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Scattering from highly packed disordered colloids

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Online at stacks.iop.org/JPhysCM/21/332102**Abstract**

We discuss the measurable structure factor $S_M(q)$ of highly concentrated nanoemulsions in a glassy amorphous state. Neutron scattering data show that the primary structure factor peak decreases with increasing concentration and eventually drops below unity. We find very good quantitative agreement between the experimental $S_M(q)$ and analytical predictions for a polydisperse hard sphere fluid. Subunity structure factor peaks are predicted for dense fluids near and above the jamming transition.

(Some figures in this article are in colour only in the electronic version)

 Supplementary data are available from stacks.iop.org/JPhysCM/21/332102

The relationship between the structure and phase behavior of hard sphere fluids has been one of the most discussed topics in classical statistical mechanics over the last century [1]. Lacking any specific interaction, the statistical physics of hard spheres is temperature-independent, and the only relevant parameter is the volume fraction of spheres, ϕ . Many real systems can be described as hard spheres as long as the interaction is repulsive and short ranged. As a consequence the hard sphere (HS) model finds applications ranging from molecular liquids, such as liquid argon or liquid metals, supramolecular fluids to granular materials and even to the question of macroscopic packing of candy [1–6]. The HS-model is particularly well suited for describing the properties of many supramolecular, or colloidal, systems, when the range of repulsive interactions can be limited to a few nanometer or less. Such colloidal particles, having typical sizes in the range 10–1000 nm, can be made almost perfectly spherical. A wealth of experimental, theoretical, and numerical results have been reported over the last decades. These results have largely shaped our current quantitative understanding of the liquid state [1, 7, 8].

One of the main reasons for this success is the fact that the structure factor $S(q)$ of bulk colloidal systems can be assessed directly by the scattering of electromagnetic radiation or neutrons, where q is the scattering wavenumber: $S(q) = 1 + \rho_0 \int e^{iqr} [g(r) - 1] d^3r$ is essentially the Fourier transform of the radial distribution function $g(r)$ that completely characterizes the structural properties of an isotropic liquid at a given average number density ρ_0 [1]. For an assembly of identical hard spheres, where crystallization is suppressed due to rapid quenching, the structure factor evolves continuously: the low q scattering intensity is suppressed due to a decreased compressibility $S(q \rightarrow 0) = \rho_0 k_B T \chi_T$ and a correlation peak appears at $q \simeq \pi/a$. With increasing ϕ the peak increases in height and becomes sharper up to the random close packing (rcp) density $\phi_{rcp} \simeq 0.64$ where the system becomes *jammed* [9–11]⁴.

Recently a detailed scattering study of the liquid structure factor reported on an unusual observation: small angle

⁴ Recently a more general concept of a *maximally random jammed* (MRJ) state has been introduced to replace the *random close packing* picture [6]. The maximally random jammed (MRJ) state is then defined as the least ordered all jammed packings [10]. For monodisperse hard spheres $\phi_{MRJ} \approx 0.64$.

neutron scattering (SANS) from highly concentrated, fairly uniform nanoemulsions showed that the primary structure factor peak can decrease with increasing volume fraction and eventually fall below one [12]. In the present letter, we provide an explanation for the reported paradoxical behavior. We demonstrate that for dense suspensions at random close packing (and beyond) moderate polydispersity can indeed lead to a subunity primary peak in the measurable structure factor. We are able to quantitatively model the measured structure factors based on an analytical solution for a Percus–Yevick fluid with Schultz distributed particle radii. Our results demonstrate the general importance of polydispersity with respect to scattering from structured liquids especially at high ϕ near and above *jamming*.

For an assembly of identical spheres the scattered intensity $I(q)$ is proportional to the scattering cross section, or form factor, of an individual sphere $F(q)$ and the liquid structure factor $S(q)$, hence $I(q) \propto F(q)S(q)$ [13]. In an experiment the form factor $F(q)$ can always be obtained from a measurement on a highly diluted sample, where for $\phi \rightarrow 0$ one finds $S(q) \equiv 1$, and thus $S(q) \propto I(q)/F(q)$ for a denser system. However by contrast to atoms, molecules, and some biological macromolecules, colloidal particles are typically prepared in such a way that there is always a remaining finite distribution of radii $N(a)$. The polydispersity index $\sigma = \delta a/\bar{a}$, defined by the standard deviation δa of $N(a)$ divided by its mean \bar{a} , can be as low as 1% or as high as 100% in some cases. Fortunately, many physical properties only depend weakly on polydispersity. The theoretical or numerical results for assemblies of identical particles can often be applied directly to the (weakly) polydisperse case. For example the volume fraction for random close packing increases gradually from $\phi_{\text{rcp}} \simeq 0.64$ for a monodisperse system to $\phi_{\text{rcp}} \simeq 0.71$ for a polydispersity of $\sigma = 30\%$ [9]. On the other hand already small amounts of polydispersity are known to affect the location of the freezing transition for HS fluids. Polydispersity can also lead to fractionation in the fluid–solid coexistence [14]. For values of $\sigma \geq 12\%$ crystallization is suppressed and the system remains amorphous at all densities [7, 15]. Suppression of freezing can be an advantage since it allows convenient access to the fascinating physics of the glass transition [4, 7, 8, 16, 17]. Polydispersity is thus often introduced artificially both in experiments and numerical simulations [16, 17].

Although the physics of the liquid state is typically only gradually affected by polydispersity, the same is not true for the scattering problem [5, 18, 19]. In the presence of polydispersity, the relationship between the measured $I(q)$ and the liquid structure factor $S(q)$ is by no means as simple any more [13]. For a discrete distribution of p particle species with different radii a_α the scattered intensity is now given as a sum of partial structure factors $S_{\alpha,\beta}(q)$ weighted by the scattering amplitudes $b_\alpha(q)$, $b_\beta(q)$:

$$I(q) \propto \sum_{\alpha,\beta}^p b_\alpha(q)b_\beta(q)S_{\alpha\beta}(q). \quad (1)$$

It is therefore not possible to extract $S_{\alpha,\beta}(q)$ or the total structure factor of a polydisperse liquid $S(q) =$

$\sum_{\alpha,\beta}^p c_\alpha c_\beta S_{\alpha\beta}(q)$ directly from a scattering experiment (c_α is the concentration of the α component). Nevertheless for moderate volume fractions up to $\phi = 30\%$ and small polydispersities of the order of 5–10% the overall difference to the corresponding monodisperse $S(q)$ is small. Polydispersity however still strongly increases scattering at small $q \ll \pi/a$. Since scattering in this limit is directly related to the isothermal compressibility χ_T care has to be taken interpreting experimental data. Polydispersity effects also have a major influence on quasielastic and inelastic scattering at small values of q . With increasing density, particle dynamics in this q -range is normally dominated by collective motion. Enhanced low- q scattering due to polydispersity adds contributions from self-diffusion that may even become dominant [20].

Most theoretical discussions of the structure of liquids are based either on numerical simulations or on a solution of the Ornstein–Zernike equation. For the latter the well known Percus–Yevick closure provides an analytical expression for the liquid structure factor $S(q)$ [21, 22]. This is widely recognized as an attractive feature of the hard sphere case and the model has been tested and validated extensively. Moreover analytical solutions including polydispersity exist for both the structure factor $S(q)$ and the measurable structure factor $S_M(q)$ [18, 19]. The Percus–Yevick equation has some known shortcomings such as a slight deviation at high densities from the Carnahan–Starling equation of state for the compressibility of hard spheres [1]. It is also known to overestimate the height of the primary peak of $S(q)$ for monodisperse systems at higher concentrations [1]. However, for polydisperse systems the convolution with a distribution of particle sizes leads to a better quantitative agreement [5]. Overall, the predicted structure factors have been shown to compare well with experiments [4] and numerical simulations over the full range explored previously up to $\phi = 0.5$: Frenkel and co-workers compared the Percus–Yevick result for polydisperse hard spheres to Monte Carlo simulations [5]. Within the numerical accuracy they found good agreement at $\phi = 0.5$ and polydispersities up to 80%.

Mason and co-workers reported on a systematic set of SANS experiments using fairly uniform fractionated nanoemulsions [12]. These nanoemulsions are very interesting model systems for simple liquids [12, 23]. They can be prepared in bulk quantities using a microfluidic homogenizer and they are true metastable emulsions that do not evolve on the timescales of months. The droplets interact via a very short ranged screened charged repulsions and can therefore be treated as effective hard spheres at most ϕ [24]. While disordered packings of hard spheres jam at ϕ_{rcp} the residual softness of the Debye layer [24] and compressed nanoemulsion droplet deformation allows them to fill space more efficiently. Thereby effective volume fractions well above ϕ_{rcp} can be reached.

For the SANS experiments shown in figure 1, a concentrated stock of silicone oil-in-water nanoemulsion droplets has been prepared by ultracentrifugation at $\phi = 0.72$ and 10 mM SDS in D_2O . This highly elastic stock nanoemulsion was subsequently diluted with a surfactant solution identical to that of the continuous phase (for details

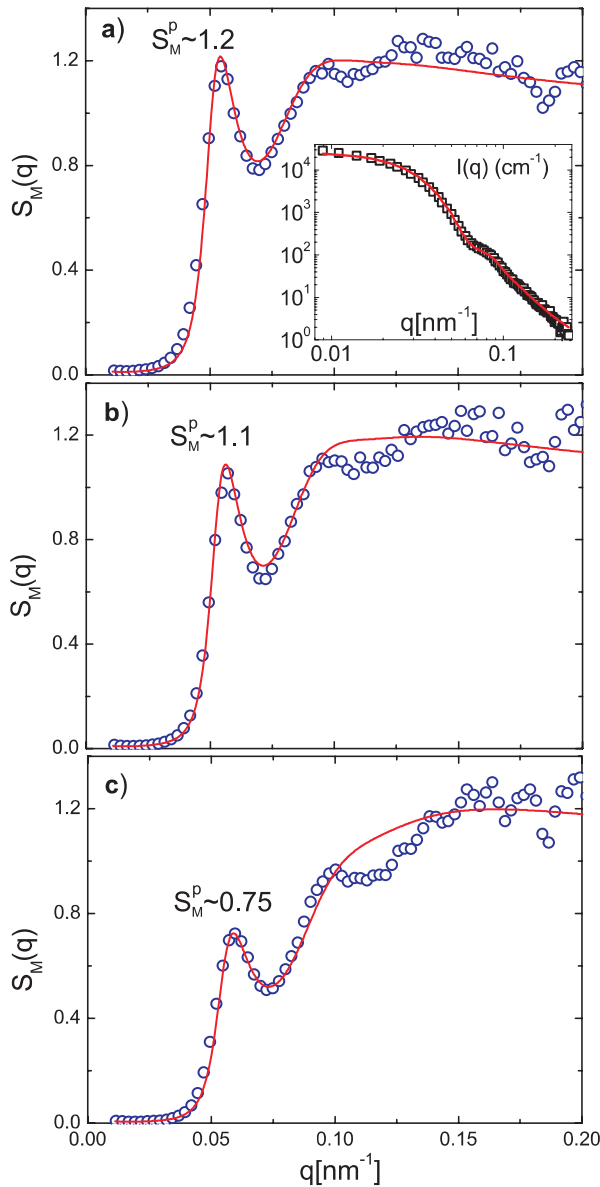


Figure 1. Measurable structure factor $S_M(q)$ for highly concentrated nanoemulsions. Open circles: small angle neutron scattering (SANS) data reproduced from [12] for (a) $\phi = 0.6$, (b) $\phi = 0.67$, (c) $\phi = 0.72$. The original published data, normalized to one at high q , have been scaled up by a factor 1.2 ± 0.03 . Solid lines show the best fit with a polydisperse Percus–Yeivick model [19]. Fit parameters are given in table 1. Inset: SANS intensity for a dilute droplet volume fraction $\phi = 0.005$ (open squares). A polydisperse fit (solid line) yields a number weighted mean radius $\bar{a} = 65$ nm and polydispersity $\sigma = 0.19$.

see [12]). The inset of figure 1(a) shows the SANS intensity at a dilute $\phi = 0.005$ volume fraction. From a fit with a polydisperse form factor $\overline{F}(q)$ we obtain a mean radius $\bar{a} = 65$ nm and a polydispersity $\sigma = 0.19$.⁵ We include polydispersity via a Schultz number distribution of radii $N(a) = a^z/z! [z + 1/\bar{a}]^{z+1} \exp[-a(z + 1)/\bar{a}]$ with a mean radius \bar{a} and polydispersity index $\sigma^2 = 1/(z + 1)$.

⁵ We have neglected the wavelength distribution of the neutron beam in our analysis. Taking into account a wavelength spread of typically $\delta\lambda/\lambda \approx 10\%$ would lower the polydispersity value to $\sigma \approx 0.15$.

Table 1. Parameters for a best fit of the polydisperse Percus–Yeivick prediction to the SANS data.

| ϕ | ϕ_{eff} | $\lambda_{D,\text{eff}}$ (nm) | \bar{a}_{eff} (nm) | σ_{eff} |
|--------|---------------------|-------------------------------|-----------------------------|-----------------------|
| 0.6 | 0.7 | 3.4 | 70.5 | 0.207 |
| 0.7 | 0.72 | 1.6 | 69 | 0.203 |
| 0.72 | 0.77 | 1.5 | 67.5 | 0.21 |

To allow comparison between theory and experiment over the full range of densities and polydispersities the so-called measurable structure factor $S_M(q)$ is usually considered, being defined via $I(q) \propto \overline{F}(q)S_M(q)$. In figures 1(a)–(c) $S_M(q)$ is plotted for the highest densities accessible $\phi = 0.6$ – 0.72 . The results clearly reveal the unusual features of the scattering from highly concentrated nanoemulsions. Strikingly the first peak of the measurable structure factor lies close to or even below unity.

Our attempt to model the data in figure 1 is based on the ad hoc assumption that the Percus–Yeivick closure is still a useful approximation at such high densities. We calculate $S_M(q\bar{a}, \sigma)$ based on the analytical expressions given in [19]⁶. The effective volume fraction ϕ_{eff} , the effective mean particle size \bar{a}_{eff} and the polydispersity σ_{eff} are all slightly adjusted to obtain a best fit to the data. We find our fits in excellent agreement with the experimental data in particular for the q -range associated with the primary peak of $S_M(q)$. As second aspect, the small dip seen at higher $q \approx 0.12$ nm⁻¹, most pronounced for the highest density $\phi = 0.72$, is not accounted for by the fit. We tentatively attribute this feature to small changes in the particle form factor due to the droplet deformation not taken into account in our analysis. In a next step, we analyze the fitting parameters required to obtain the good quantitative agreement (table 1). Due to the finite Debye screening length λ_D , the effective radius is increased and we expect the effective volume fraction obtained from a fit to be somewhat higher than the actual volume fraction of the oil droplets. This is indeed observed at all concentrations considered. An estimate of the screening length is given by $\lambda_{D,\text{eff}} = \bar{a}[(\phi_{\text{eff}}/\phi)^{1/3} - 1]$. The value for $\lambda_{D,\text{eff}} = 3.4$ nm found for the lowest density is in excellent agreement with the Debye length $\lambda_D \approx 3.5$ nm of a 10 mM SDS solution [25]. Due to the softness of the interaction potential we expect the Debye layer to be compressed at even higher densities [24]. Also, this dependence is reproduced by the fit. Even more striking the average interparticle distance $2\bar{a}_{\text{eff}}$, which is essentially given by the position of the primary peak q_{peak} , shows the same trend. The polydispersity σ_{eff} is found to be slightly higher than the value obtained from the form factor fit. We think this might be a signature of droplet deformation, which is typically of the order of 7% or less in this regime [26]. Although a minor correction in our case, droplet deformation (or compression of soft solids) can lead to some degree of random rearrangements of the particles center of mass, thus increasing the apparent polydispersity contribution to $S(q)$.

To demonstrate the validity of our approach, we present in figure 2 another comparison: light scattering from a submicron

⁶ See also, the supplementary data available at stacks.iop.org/JPhysCM/21/332102.

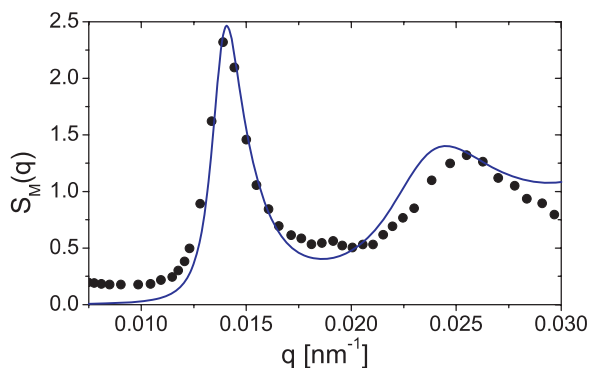


Figure 2. Measurable structure factor $S_M(q)$ for a highly compressed refractive index matched submicron emulsion (light scattering data reproduced from [27]). Solid line: best fit with the polydisperse Percus–Yevick model, $\phi_{\text{eff}} = 0.73$ ($\phi = 0.7$), $\bar{a}_{\text{eff}} = 279.5$ nm ($\bar{a} = 256$ nm) and polydispersity $\sigma_{\text{eff}} = 0.13$ ($\sigma = 0.12$).

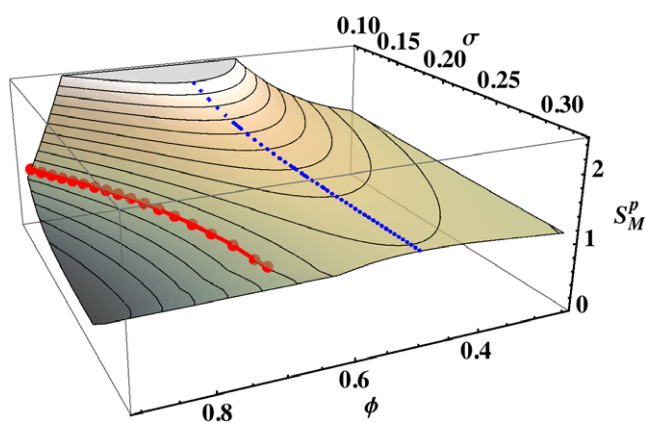


Figure 3. Percus–Yevick prediction for the height of the primary peak in the measurable structure factor S_M^p as a function of volume fraction ϕ and polydispersity σ . Line with solid circles: threshold value of $S_M^p = 1$. At very high ϕ and σ , no primary peak exists. Dotted line: maximum peak value as a function of density, $\partial S_M^p(\phi, \sigma)/\partial \sigma = 0$. At $\sigma < 0.14$ the maximum peak value exceeds 2.5, the highest value shown here.

emulsion, having a droplet size 265 nm and a somewhat lower polydispersity of $\sigma \simeq 0.12$ [27]. The agreement is again very good keeping in mind the extreme conditions (near refractive index matching at a volume fraction of $\phi = 0.7$) and the likely contribution of multiple scattering at low values of q as pointed out by the authors [27].

These findings will be of significance for many scattering experiments on dense colloidal systems with short range repulsive interactions. Figure 3 summarizes the peak height dependence $S_M^p(\phi, \sigma)$ over the whole range of interest $0.3 \leq \phi \leq 0.9$ and $0.1 \leq \sigma \leq 0.3$. Note that the peak position $q_{\text{peak}} \simeq \pi/a$ changes only marginally. At constant polydispersity, the peak height goes through a shallow maximum as a function of density ϕ . Subunity peaks are found close to or above ϕ_{rcp} . Our results thus indicate that some softness in the interaction potential (or particle deformability) favors the observation of subunity peaks in the measurable structure factor. The polydispersity dependence can be summarized as follows: for densities $\phi < 0.6$ polydispersity smears out the peak. Typically for $\sigma > 0.25$

one finds $1 < S_M^p < 1.5$. This is the behavior commonly reported in the literature [5, 19, 20, 28]. For densities $\phi > 0.68$ subunity peaks are predicted in a range $0.10 < \sigma < 0.28$. At even higher values of σ the subunity peak reduces to a shoulder and then disappears entirely.

In conclusion, we have shown, that polydispersity effects can lead to unexpected qualitative changes in the measurable structure factor. Our findings for polydisperse highly packed fluids furthermore imply that the Percus Yevick approximation, and other similar closure relations, extend to densities much higher than previously considered.

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