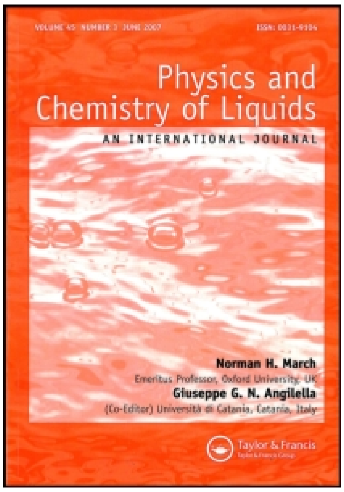

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The Second Virial Coefficient and "Liquid–Vapour" Phase Transition in Sterically Stabilized Colloidal Dispersions

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The observed temperature dependence of the second virial coefficient in dispersions of sterically stabilized colloids is explained using a macroparticle interaction potential that allows for a decrease of the effective hard core diameter with increasing temperature. Such assumptions also account for the "liquid-vapour" phase transition.

Key Words: Interaction potential, effective hard core.

The effects of temperature (T) variation on non-aqueous dispersions of sterically stabilized silica spheres have recently attracted considerable experimental attention.[1–7]. The most interesting aspect of such studies has been the observation of two critical flocculation temperatures in the phase diagram[1–4] and a non-monotonic T-dependence of the second virial coefficient B_2.[7] To date these properties have been not correlated and one reason for this has been the lack of a suitable macroparticle interaction model for the systems. Jansen *et al.*[7] proposed a simple model interaction with a T-independent hard core plus a T-dependent attractive square well. At low temperatures, this potential describes the concave-down phase coexistence curve and the $B_2(T)$ behaviour for dispersions of sterically stabilized silica spheres in toluene. However, it does not explain the observed non-monotonic behaviour of B_2 at higher temperatures (shown in Figure 1) or the appearance of a concave-up coexistence curve in similar systems with *n*-alkane solvents.[1–4]

In this paper, we relate these two dispersion properties using a macroparticle interaction potential $U(r)$ with a T-dependent double Yukawa (DY) form that was introduced in another paper where we studied the qualitative behaviour of the phase diagram.[8] Here we present a quantitative description of both $B_2(T)$ and the "liquid–vapour" phase transition observed for these systems.

We begin with the classical definition of B_2 from an expansion of the osmotic pressure Π in powers of the macroparticle number density n with[9]

$$\Pi/k_BT \cong n[1 + B_2 n + \theta(n^2)], \tag{1}$$

where k_B is Boltzmann's constant and

$$B_2 = (2\pi N_A/M)\int_0^\infty [1 - \exp(-U(r)/k_BT)]r^2\,dr. \tag{2}$$

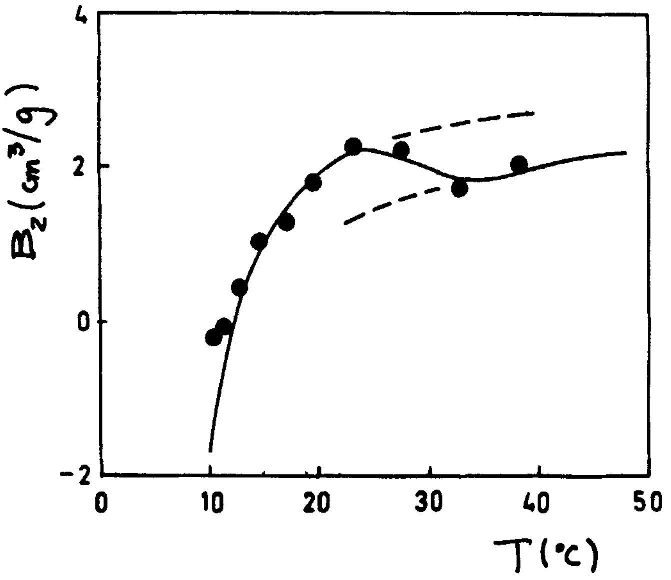

Figure 1 Temperature dependence of the second virial coefficient B_2 for C_{18} stabilized silica spheres dispersed in toluene. The dots (●) are experimental values,[7] and the solid line is the result of this work. The dashed line extensions of the solid line indicate the behaviour of B_2 that follows from fixing λ at a constant value appropriate to either high- or low-T régimes. We used σ = 70 nm and $M = 1.35 \times 10^8$ g. mole^{-1}.

N_A is Avogadro's number and M the molar mass of the particles.[7]

The T-dependent DY form for $U(r)$ is defined by

$$U(r, T)/\varepsilon = (E/x)\{\exp[-A\,(x\lambda(T) - 1)] - \exp[-B(x - 1)]\}, \quad (3)$$

where ε is the potential well depth, $x \equiv r/\sigma$ and σ represents an effective diameter for the macroparticles at $\lambda(T) = 1$. This interaction potential contains a new element in the empirical $\lambda(T)$-function which provides a measure for changes in the repulsive part of the interaction potential that can be related to changes in the polymer layer thickness with increasing T. The DY-coefficients A, B and E are chosen so as to allow $U(r)$ to mimic the 12-6 Lennard-Jones potential function and, hence, the van der Waals forces when $\lambda \equiv 1$ as discussed in [10]. Thus B_2 can be easily evaluated numerically from Eqs (2) and (3) once $\lambda(T)$, M, σ and ε are specified. In this work ε is taken to be a function of T. This reflects the T-dependence of the Hamaker constant, A_H, that characterises the magnitude of the van der Waals interaction.

Following the work of Jansen *et al.*[7] we assume that at low T the form of the silica particle and its terminally attached C_{18} chain coat is essentially T-independent and set λ to a constant value. At lower temperatures the attached chains are fully stretched and likewise the repusive part of the DY potential is fully extended. The T-variation of ε (or, alternatively, A_H) is then chosen to ensure that the low T behaviour of B_2 is correctly reproduced.

At intermediate temperatures we use, for simplicity, a linear T-dependence for λ. This allows for a small change of the associated effective core diameter of the sterically stabilized colloids with temperature. As indicated in [8], the introduction of $\lambda(T)$ can explain the existence of an upper coexistence curve in terms of a small decrease of the attached chain layer thickness with increasing T. At higher temperatures λ once more tends to a constant value due to a natural compaction of the attached chain layer. Although it is believed that the terminally-attached C_{18} chains are relatively close-packed on the surface of the silica particles,[3] small conformational changes will still occur with increasing T due to the T-dependence of the chain-solvent interaction. We note, in passing, that the T-dependent repulsive Yukawa term used here is much more sensitive to changes in the range of steric repulsion than the similar, but not identical, DY-function proposed to describe the phase separation curves of micellar solutions.[11–13] The principle difference between this and our previous qualitative study[8] lies in the simplifying assumptions used.

In Figure 1 we compare our results for $B_2(T)$ with the experimental data for C_{18} stabilized dispersions of silica spheres in toluene.[7] The

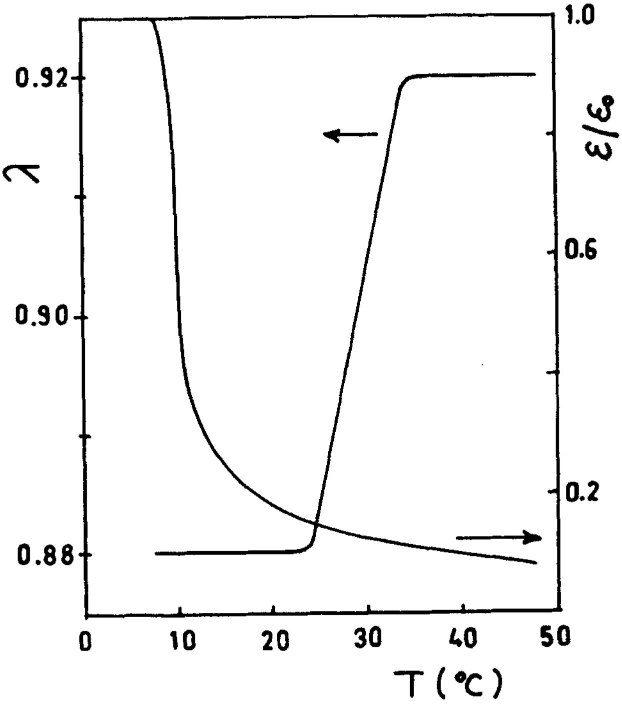

Figure 2 The DY interaction parameters λ and ε as a function of temperature which reproduce the second virial coefficient behaviour shown in Figure 1. Here $\varepsilon_0/k_B = 661.1$ K.

agreement is excellent for the continuous $\lambda(T)$ and $\varepsilon(T)$ curves shown in Figure 2. It is important to note that the "anomalous" experimental points of B_2 at higher T are within the experimental uncertainties.[7]

The key role played by the T-dependence of λ and ε is revealed by plotting the macroparticle interaction potential as a function of T as shown in Figure 3. A linear variation of λ with T at intermediate temperatures allows a small decrease of the effective core size of the pair potential with increasing T that corresponds to a small decrease in the grafted chain layer thickness. Note from Figure 2 that $\varepsilon(T)$ decreases almost linearly with T in the range of the linear increase of $\lambda(T)$. The interplay of these two effects results in the well depth of our DY potential taking on almost "constant" values at those temperatures. This gives rise to the non-monotonic behaviour seen in B_2 as a function of T for the sterically stabilized dispersion in toluene.

When λ is T-independent and $\varepsilon = \varepsilon(T)$ we obtain only monotonic forms for $B_2(T)$ which result from the decreasing magnitude of the

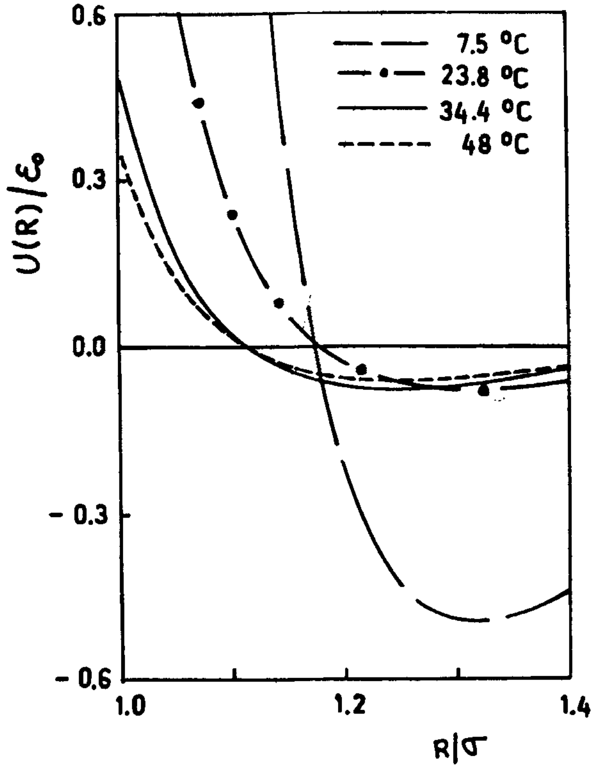

Figure 3 The macroparticle interaction potential function at different temperatures across the experimental range given by the model DY form with the parameters displayed in Figure 2.

attractive interaction with increasing T. Such behaviour is illustrated in Figure 1 by the dashed line extensions to the solid line with λ taking constant values in the low- and high-T limits of λ shown in Figure 2. However, if $\lambda(T)$ is not constant, we suggest that the model DY interaction for $U(r, T)$ reproduces, and enables us to interpret, the available $B_2(T)$ data of sterically stabilized colloids over the entire measured T-interval.

The DY-potential deduced from the $B_2(T)$ data can be checked by computing the phase diagram for the system and comparing with experiment. Figure 4 shows the calculated phase diagram in the T–c plane obtained by using the Gibbs–Bogolyubov inequality variational approach.[8] This is to be compared with the experimentally determined cloud-point temperatures as a function of concentration.[7] It can be seen that the measured cloud-point temperatures are well reproduced by the

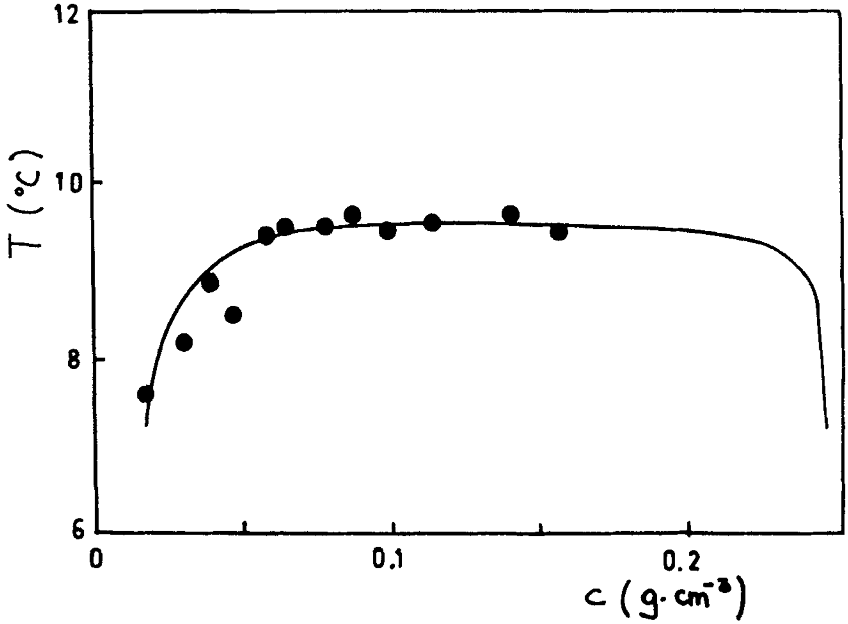

Figure 4 Experimental cloud-point temperatures against concentration (●) and calculated phase coexistence curve (————) using the same DY-potential parameters which fit the $B_2(T)$ data. Note that $T^* = (1/611.1) \times (\varepsilon_0/\varepsilon) \times T$ and $\rho^* = N_A \times M \times \sigma \times c$, N_A being Avogadro's number.

T-dependent interaction potential proposed here. We conclude thus that the reported "liquid–vapour" phase transition and the "anomalous" $B_2(T)$ data of C_{18} stabilized silica spheres in toluene are consistent with a macroparticle interaction that allows for small changes in steric repulsion with T.

We have previously shown that the equilibrium phases of C_{18} stabilized silica spheres dispersed in n-alkanes may also be described using the T-dependent DY potential as given in Eq. (3).[8] The temperature dependent ε deduced here, for C_{18} stabilized silica spheres dispersed in toluene, would preclude the existence of a concave-up phase coexistence curve in the temperature range studied, and experiments appear to confirm this prediction.[7] A much deeper "anomaly" in $B_2(T)$ would be necessary to produce both upper and lower temperature phase coexistence curves in the phase diagram. This could only happen if the transition in $\lambda(T)$ occurred at higher temperatures when $\varepsilon(T)$ approached a constant value.

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