3. Quenched amorphous materials as a supermolecule

Consider a liquid sorbed by an amorphous solid. We will assume that the fluid is at equilibrium, and that the structure of the disordered porous material is essentially quenched. On large length scales, this non-equilibrium system is homogeneous. We shall view the solid material as one huge ubiquitous molecule. The Fourier transform of its ω-function, (2.8), is the structure factor of the material

$$\hat{\omega}_m(k) = \frac{1}{N} \sum_{\alpha,\gamma=1}^{N} \langle \exp[i k \cdot (r_m^{(\alpha)} - r_m^{(\gamma)})]\rangle_m. \tag{3.1}$$

The positions of the material sites, $\{r_m^{(\alpha)}\}$, are characterized statistically by a distribution which is unaffected by the fluid. The angular brackets, $\langle\ldots\rangle_m$, indicate the average over that distribution. The resulting $\hat{\omega}_m(k)$ is independent of the orientation of k.

With this perspective, we construct a reduced RISM equation. For simplicity, consider a solid material where there is only one non-equivalent site. While macroscopic in extent, there is but one material 'molecule' in the system. As such, the chains to be summed in (2.1) should contain no more than one ω_m-function. In particular, for a simple one-component atomic fluid of density ρ_f, this consideration yields

$$\hat{h}_{fm}(k) = \hat{c}_{fm}(k)\hat{\omega}_m(k) + \hat{c}_{ff}(k)\rho_f \hat{c}_{fm}(k)\hat{\omega}_m(k) + \hat{c}_{ff}^2(k)\rho_f^2 \hat{c}_{fm}(k)\hat{\omega}_m(k) + \cdots$$

$$= [1 + \rho_f \hat{C}_{ff}(k)]\hat{c}_{fm}(k)\hat{\omega}_m(k) \tag{3.2}$$

where

$$\hat{C}_{ff}(k) = \hat{c}_{ff}(k)[1 - \rho_f \hat{c}_{ff}(k)]^{-1}. \tag{3.3}$$

Here, $c_{ff}(r)$ is the direct correlation function between pairs of fluid particles, and $\hat{c}_{ff}(k)$ is its Fourier transform; $h_{fm}(r)$ and $c_{fm}(r)$ refer to the pair correlation function and direct correlation function, respectively, between a fluid particle and any of the material sites. Since the N sites are all equivalent, $h_{fm}(r)$ and $c_{fm}(r)$ are independent of a specific site label. Equation (3.2) is derived by summing over all equivalent sites as exhibited in (2.7). Similarly, consider the contribution to the fluid–fluid pair correlation function, $h_{ff}(r)$, from chains with two c-functions and one ω-function:

$$\sum_{\alpha,\gamma} \hat{c}_{fm}(k)\frac{1}{V}\hat{\omega}_{\alpha\gamma}(k)\hat{c}_{mf}(k) = \hat{c}_{fm}^2(k)\rho_m\hat{\omega}_m(k) \tag{3.4}$$

where $\rho_m = N/V$ is the density of sites comprising the material. The sum over all such chains with no or one ω_f-function yields

$$\hat{h}_{ff} = \hat{C}_{ff}(k) + [1 + \rho_f\hat{C}_{ff}(k)]^2\hat{c}_{fm}^2(k)\rho_m\hat{\omega}_m(k). \tag{3.5}$$

Equations (3.2) and (3.5) are Madden and Glandt's Ornstein–Zernike-type equations for an atomic fluid in equilibrium with a porous material [6, 7]. In the notation of [6] and [7], $\hat{\omega}_m(k)$ corresponds to $1/[1 - \rho_m\hat{c}_{mm}(k)]$. Notice that the term containing $\hat{\omega}_m(k)$ in (3.5) would not contribute if the material was confined to an infinitesimal fraction of the volume available to the fluid. In that case, $c_{ff}(r)$ would be the pure bulk fluid direct correlation function, and the Madden–Glandt equations would reduce to more standard Ornstein–Zernike or Chandler–Andersen equations. This limit would be pertinent if, for example, the material were confined to a planar region as might be done to treat a fluid in equilibrium with a surface.

Also notice that $C_{ff}(r)$ plays no role in (3.2) when $\rho_f \to 0$. In that case, (3.2) coincides with the Ornstein–Zernike equation for a fluid at low concentrations in equilibrium with an *annealed* material with density–density correlation function $\rho_m\omega_m(|r - r'|)$. This correspondence is the correct result in this limit. In particular, consider the statistical behaviour of a single molecule in a macroscopic equilibrium material. It is the same as that for a single molecule that is allowed to equilibrate to (i.e., wander throughout) a rigid system whose configuration is one member of its own equilibrium ensemble.

4. Flexible polyatomic molecules in equilibrium with quenched material

Madden and Glandt's derivation [6, 7] of (3.2) and (3.5) is based upon a topological reduction of the cluster series for a fluid perturbed by a quenched material. The heurestic derivation given in the previous section suggests a generalization of the Madden–Glandt equations appropriate for polyatomic fluids. Specifically, in the chain sums for this more general case, the ω-functions of the fluid molecules, $\omega_{ff'}(r)$, should appear at the fluid particle vertices. The subscripts f and f' refer to the finite number of sites in the polyatomic fluid molecules. The sums of all chains with no ω_m-functions now become the matrix of functions given in k-space by

$$\hat{C}(k) = \hat{\omega}(k)\hat{c}(k)[1 - \rho_f\hat{\omega}(k)\hat{c}(k)]^{-1}\hat{\omega}(k) \tag{4.1}$$

where $\hat{\omega}(k)$ is the matrix with elements $\hat{\omega}_{ff'}(k)$, similarly, $\hat{c}(k)$ refers to the direct correlation functions, $\hat{c}_{ff'}(k)$. With this notation, the sums with one or no ω_m-function yield

$$\hat{h}_{fm}(k) = \sum_{f'} [\hat{\omega}_{ff'}(k) + \rho_f \hat{C}_{ff'}(k)] \hat{c}_{f'm}(k) \hat{\omega}_m(k) \tag{4.2}$$

and

$$\hat{h}_{ff'}(k) = \hat{C}_{ff'}(k) + \sum_{f''f'''} [\hat{\omega}_{ff''}(k) + \rho_f \hat{C}_{ff''}(k)]$$

$$\times \hat{c}_{f''m}(k) \rho_m \hat{\omega}_m(k) \hat{c}_{mf'''}(k) [\hat{\omega}_{f'''f'}(k) + \rho_f \hat{C}_{f'''f'}(k)] \tag{4.3}$$

The sums over f', f'' and f''' span the sites of the polyatomic fluid molecule. Note that $c_{fm}(r) = c_{mf}(r)$.

Equations (4.2) and (4.3) are the polyatomic fluid generalizations of (3.2) and (3.5). Obvious extensions of (3.7) and (3.8) include the case of a multi-component fluid.

With closure relations such as (2.3), these equations can be solved for the pair correlation functions $h_{fm}(r)$ and $h_{ff'}(r)$ in terms of $\omega_{ff'}(r)$ and $\omega_m(r)$. When the polyatomic molecules are flexible compounds, their ω-functions could differ substantially from those of the free molecule. To compute the influence of the environment on $\omega_{ff'}(r)$, note that the full n-site intra-molecular distribution is given by

$$s(r^{(1)}, \ldots, r^{(n)}) = c s^{(0)}(r^{(1)}, \ldots, r^{(n)}) y(r^{(1)}, \ldots, r^{(n)}) \tag{4.4}$$

where $s^{(0)}(r^{(1)}, \ldots)$ is the free molecule distribution, $y(r^{(1)}, \ldots)$ is the cavity distribution function or influence functional [13, 14], and c is the normalization constant. The integrating of $s(r^{(1)}, \ldots)$ over all coordinates except $r^{(f)}$ and $r^{(f')}$ yields $\omega_{ff'}(|r^{(f)} - r^{(f')}|)$. In practice, this integration can be simplified by considering only the relatively few accessible conformations.

Possible uncertainties in the y-functions can be the most serious obstacle in employing (4.4). For this problem, a reasonable solution may be the estimate that has proven useful for isomorphic electron polymers [11, 15],

$$y(r^{(1)}, \ldots, r^{(n)}) \approx \exp \left\{ \frac{1}{2} \sum_{f,f'=1}^{n} v_{ff'}(|r^{(f)} - r^{(f')}|) \right\} \tag{4.5}$$

where $v_{ff'}(r)$ is the solvent induced interaction (in units of $-k_B T$) between sites f and f'. This interaction is akin to a reaction field coupling between pairs of sites. As such, its topological structure should be chains originating with a c-bond at one site and ending with a c-bond at the other; in between, there should be at least one sorbate or material site. The sum of all these chains is

$$\hat{v}_{ff'}(k) = [\hat{\omega}^{-1}(k) \hat{C}(k) \rho_f \hat{c}(k)]_{ff'} + \sum_{f''f'''} [1 + \rho_f \hat{\omega}^{-1}(k) \hat{C}(k)]_{ff''}$$

$$\times \hat{c}_{f''m}(k) \rho_m \hat{\omega}_m(k) \hat{c}_{mf'''}(k) [1 + \rho_f \hat{C}(k) \hat{\omega}^{-1}(k)]. \tag{4.6}$$

The inverse ω-matrices insure that the chains begin and end with c-functions and not ω-functions. Equation (4.6) applies to the fluid in equilibrium with the quenched material. It generalizes formulae pertaining to annealed surroundings. Compare it, for example, with (6.10) of [15].

This estimate of the intramolecule structure is a self-consistent theory. The c-functions depend upon the ω-functions through the solutions to (4.2) and (4.3) and their closures. The ω-functions depend upon the c-functions through (4.4)-(4.6).

5. Variational principle

Consider now the method of solving (4.2) and (4.3) with the specific closure (2.3). A variational procedure follows from the observation that

$$\delta I/\delta c_{fm}(r) = 2\rho_m[1 + h_{fm}(r)] \tag{5.1a}$$

and

$$\delta I/\delta c_{ff'}(r) = \rho_f[1 + h_{ff'}(r)] \tag{5.1b}$$

with

$$I = \int dr \left[\rho_f \sum_{f,f'} c_{ff'}(r) + 2\rho_m \sum_f c_{fm}(r) \right] - \frac{1}{\rho_f(2\pi)^3}$$

$$\times \int dk \left\{ \text{tr } \rho_f \hat{\omega}(k) c(k) + \ln \det[1 - \rho_f \hat{\omega}(k)\hat{c}(k)] \right.$$

$$\left. - \rho_f \sum_{f,f'} \hat{c}_{f'm}(k)\rho_m \hat{\omega}_m(k)\hat{c}_{mf}(k)[\hat{\omega}(k)(1 - \rho_f \hat{c}(k)\hat{\omega}(k))^{-1}]_{ff'} \right\} \tag{5.2}$$

where tr and det denote the matrix trace and determinant, respectively. In view of (2.3a) and (5.1), it is seen that the closure (2.3) together with (4.2) and (4.3) are equivalent to adjusting $c_{fm}(r)$ and $c_{ff'}(r)$ in the range $0 < r < d_{fm}$ and $0 < r < d_{ff'}$, respectively, so as to make $I[c_{fm}(r), c_{ff'}(r)]$ stationary with respect to these variations. The functional is positive, and the variational solutions correspond to determining its minimum. For computational efficiency, variational solutions are generally preferable to standard iterative procedures provided the unknown functions are short ranged. In the present case, the unknowns are the c-functions at short distances. Variational formulations of more general closures are readily deduced from (5.1).

For notational clarification, it is perhaps useful to consider (5.2) for the case of a simple fluid sorbate. In this case, the functional I simplifies to

$$I_{MG} = \int dr \, [\rho_f c_{ff}(r) + 2\rho_m c_{fm}(r)] - \frac{1}{\rho_f(2\pi)^3} \int dk \, \{\rho_f \hat{c}_{ff}(k)$$

$$+ \ln[1 - \rho_f \hat{c}_{ff}(k)] - \rho_f \hat{c}_{fm}^2(k)\rho_m \hat{\omega}_m(k)/[1 - \rho_f \hat{c}_{ff}(k)]\}. \tag{5.3}$$

One may verify that (5.1) with $I = I_{MG}$ yields the Madden–Glandt equations, (3.2) and (3.5).

6. Discussion

This article outlines a computationally convenient theory for the structure of a poly-atomic fluid sorbed by a quenched amorphous material. The correlation functions so obtained can be employed to estimate the thermodynamic properties of such systems. It remains to investigate the most efficient and accurate routes to these estimates.

In addition to exploring these applications, the present article possibly foreshadows other uses of the RISM theory for complex systems. For example, the supermolecule view might be convenient for treating fluids confined to the micropores of crystalline molecular sieves. This view may also be of use in constructing theories for fluids at the interfaces of disordered solids or membranes. Here, the supermolecule may be a planar or nearly planar assembly. For the cases in which these assemblies can fluctuate, one will need to consider how the associated $\omega_m(k) = \omega_m(k_\parallel, k_\perp)$ is affected by the neighbouring fluid.

Even without these extensions, the perspective drawn in the simplest case, that of the Madden–Glandt equations, may be of some pedagogical interest. The variational formulation of their equations should be of practical use too.

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