APPENDIX B

REPRINTS

LIGHT SCATTERING OF A CONCENTRATED MICROEMULSION

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Applicability of the square-well potential for a concentrated microemulsion is tested by calculating the Rayleigh ratio under the mean spherical model approximation. The good agreement obtained suggests that the structure of such emulsions can be represented by a square-well model.

Recent advances in statistical mechanics of simple fluids employing perturbation methods [1,2] suggest that a similar approach may be useful for concentrated microemulsions [3]. A perturbation version of the Percus–Yevick (PY) hard-sphere model [4] is the mean spherical model (MSM) approximation [5].

In MSM the direct correlation function, $C(r)$, can be written as [6]

$$C(r) = C_{WT}(r), \qquad 0 < r \leqslant \sigma, \tag{1}$$

$$= -u(r)/k_B T, \qquad r \geqslant \sigma, \tag{2}$$

where $C_{WT}(r)$ is the Wertheim–Thiele solution of the PY equation for hard-sphere systems [4] and $u(r)$ is the pair potential, being presently represented by a square-well potential, and k_B is the Boltzmann constant. $C(k)$, the Fourier transform of $C(r)$ is related to the structure factor, $S(k)$, by [6]

$$S(k) = [1 - \rho C(k)]^{-1}. \tag{3}$$

The final form of $C(k)$ is given elsewhere [6] and its value in the limit $k \to 0$ is

$$\rho C(0) = (1 - \alpha) + 8\eta\epsilon(\lambda^3 - 1)/k_B T, \tag{4}$$

where

$$\alpha = (1 + 2\eta)^2/(1 - \eta)^4. \tag{5}$$

Here the packing fraction η is related to the hard-sphere diameter σ by $\eta = \pi\rho\sigma^3/6$, ρ being the average number density. λ and ϵ correspond to the width and depth of the square well used.

According to Debye the light scattering ratio, R_{90}, can be represented as [7]

$$R_{90} = KcM/[1 - \rho C(0)], \tag{6}$$

with

$$K = 2\pi^2 n^2 (dn/dc)^2 (\lambda_0^4 N)^{-1}. \tag{7}$$

M is the particle molar mass, c is the weight density ($c = \rho M/N$), n is refractive index and λ_0 is the wavelength "in vacuo" of unpolarized light.

Eqs. (4)–(7) have been used to compute R_{90} for a concentrated microemulsion [7] and the results are shown in fig. 1. The potential parameters have been determined by fitting eq. (6) with the experimental

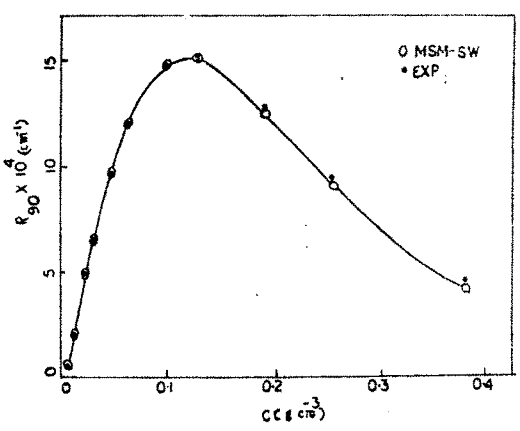

Fig. 1. Light scattering of a microemulsion. Potential parameter values: $\lambda = 1.25$; $\epsilon/k_B T = 0.62$.

value at the first peak position and the parameters thus obtained are given in fig. 1.

The agreement obtained is quite satisfactory and suggests that the concept of pairwise interaction is a useful one even in the theory of concentrated micro-emulsions. Calculations of $S(k)$ at various values of k and the diffusion coefficient are in progress and the results will be published in future communications.

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