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A simple and accurate method for calculation of the structure factor of interacting charged spheres

Chu Wu^{1,2}, Derek Y. C. Chan*^{1,2,3} and Rico F. Tabor*⁴

¹ Particulate Fluids Processing Centre, University of Melbourne, Parkville, VIC 3010, Australia

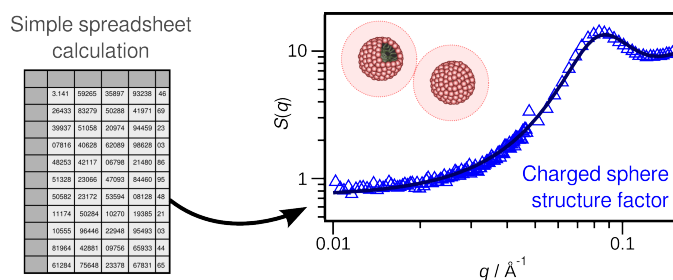
² Department of Mathematics and Statistics, University of Melbourne, Parkville, VIC 3010, Australia

³ Department of Chemistry and Biotechnology, Swinburne University of Technology, Hawthorn 3122, Australia

⁴ School of Chemistry, Monash University, Clayton, VIC 3800, Australia

[*d.chan@unimelb.edu.au](mailto:d.chan@unimelb.edu.au), rico.tabor@monash.edu

Calculation of the structure factor of a system of interacting charged spheres based on the Ginoza solution of the Ornstein-Zernike equation has been developed and implemented on a stand-alone spreadsheet. This facilitates direct interactive numerical and graphical comparisons between experimental structure factors with the pioneering theoretical model of Hayter-Penfold that uses the Hansen-Hayter renormalisation correction. The method is used to fit example experimental structure factors obtained from the small-angle neutron scattering of a well-characterised charged micelle system, demonstrating that this implementation, available in the Supplementary Information, gives identical results to the Hayter-Penfold-Hansen approach for the structure factor, $S(q)$ and provides direct access to the pair correlation function, $g(r)$. Additionally, the intermediate calculations and outputs can be readily accessed and modified within the familiar spreadsheet environment, along with information on the normalisation procedure.



Graphical abstract

Introduction

In its simplest terms, the structure factor of a system describes local correlations, related to the probability of finding a particle at a given separation from another. In scattering experiments, the structure factor is a measure of the interference of radiation scattered from different objects, and thus the correlations observed provide a measure of local order. These correlations are dependent on the way particles interact, from simple volume exclusion effects to ‘sticky’ pair potentials for attractive particles and the screened Coulombic repulsion of like-charged objects.^{1,2} The structure factor is often given the symbol $S(q)$, measured in scattering experiments as a function of the scattering vector, q . The functional form of $S(q)$ depends on the number concentration of objects as well as the range, intensity and type of interactions that they experience. The Fourier transform of the structure factor gives the pair correlation function, $g(r)$, that gives the probability, $4\pi r^2 g(r) dr$, of finding two particles in the separation interval r to $r + dr$. Its value tends to unity at large separations where correlations are no longer significant.

In a large number of systems, particularly where water is the solvent, particles will experience interactions dominated by the repulsions between their surface charges. These repulsions are screened by dissociated counterions and added salt, resulting in a classical Gouy-Chapman double-layer interaction that can be modelled with the Poisson-Boltzmann theory.³ Well-studied examples include micelles formed from ionic surfactants, polymer, metal and oxide particles and charged globular proteins and polyelectrolytes.¹

As well as wide applications in the analysis and quantitative modelling of data from small-angle X-ray, neutron and light scattering, the charged-sphere structure factor is central to many other correlative analyses of fluid systems including theoretical studies of colloidal glasses,⁴ structural forces in rigid and deformable systems^{5,6} and Monte Carlo simulations of interacting systems.⁷ Thus, a method to quickly and easily calculate charged-sphere structure factors while still having access to the fitting equations and process is of interest to a number of fields.

The most widely used construction to obtain the structure factor for such interacting charged systems, modelled as charged spheres, was derived more than 30 years ago by Hayter and

Penfold.⁸ The charged spheres are assumed to interact *via* a hard core with diameter, σ , that implies $g(r) = 0$ for $r < \sigma$, plus a repulsive screened Coulomb or Yukawa⁹ pair potential: $u(r) = (u_0/r) \exp(-\kappa r)$, for $r > \sigma$, where the constant, $u_0 > 0$. This work underpinned diverse advances in the field of particle and soft matter systems over the past three decades by allowing rapid and precise calculations and modelling to be performed.

The model for calculating the structure factor, $S(q)$ uses the known solution^{10,11} of the Ornstein-Zernike equation¹² with a direct correlation function, $c(r)$ that has a screened Coulomb or Yukawa form when the spheres are not in contact ($r > \sigma$). In the Mean Spherical Approximation (MSA), used in the Hayter and Penfold model,⁸ the assumption that $c(r) = -u(r)/(k_B T)$ for $r > \sigma$ is used where k_B is Boltzmann's constant and T the absolute temperature. For low volume fractions of particles, the MSA can give the unphysical result, namely, $g(r) < 0$ at small separations - that is, a negative probability of finding a particle at a finite separation. Hansen and Hayter proposed a 'renormalisation' method¹³ in which the hard core diameter is increased to a larger value σ' , with the scaling parameter $s = \sigma/\sigma' < 1$ chosen so that $g(r = \sigma') = 0$ at the same particle number density. Thus the theoretical basis for modelling screened Coulombic interactions between colloidal particles is to relate the constant u_0 to physical quantities such as particle charge, relative dielectric permittivity of the solvent and the Debye screening parameter, κ that is related to the salt concentration by: $\kappa^{-1} = [\epsilon_r \epsilon_0 k_B T / (2 N_A e^2 I)]^{1/2}$ where ϵ_r and ϵ_0 are the relative permittivity of the solvent and the vacuum permittivity respectively, N_A is Avogadro's number, e is the fundamental charge and I is the solution ionic strength. A popular option is to use the linear Debye-Hückel model or the non-linear Poisson-Boltzmann model to calculate the constant u_0 and the screening parameter, κ .

Different approaches to the numerical evaluation of the original analytic solution by Waisman¹⁴ have been considered^{15,16}. The most convenient is that based on the alternate analytic solution by Ginoza^{17,18} that is adopted here.

Methods

The Hayter-Penfold/Hansen-Hayter model has been implemented within closed, stand-alone

software packages on a number of platforms such as SASView¹⁹ (international large scale facilities collaboration), FISH²⁰ (Rutherford Appleton Laboratories), the NIST fitting macros²¹ produced for IGOR Pro (NIST, Gaithersburg, MD) and SASfit²² (Paul Scherrer Institut). The computational details of these packages are not readily accessible to users so there is limited scope for modifying the code. Given the current capabilities of personal computers and tablets and the common availability of spreadsheet programs on these platforms, it is timely to make the Hayter-Penfold/Hansen-Hayter model available on a broader platform with the additional advantage that details of the computational steps are openly available for users to study and modify, and the type of input parameters (physical quantities or non-dimensional values) can be chosen by the user.

The standard implementations of the Hayter-Penfold model⁸ are based on the Waisman solution¹⁰ of the Ornstein-Zernike equation with a Yukawa form for the direct correlation function, $c(r)$. They involve first finding numerically the correct zero of a quintic polynomial and then an iterative Newton algorithm is used to determine the scaling parameter $s = \sigma/\sigma'$ of the Hansen-Hayter renormalisation.¹³

Here we use the Ginoza solution¹⁸ of the same equation. For repulsive interactions, this involves finding a unique positive zero of a non-linear equation from which all other parameters are easily determined (see Electronic Supplement for details). The correct scaling parameter, s is found interactively within the spreadsheet.

The structure factor, $S(k)$ determined by the Ornstein-Zernike equation¹² with a single-component Yukawa form⁹ for the direct correlation function: $c(x) = -(\gamma/x) \exp(-kx)$, $x = r/\sigma > 1$, and $g(x) = 0$ for $x < 1$, is determined by only 3 fundamental non-dimensional parameters: the volume fraction: $\eta = \pi n \sigma^3/6$, where n is the number density of particles, the dimensionless screening parameter: $k = \kappa \sigma$, and the constant: $\gamma = u_o/(k_B T) > 0$ that characterises the strength of the repulsive interaction. However, current implementations of the Hayter-Penfold/Hansen-Hayter model^{8,13} mentioned above require specification of physical parameters such as the particle charge, the relative permittivity, particle radius, salt concentration of a univalent electrolyte, temperature and particle volume fraction. The precise relation between between these

physical parameters to the 3 non-dimensional parameters (η, k, γ) depends on an assumed model of the electric double layer repulsion and is independent of the solution of the Ornstein-Zernike equation for $S(k)$. In the Hayter-Penfold/Hansen-Hayter model, the superposition or weak coupling approximation of the linear Debye-Hückel model is assumed with: $u_o = (Ze)^2 \exp(\kappa\sigma) / [\pi \epsilon_o \epsilon \sigma (2 + \kappa\sigma)^2]$, where (Ze) is the charge on the particle and $(\epsilon_o \epsilon)$ is the dielectric permittivity of the solvent and both added salt and intrinsic counter-ions, restricted to be univalent, contribute to the Debye screening parameter, κ .

In our implementation of the Ginoza form of the solution, which gives the same numerical results as those given by current implementations of the Hayter-Penfold/Hansen-Hayter model, we offer the option of calculating $S(k)$ in terms of the 3 non-dimensional parameters (η, k, γ). This option affords the flexibility of using a different model of the electric double layer repulsion, such as the non-linear Poisson-Boltzmann model and electrolytes of different valencies,²³ to relate physical parameters to the 3 fundamental non-dimensional parameters (η, k, γ) of the Ornstein-Zernike equation. Furthermore, our implementations allows the user to specify the ionic strength of the added salt and the valence of the intrinsic counter-ions whereas all current implementations of the Hayter-Penfold/Hansen-Hayter model^{8,13} are restricted to univalent salts and counter-ions.

By implementing our solution on a spreadsheet, we take advantage of the widespread familiarity with this common computational environment and its general capabilities. It is easy also to import and manipulate experimental data in a spreadsheet format. The built-in graphing options of the spreadsheet are used to provide real time feedback during fitting and comparison between model and experiment. Users have the flexibility to use the spreadsheet environment to either modify details of the model or export the results to other applications. The open nature of the implementation further provides pedagogic value to newcomers to the field.

Results and discussion

To demonstrate the ability of the routine to accurately model experimental structure factors, comparison was made with structure factors obtained from small-angle neutron scattering of

charged sodium dodecyl sulfate (SDS) micelles in water (Fig. 1). The scattering data were obtained from previous work,⁵ and pseudo-structure factors were calculated by dividing the raw scattering data by the calculated micelle volume fraction and a form factor used consistently across all concentrations, representing hard spheres of radius 18.5 Å, after Bartlett and Ottewill.²⁴ This method, although somewhat crude in its assumptions (*i.e.* that the form factor is concentration independent), provides an relatively accurate approximation of the structure factor in the low q range, where the contribution from the form factor is approximately constant. It is assumed that the background electrolyte contribution comes from the non-aggregated surfactant monomers, and the best fit value for these data is 5 ± 1 mM. The data can then be consistently fit to the level of agreement shown in Fig. 1 by assuming 26 charges per particle (micelle) and particle volume fractions of 0.011, 0.022 and 0.044 for 50, 100 and 200 mM SDS respectively.

A much more precise procedure for obtaining experimental structure factors from small-angle scattering utilises contrast variation to obtain data sets for compositionally equivalent samples at different contrast conditions.² A simultaneous model fit constraining structure factor across the data sets then provides an accurate measure of the structure factor. However, this was not possible with the data available here, and the proof of principle for obtaining structure factors with experimentally reasonable physical quantities is evident.

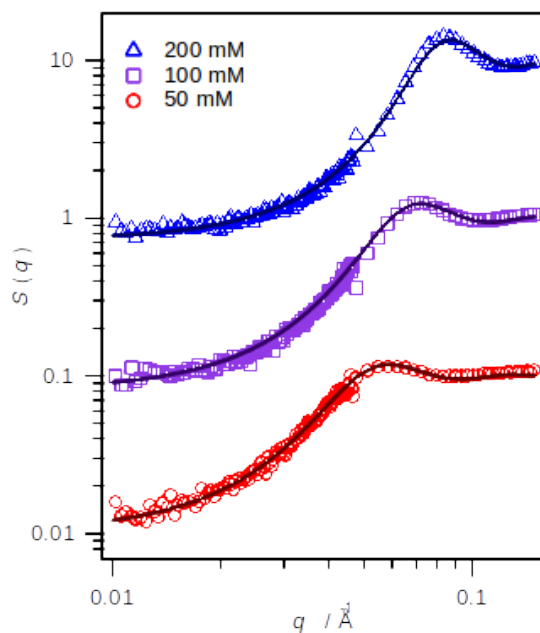


Fig. 1. Pseudo-structure factors from small-angle neutron scattering of SDS micelles at different

surfactant concentrations. Symbols are experimentally-derived structure factors and solid lines are fits using the spreadsheet method described in the text. The traces are offset vertically by multiplication as noted, for clarity of presentation.

The spreadsheet-derived structure factors fit the experimentally obtained data well across the low- q range, with physical parameters that take reasonable values in line with literature reports on SDS micelles.^{25,26} The fitting is also identical to that obtained using the same parameters in the SASView fitting program,¹⁹ indicating that the Ginoza implementation here is equivalent to the Waisman solution conventionally used.

Conclusion

We have presented a new method for calculating the structure factor for interacting charged spheres, based on the Ginoza solution¹⁸ to the Ornstein–Zernike equation¹² with renormalisation. To test the efficacy of the calculation, we fitted structure factor data obtained from small-angle neutron scattering of negatively charged surfactant micelles in aqueous solution.⁵ In providing a flexible solution to the problem of inter-particle structure factors and pair correlation functions on a spreadsheet platform, we broaden the accessibility of an important tool that has been indispensable in modelling data obtained by neutron, x-ray or light scattering.^{1,2,8,13} The open nature of the implementation further provides pedagogic value to newcomers to the field and allows direct access to the input type, equations and fitting procedure, in order to better control and understand structure factors for a wide range of systems.

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