Concentration dependence of static and dynamic structure in a spherical microemulsion system

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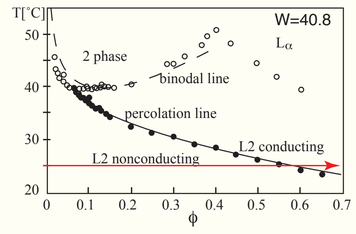
motivation

Microemulsion composed of water, oil, and surfactant forms various kind of self-assembled structures in nano-meter length scale. One of the typical microemulsion systems are water, oil, and AOT system. When the molar ratio between water and AOT is kept constant with changing oil concentration, it is known that the system forms water-in-oil droplet structure at room temeprature. At the dilute corner of the phase diagram, the structure and dynamics have been well established. However, at the dense droplet region, both structure and dynamics have not yet been clarified.

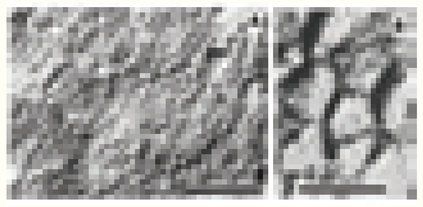
Especially, droplet concentration dependence of the structre and dynamics has not been analyzed universaly (within the same concept of the data analysis procedure).



originally drawn by Cametti et al., Phys. Rev. A 45, R5338 (1992).

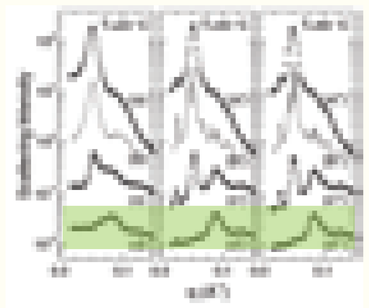
So far, dilute region or dense region has been well explained using scattering technique. However, in semi-dilute region, not many structure information has been elcidated. Universal understanding for the structure and dynamics onto the red line is necessary to discuss self-assembly at the semi-dilute to dense droplet region.

De Geyer and co-workers showed that SDS/water/oil/alcohol system shows a polyhedral shape of unit particles at the crowded environment.



TEM image taken by de Geyer et al., J. Chem. Phys. B, 104, 6610 (2000).

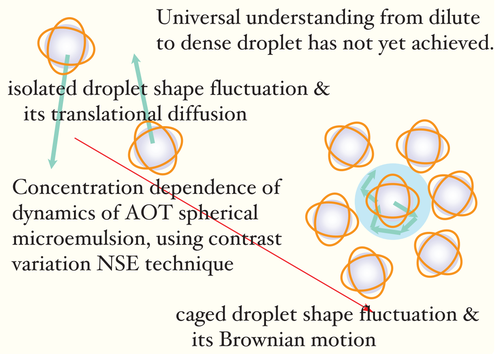
In this situation, dynamic properties of membranes must be affected by the nearest membranes. Molle et al. carried out a neutron spin echo (NSE) experiment in the system, using contrast variation neutron scattering technique. They measured NSE profile at a matching point, where scattering peak in small-angle profile was matched out.



SANS & SAXS profiles for various scattering contrast in SDS, brine, toluene, and alcohol taken by Molle et al., Phys. Rev. Lett. 90, 068305 (2003).

effective diffusion constant in SDS/brine/toluene/alcohol system shown by Molle et al., Phys. Rev. Lett. 90, 068305 (2003).

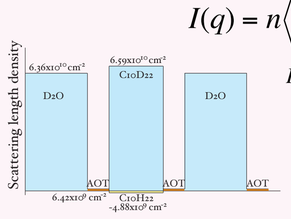
They described shape and structure fluctuation modes for each contrast data. The evaluated effective diffusion constant from the peak matching contrast showed a peak, indicating shape fluctuation mode of droplets. They found the relaxation time of the shape fluctuations is about 170ns. This time scale is much longer than that in a dilute droplet (8 ns) measured by another group. Thus, they expect the rigid membranes in crowded environment.



Relative Form Factor and Relative Intermediate Form Factor

small-angle scattering intensity from monodisperse systems

$$I(q) = n\left\langle \left| f(q) \right|^2 \right\rangle \left\langle s(q) \right\rangle = nF(q)S(q)$$

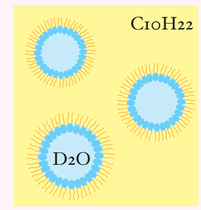


$$F(q) = \left| \int \Delta\rho(r) \exp(-iqr) dr^2 \right|$$

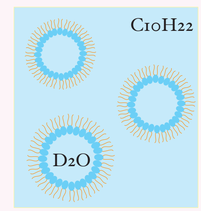
form factor of the unit particle; depends on the scattering contrast

$$S(q) = \frac{1}{nV} \iint \exp\left[iq\left(r_i - r_j\right) \right] dr_i dr_j$$

structure factor of the system; independent of the scattering contrast



bulk contrast



film contrast

relative form factor

$$R(q) = \frac{I_b(q)}{I_f(q)} = \frac{F_b(q)}{F_f(q)}$$

no need to assume any shape of structure factor

Nagao et al., Phys. Rev. E 75, 061401 (2007).

the same analogy is applied to understanding the intermediate scattering functions, $I(q,t)/I(q,0)$s', observed by NSE

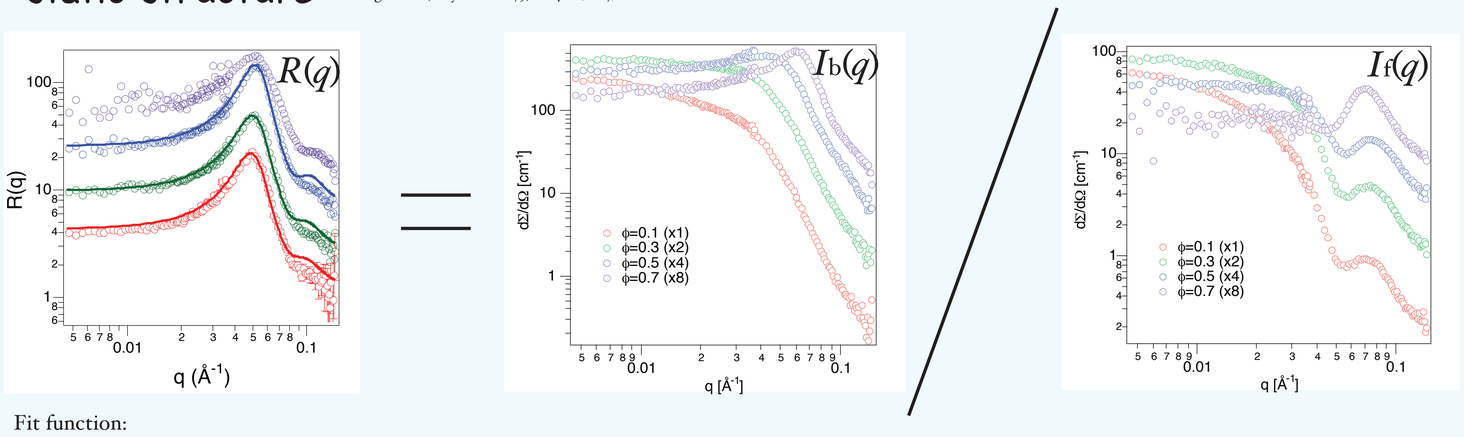
relative intermediate form factor

$$R(q,t) = \frac{\left[I(q,t)/I(q,0) \right]_b}{\left[I(q,t)/I(q,0) \right]_f} \approx \frac{\left[F(q,t)/F(q,0) \right]_b}{\left[F(q,t)/F(q,0) \right]_f}$$

Nagao and Seto, Phys. Rev. E 78, 011507 (2008).

static structure

Nagao et al., J. Appl. Crystallogr. 36, 602 (2003).
Nagao et al., Phys. Rev. E 75, 061401 (2007).



Fit function:
Model form factor for the core-shell model spherical form factor.

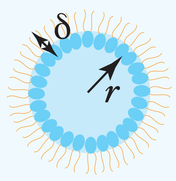
$$F(q) = \int h(r) \left| f(q,r) \right|^2 dr$$

$h(r)$; Gaussian or Lognomal distribution function

$$f(q,r) = \frac{4\pi}{3}\left(\rho_w - \rho_s\right)\left[r^3 j_0(qr) - \frac{\rho_o - \rho_s}{\rho_w - \rho_s}(r+\delta)^3 j_0\{q(r+\delta)\} \right]$$

$j_0(x)$; spherical Bessel function of the 0-th order

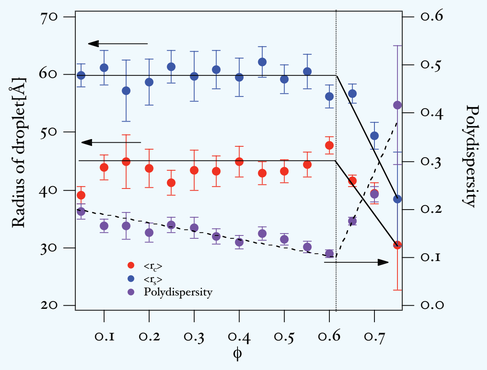
parameters



droplet radius r

shell thickness δ

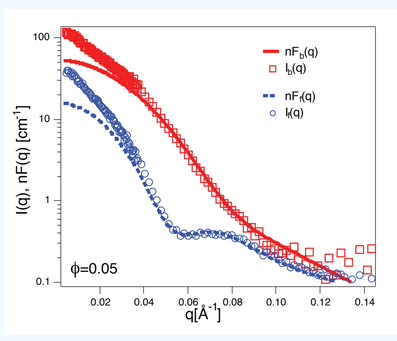
polydispersity $p = \frac{\Delta r}{\langle r \rangle}$

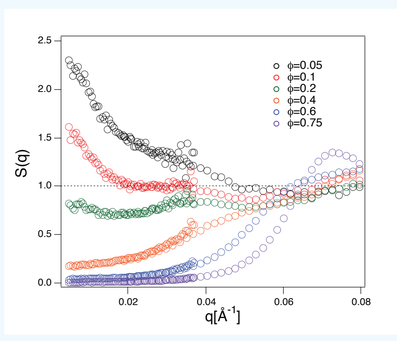


ϕ<0.65
constant r, δ
decrease of p

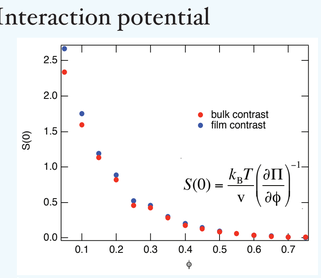
ϕ≥0.65
decrease of r, δ
increase of p
-> no more droplet structure is stabilized

Decoupled Form Factor and Structure Factor





Interaction potential

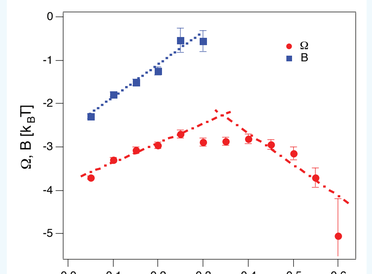


$$\frac{\Pi v}{k_B T} = \phi + \left[4 - \exp\left(-\frac{B}{k_B T} \right) \right] \phi^2 + \cdots$$

cluster model: binding energy of droplet B
Koper et al., J. Phys. Chem. 99, 13291 (1995).

$$\frac{V(r)}{k_B T} = \begin{cases} +\infty & 0 < r < R' \\ \Omega & R < r < R' \\ 0 & R' < r \end{cases}$$

square well potential model: potential depth Ω
Baxter et al., J. Phys. Chem. 49, 2770 (1968).

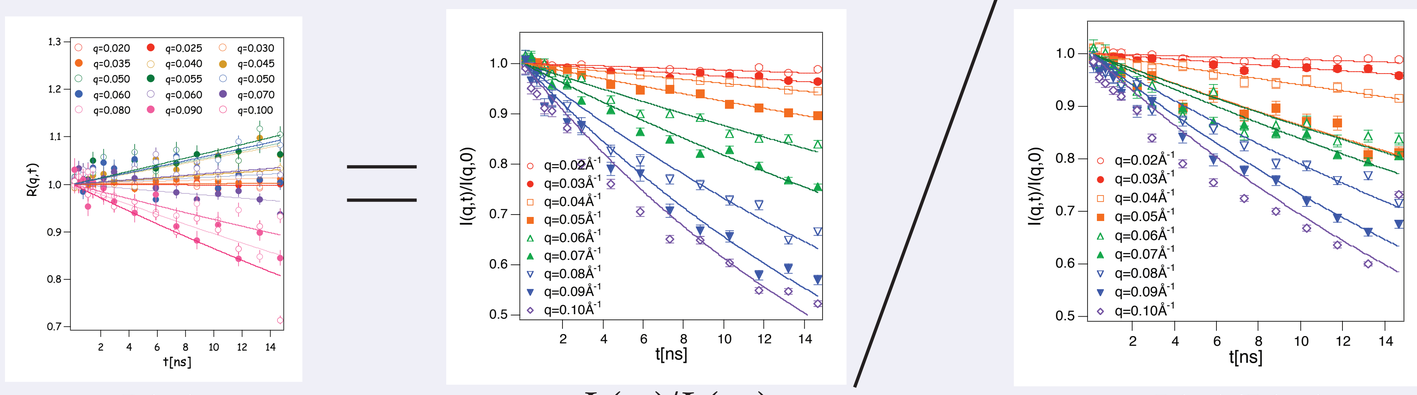


ϕ<0.3: attractive interaction decreases
ϕ>0.4: attractive interaction increases

at least two kinds of dominant interaction between droplets

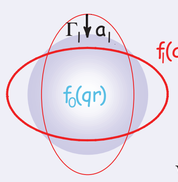
dynamic structure

Nagao and Seto, Phys. Rev. E 78, 011507 (2008). Selected for the Virtural Journal of Nanoscale Science & Technology, 18-6 (2008).



Fit function:
single particle shape fluctuation dynamics is applied

$$\frac{I(q,t)}{I(q,0)} = \exp\left(-\Gamma_{eff} t \right)$$



$$\Gamma_{eff} = \Gamma_0 + \Gamma_{def} = D_0 q^2 + \frac{5\Gamma_2 f_2(qr)\left\langle |a_2|^2 \right\rangle}{4\pi f_0(qr) + 5 f_2(qr)\left\langle |a_2|^2 \right\rangle}$$

$$R(q,t) = \exp\left[-\left(\Gamma^b_{eff} - \Gamma^f_{eff} \right) t \right] = \exp\left[-\left(\Gamma^b_{def} - \Gamma^f_{def} \right) t \right]$$

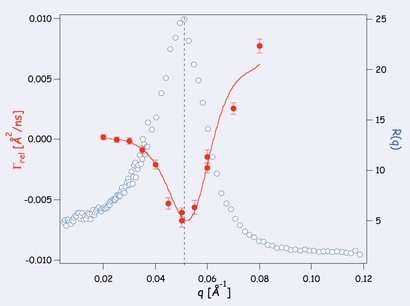
where $D^b_o = D^f_o$ is assumed

parameters

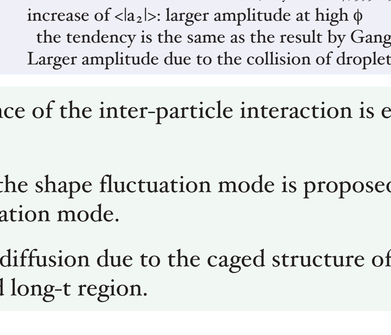
translational diffusion constant: D_0

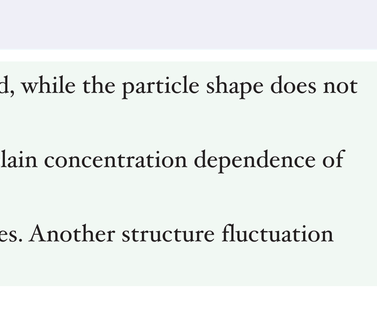
decay rate for the second mode: Γ_2

amplitude for the second mode: $\langle |a_2| \rangle$



Decoupled Form and Structure Factor Fluctuations





a = 0.91 ± 0.08
cf. a = 0.78 by Gang et al. (experiment)
Gang et al., Phys. Rev. E 52, 6289 (1995).
a = 1.4 by Edwards and Schwartz (theory)
Edwards and Schwartz, Physica A 167, 595 (1990).
increase of $\langle |a_2| \rangle$: larger amplitude at high ϕ
the tendency is the same as the result by Gang et al.
Larger amplitude due to the collision of droplets

center-of-mass diffusion decrease with ϕ
the dip position corresponds to the peak position of S(q) which is shown above.

Summary

We proposed the relative methods to analyze contrast variation neutron scattering data.

We have decoupled contributions from form and structure factors and those fluctuations in a microemulsion system.

A complex concentration dependence of the inter-particle interaction is evaluated, while the particle shape does not change drastically.

A collision driven enhancement of the shape fluctuation mode is proposed to explain concentration dependence of the parameters for the shape fluctuation mode.

A slow down of the center-of-mass diffusion due to the caged structure of particles. Another structure fluctuation mode is suggested in the high-q and long-t region.