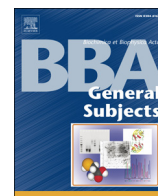




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Coarse-grained empirical potential structure refinement: Application to a reverse aqueous micelle[☆]

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ABSTRACT

Conventional atomistic computer simulations, involving perhaps up to 10^6 atoms, can achieve length-scales on the order of a few 10s of nm. Yet many heterogeneous systems, such as colloids, nano-structured materials, or biological systems, can involve correlations over distances up 100s of nm, perhaps even $1\ \mu\text{m}$ in some instances. For such systems it is necessary to invoke coarse-graining, where single atoms are replaced by agglomerations of atoms, usually represented as spheres, in order for the simulation to be performed within a practical computer memory and time scale. Small angle scattering and reflectivity measurements, both X-ray and neutron, are routinely used to investigate structure in these systems, and traditionally the data have been interpreted in terms of discrete objects, such as spheres, sheets, and cylinders, and combinations thereof. Here we combine the coarse-grained computer simulation approach with neutron small angle scattering to refine the structure of a heterogeneous system, in the present case a reverse aqueous micelle of sodium-dioctyl sulfosuccinate (AOT) and iso-octane. The method closely follows empirical potential structure refinement and involves deriving an empirical interaction potential from the scattering data. As in traditional coarse-grained methods, individual atoms are replaced by spherical density profiles, which, unlike real atoms, can inter-penetrate to a significant extent. The method works over an arbitrary range of length-scales, but is limited to around 2 orders of magnitude in distance above a specified dimension. The smallest value for this dimension is of order 1 nm, but the largest dimension is arbitrary. This article is part of a Special Issue entitled "Recent Advances in Bionanomaterials" Guest Editor: Dr. Marie-Louise Saboungi and Dr. Samuel D. Bader.

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1. Introduction

In the past decade or so empirical potential structure refinement (EPSR) has become a frequently used method for interpreting the atomistic structure of liquids and glasses based on X-ray and neutron total scattering data [1–8]. The EPSR method, which originally derived from the reverse Monte Carlo (RMC) method of McGreevy and Pusztai [9], uses the scattering data to generate an empirical potential which perturbs the starting seed potential (also known as the reference potential) in a manner so that the simulated structure reproduces the experimental measurements as closely as practical. [10–12] EPSR is mostly invoked when systems contain complex molecules so that they would, via the reference potential, remain in a physically realistic region of the huge possible phase space in which such systems could possible exist. It also works well in the case of complex atomistic glasses [2,5]

by means of making use of the known ionic Coulomb forces in such systems to prevent unphysical local atom coordinations.

Currently EPSR has a technical limit of $\sim 150,000$ atoms [13], which is partly imposed by the constraints of the small computing architectures on which it is typically run. A significant constraint on making EPSR simulations arbitrarily large however is that as the system becomes larger, corresponding to longer ranged measured structure, the empirical potential has also to become correspondingly longer ranged if it is going to fit that structure. Conventional optimisations based on keeping interaction potentials short-ranged that are typically available for conventional large scale molecular dynamics simulations [14,15] may therefore not be usable in this case. Hence, although larger atomistic systems are in principle possible with the EPSR technique, the problem of summing interaction potentials over thousands of atom neighbours with each atom move becomes prohibitive as the required range of the empirical potential increases.

The alternative is to dispense with the atomistic information, and fit only the longer-ranged structure. This is the basis for coarse-grained computer simulations – see for example [16,17] and references therein. The reason this is required experimentally is that since 2009 a new diffractometer has been operating at the ISIS Pulsed Neutron Facility, the

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Near and Intermediate Range Order Diffractometer (NIMROD) [18]. NIMROD can resolve atom separations but can also sample longer ranged heterogeneities which may be present up to distances of ~30 nm. NIMROD presents a serious challenge to computer data modelling regimes because it samples correlations at large and small inter-atomic distances simultaneously. Since it is currently not possible to fit the full range of distances present in NIMROD data in a single atomistic simulation, the present work seeks to address the intermediate length scale which lies beyond the immediate atomistic information in the region 0 to ~2 nm.

The ideas presented in this work derive from a number of previous sources. Perhaps the earliest, by Hayter and Penfold, [19] uses the Mean Spherical Approximation [20] to calculate the particle-particle structure factor, $H_{pp'}(Q)$ (see Eq. (6) below). In that case an entire micelle is described by a single spherical particle, with the surfactant appearing as a layer on top of the core particle. More recently a number of authors have pursued analogous ideas to those given here, primarily using RMC-type methods to refine the structure of a set of spheres against small angle scattering data. [21–25] More complex structures are then built up by bonding these spheres in particular sequences [22]. An alternative approach to modelling small angle scattering data is to fit a series of 3-dimensional shapes to the scattering data, such as is done in the FISH and other packages, for example [26,27]. Given the huge amount of prior experience in the field of refining small angle scattering data, the present work is a preliminary account of applying the EPSR technique to small angle structural analysis, to see what, if any, are the advantages of this approach.

2. Theory

The structure of any material, liquid or solid, homogeneous or heterogeneous, can be characterised by a set of site-site radial distribution functions (RDF), $g_{\alpha\beta}(r)$, which in turn are related by Fourier transform, within the Faber-Ziman formalism [28], to a corresponding set of partial structure factors (PSF):

$$H_{\alpha\beta}(Q) = 4\pi\rho_A \int r^2 \left(g_{\alpha\beta}(r) - 1 \right) \frac{\sin Qr}{Qr} dr. \quad (1)$$

There is one such RDF, PSF pair for each pair of atom types, (α, β) , and $\rho_A = N_A/V$ is the total number of atoms per unit volume of the material. Here Q is the wave vector and relates to the scattering angle, 2θ , and radiation wavelength, λ , used in the scattering experiment: $Q = \frac{4\pi \sin \theta}{\lambda}$. Indeed the differential scattering cross section (DCS) measured in a scattering experiment relates directly to these PSFs:

$$F(Q) = \sum c_\alpha b_\alpha^2 + \sum (2 - \delta_{\alpha\beta}) c_\alpha c_\beta b_\alpha b_\beta H_{\alpha\beta}(Q) \quad (2)$$

where $c_\alpha = N_\alpha/N$ is the atomic fraction of α type atoms, and b_α is either a number (for neutrons) which depends on the isotope and spin state of each nucleus, or (for X-rays) is a form factor dependent on Q ,

$$b_\alpha \rightarrow f_\alpha(Q) = 4\pi \int r_e^2 \rho_\alpha^{(e)}(r_e) \frac{\sin Qr_e}{Qr_e} dr_e \quad (3)$$

which is the Fourier transform of the electron density distribution, $\rho_\alpha^{(e)}(r_e)$, around the respective atom. Since X-rays are scattered primarily by the core electrons, it is traditionally assumed this form factor is independent of the bonding state of the atom – the so-called independent atom form factors. The angular brackets in Eq. (2), which represent averages over the spin and isotope states of the nuclei, only apply to neutron scattering and are also assumed to be independent of the bonding state of the atoms. Note that with this formalism $g_{\alpha\beta}(r)$ and $H_{\alpha\beta}(Q)$ are symmetric with respect to interchange of (α, β) .

The first term in Eq. (2) represents the “single atom” scattering level at high Q (where the second term structure function has decayed to

zero). It is structurally uninteresting, but it is important in putting the measured scattering data on to an absolute scale of differential scattering cross section. This absolute scale is essential if the results of a computer modelling fit to the data are to be reliable.

2.1. Introduce coarse graining

The reason why the neutron scattering length is normally independent of Q , is because the wavelength of the neutron used in scattering experiments, ~0.1 nm, is vastly larger than the typical nuclear dimension (~10 fm) and so the neutron is unaware of the nuclear structure. On the other hand for X-rays the electron density distribution has a width of around ~0.3 nm so the X-ray of wavelength ~0.1 nm is sensitive to the electron distribution around the atomic nucleus. As a result the raw X-ray diffraction signal from a material has a strong Q dependence, with the scattering level decaying rapidly with increasing Q . This Q dependence is usually removed by dividing the raw data by either $[\sum c_\alpha f_\alpha(Q)]^2$ or $\sum c_\alpha [f_\alpha(Q)]^2$ [29]. The X-ray form factor provides the analogy for introducing coarse graining into the current work.

In essence, the idea is to replace individual atom types, α , with a set of spherical scattering particles p with scattering length density distributions $n_p(r_p) = [\sum N_\alpha^{(p)} b_\alpha] \rho_p(r_p)$. Here $N_\alpha^{(p)}$ is the number of atoms of type α in particle p , and $\rho_p(r_p)$ is normalised so that $4\pi \int r_p^2 \rho_p(r_p) dr_p = 1.0$. Associated with this density distribution is a form factor

$$f_p(Q) = 4\pi \int r_p^2 \rho_p(r_p) \frac{\sin Qr_p}{Qr_p} dr_p \quad (4)$$

with $f_p(0) = 1$.

The number of particles of type p is N_p with particle fractions $c_p = N_p/\sum N_q$, the total number of atoms in particle p is $N_A^{(p)} = \sum N_\alpha^{(p)}$, and the average number of atoms of type α per particle is $\bar{N}_\alpha = \sum c_p N_\alpha^{(p)}$. The average total number of atoms per particle is then $\bar{N}_A = \sum \sum c_p N_\alpha^{(p)} = \sum c_p \sum N_\alpha^{(p)}$ so that $c_\alpha = \bar{N}_\alpha / \bar{N}_A = \sum c_p N_\alpha^{(p)} / \bar{N}_A$.

With these definitions, the coarse-grained differential cross section (CG-DCS) can be written by analogy with Eq. (2):

$$F_{CG}(Q) = \frac{1}{\bar{N}_A} \left[\begin{aligned} & \sum \sum c_p N_\alpha^{(p)} b_\alpha^2 \\ & + \sum c_p \left[\sum N_\alpha^{(p)} (N_\alpha^{(p)} - 1) b_\alpha^2 + 2 \sum N_\alpha^{(p)} b_\alpha N_\beta^{(p)} b_\beta \right] f_p^2(Q) \\ & + \sum (2 - \delta_{pq}) c_p c_q \left[\sum N_\alpha^{(p)} b_\alpha \right] f_p(Q) \left[\sum N_\alpha^{(q)} b_\alpha \right] f_q(Q) H_{pq}(Q) \end{aligned} \right], \quad (5)$$

where the denominator $1/\bar{N}_A$ is introduced because measured differential cross sections are typically expressed per atom of material in the radiation beam. The particle-particle PSF is defined by

$$H_{pp'}(Q) = 4\pi \rho_p \int r^2 \left(g_{pp'}(r) - 1 \right) \frac{\sin Qr}{Qr} dr \quad (6)$$

with ρ_p now the total particle number density.

2.2. The single particle scattering

The first term in Eq. (5) is identically the single atom scattering seen in Eq. (2). It will be noted however that there are extra terms appearing in Eq. (5) compared to Eq. (2). These arise because each particle may contain more than one atom of any given type. Since the atoms in each particle are assumed to be distributed statistically through the particle according to the same $\rho_p(r_p)$ for all atom types their relative positions within the particle are uncorrelated and the same particle form factor $f_p(Q)$ applies to all of them. Nonetheless if $N_\alpha^{(p)} > 1$ there will be *intra-particle* distinct atom contributions to the overall differential cross section which would not be counted without these extra terms. Also if we wished different atom types to be associated with different particle form factors e.g. a coating on the surface of a nanoparticle,

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