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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 Rayleigh ratio, R_{90}, 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_{90}, 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

$$\begin{aligned} u(r) &= \infty && 0 < r \leqslant \sigma \\ &= \lambda\epsilon/(\lambda-1)\,(r/\lambda\sigma - 1) && \sigma < r < \lambda\sigma \\ &= 0 && r > \lambda\sigma \end{aligned} \tag{1}$$

where λ represents the breadth, ϵ represents the depth of the triangular well used and σ, 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

$$\begin{aligned} C(r) &= 1 - \exp\{u(r)/k_B T\}\, g(r) \qquad r < \sigma \\ &= -u(r)/k_B T \qquad\qquad\qquad r > \sigma \end{aligned} \tag{2}$$

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

$$\begin{aligned} C(r) = C_{WT}(r) &= -[\alpha + \beta(r/\sigma) + \gamma(r/\sigma)^3] \quad 0 < r \leqslant \sigma \\ &= -(\epsilon/k_B T)(\lambda/\lambda - 1)((r/\lambda\sigma) - 1) \quad \sigma \leqslant r \leqslant \lambda\sigma \\ &= 0 \qquad\qquad r > \lambda\sigma \end{aligned} \tag{3}$$

and

$$\begin{aligned} \alpha &= (1 + 2\eta)^2/(1-\eta)^4 \\ \beta &= -6\eta(1 + \eta/2)^2/(1-\eta)^4 \\ \gamma &= (\eta/2)(1+2\eta)^2/(1-\eta)^4 \end{aligned} \tag{4}$$

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

Fourier transforming equation (3), we get

$$\begin{aligned} \rho C(k) = {} & [-24\eta/(k\sigma)^6]\,[\alpha(k\sigma)^3(\sin k\sigma - k\sigma\cos k\sigma) \\ & + \beta(k\sigma)^2\{2k\sigma\sin k\sigma - (k^2\sigma^2 - 2)\cos k\sigma - 2\} \\ & + \gamma\{(4k^3\sigma^3 - 24k\sigma)\sin k\sigma - (k^4\sigma^4 - 12k^2\sigma^2 + 24)\cos k\sigma + 24\} \\ & + (1/\lambda - 1)(\epsilon/k_B T)(k\sigma)^2\{\lambda k\sigma \sin\lambda k\sigma \\ & + 2\cos\lambda k\sigma - (\lambda k^2\sigma^2 - k^2\sigma^2 + 2)\cos k\sigma - (2-\lambda)k\sigma\sin k\sigma\}] \end{aligned} \tag{5}$$

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

$$S(k) = [1 - \rho C(k)]^{-1} \tag{6}$$

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

$$\rho C(0) = (1-\alpha) + 2\eta\,\epsilon(\lambda^3 + \lambda^2 + \lambda - 3)/k_B T \tag{7}$$

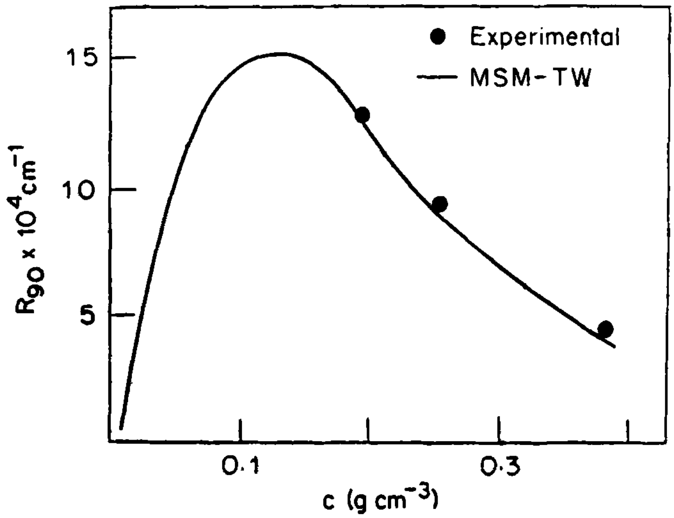

Figure 1. Rayleigh ratio, R_{90}, as a function of number density. Curve is calculated by using the triangular well-potential.

3. Results and discussions

Reduced scattering intensity of the microemulsion is

$$R_\theta = (1 + \cos^2 \theta)\, \mathscr{K}\, Mc\, [1 - \rho\, C(0)]^{-1} \tag{8}$$

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

$$R_{90} = \mathscr{K}\, CM\, [1 - \rho C(0)]^{-1} \tag{9}$$

where

$$\mathscr{K} = 2\pi^2 n^2 (\mathrm{d}n/\mathrm{d}c)^2/(\lambda_0^4 N) \tag{10}$$

where M is the particle molar mass, c is the weight density ($c = \rho M/N$), n is the refractive index and λ_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 olete 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, σ=10·25 nm. The potential parameters are λ=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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