Perturbation theory for a microemulsion with triangular well potential†

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Abstract. The perturbation approach of Barker and Henderson (1967, 1968) has
been applied to a microemulsion obeying triangular well potential as a perturbative
attractive tail over the Percus-Yevick (PY) hard sphere model by calculating the Ray-
leigh ratio, $R_{\infty}$, under the mean spherical approximations. The results are in better
agreement with experimental values.

Keywords. Triangular well potential; Rayleigh ratio; mean spherical approximations;
hard sphere; perturbation.

1. Introduction

Perturbation theories have received a lot of attention in recent years as a means of
calculating liquid state properties (Zwanzig 1954; Rowlinson 1964; Smith and Alder
1959). In this paper, we propose to apply the perturbation theory of Zwanzig (1954)
as extended by Barker and Henderson (1967) to a microemulsion (Calji et al 1977)
interacting through a triangular well-potential. Recently the authors have tested
the applicability of a square well-potential (Somasekhara Reddy and Murthy 1982)
to microemulsion (Calji et al 1977) by calculating, $R_{\infty}$, the Rayleigh ratio. It will,
therefore, be interesting to see how the triangular well-potential works with in the
framework of mean spherical model (MSM) approximation. This has been examined
in this paper.

The triangular well-potential (Reed and Gubbirs 1973) is defined as

$$u(r) = \begin{cases} 
\infty & 0 < r \leq \sigma \\
\lambda \epsilon/(\lambda - 1) \left(\frac{r}{\lambda \sigma} - 1\right) & \sigma < r < \lambda \sigma \\
0 & r > \lambda \sigma 
\end{cases}$$

(1)

where $\lambda$ represents the breadth, $\epsilon$ represents the depth of the triangular well used
and $\sigma$, the effective rigid sphere diameter.

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2. Theory

The MSM approximation can be treated as a perturbation of the Percus-Yevick (1958) (PY) hard sphere model (Wertheim 1963; Thiele 1965) and can be written as

\[
C(r) = 1 - \exp \left\{ \frac{u(r)}{k_B T} \right\} g(r) \quad r < \sigma
\]

\[
= - \frac{u(r)}{k_B T} \quad r > \sigma
\]  

(2)

where \( g(r) \) is the radial distribution function and \( C(r) \) is the so-called direct correlation function. We therefore assume

\[
C(r) = C_{WT}(r) = - \frac{u(r)}{k_B T} \quad 0 < r < \sigma
\]

\[
= 0 \quad r > \lambda \sigma
\]  

(3)

and

\[
a = \frac{1 + 2 \eta^2}{1 - \eta}^4
\]

\[
\beta = - 6 \eta (1 + \eta/2)^2/(1 - \eta)^4
\]

\[
\gamma = \left( \frac{\eta}{2} \right) \left( 1 + 2 \eta^2 \right) / (1 - \eta)^4
\]  

(4)

\( C_{WT}(r) \) is the well-known Wertheim-Thiele (1963, 1965) solution of the PY equation for hard sphere systems. The packing fraction is related to \( \sigma \) by \( \eta = \pi \rho \sigma^3/6 \), \( \rho \) being the average number density.

Fourier transforming equation (3), we get

\[
\rho \mathcal{C}(k) = \left[ - 24 \eta / (k \sigma)^4 \right] \left[ a (k \sigma)^2 \sin k \sigma - k \sigma \cos k \sigma \right] + \beta (k \sigma)^2 \left\{ 2k \sigma \sin k \sigma - (k^2 \sigma^2 - 2) \cos k \sigma - 2 \right\}
\]

\[
+ \gamma \left\{ (4k^3 \sigma^3 - 24k \sigma) \sin k \sigma - (k^4 \sigma^4 - 12k^2 \sigma^2 + 24) \cos k \sigma + 24 \right\}
\]

\[
+ (1/\lambda - 1) \left( \epsilon / k_B T \right) (k \sigma)^2 \left\{ \lambda k \sigma \sin \lambda k \sigma \right. 
\]

\[
\left. + 2 \cos \lambda k \sigma - (\lambda \kappa^2 \sigma^2 - k^2 \sigma^2 + 2) \cos k \sigma - (2 - \lambda) k \sigma \sin k \sigma \right]\}
\]  

(5)

and \( \mathcal{C}(k) \), the Fourier transform of \( C(r) \), is simply related to the structure factor, \( S(k) \) by (Gopala Rao and Murthy 1975)

\[
S(k) = [1 - \rho \mathcal{C}(k)]^{-1}
\]  

(6)

The final form of \( \rho \mathcal{C}(k) \) is given by (5) and its value in the limit \( K \to 0 \) is

\[
\rho \mathcal{C}(0) = (1 - a) + \frac{2 \eta \epsilon (\lambda^3 + \lambda^2 + \lambda - 3)/k_B T}{k_B T}
\]  

(7)
3. Results and discussions

Reduced scattering intensity of the microemulsion is

\[ R_0 = (1 + \cos^2 \theta) \chi M C [1 - \rho C(0)]^{-1} \]  \hspace{1cm} (8)

Because scattering disymmetry was absent, the light scattering ratio \( R_{90} \) can be represented by Debye (1974) as

\[ R_{90} = \chi M C [1 - \rho C(0)]^{-1} \]  \hspace{1cm} (9)

where

\[ \chi = 2\pi^2 n^2 (dn/dc)^2 / (\lambda_0^4 N) \]  \hspace{1cm} (10)

where \( M \) is the particle molar mass, \( c \) is the weight density \( (c = \rho M/N) \), \( n \) is the refractive index and \( \lambda_0 \) the wavelength in vacuo of unpolarized light.

Equations (7) and (9) have been used for computing \( R_{90} \) for a microemulsion (Calji et al. 1977) containing toluene, hexanol, potassium oleate and oleic acid and the results are shown in figure 1. The potential parameters have been determined by fitting (8) with the experimental values at the first peak position and at the hard sphere diameter, \( \sigma = 10.25 \) nm. The potential parameters are \( \lambda = 1.47 \) and \( \epsilon/k_B T = 0.64 \).

Figure 1 shows that values especially at the peak position are in better agreement with experimental results than those from the short range van der Waals attractive tail. Calculation of the structure factor at various values of \( K \), using the present potential parameters are in progress and the results will be discussed in a future communication.
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