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## On the stability of charge-stabilized colloidal dispersions

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**Abstract.** Reversible ‘liquid–vapour’ like transitions and irreversible coagulation in charge-stabilized colloidal dispersions are studied using a one-component macroparticle framework with a conventional DLVO interaction potential. The spinodal and coexistence curves are calculated as a function of salt concentration using thermodynamic perturbation theory—specifically the random-phase approximation using firstly hard spheres and then sticky hard spheres as reference systems. With the hard spheres, the hard-core location varies between the first and second zero of the DLVO potential. In the case of the sticky hard spheres, the hard core is located at the first zero of the DLVO potential; this models the deep narrow primary minimum of this potential. The irreversible coagulation is distinguished from the reversible transition by the flattening of the coexistence curve at a value of salt concentration above the range over which the ‘liquid–vapour’ transition takes place.

### 1. Introduction

Grimson (1983a, b) and Victor and Hansen (vH) (1984, 1985) have presented plausible statistical mechanics calculations of the ‘liquid–vapour’ phase separation in mono-disperse charge-stabilized dispersions of colloidal particles, whose possible existence—under favourable conditions—was suggested by Long *et al* (1972).

In the traditional one-component description of these systems, the phase behaviour of the macroparticles results from the interplay between the screened Coulomb repulsion and the van der Waals attractive forces which feature in the DLVO potential energy  $\varphi(r)$  of interaction between the macroparticles (however, see Canessa *et al* (1988)). Besides the very deep primary minimum which leads to irreversible coagulation of the macroparticles, the interplay between the two forces may give rise to a secondary minimum which is responsible for the reversible flocculation akin to the liquid–vapour equilibrium mentioned above.

Both set of papers referred to above make use of the thermodynamic perturbation theory of liquids in their work (see, e.g., Hansen and McDonald 1986). Grimson uses the random-phase approximation (RPA) with a hard sphere (HS) reference system in his first paper (Grimson 1983a) and the one-component plasma (OCP) as the reference

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system in his second paper (Grimson 1983b). VH use the more accurate Weeks, Chandler and Andersen (WCA) theory with a HS reference system together with the high-temperature approximation. However, the main differences between the two approaches are quantitative rather than qualitative when—as indicated by VH—the values of the parameters used in the calculations correspond to the system of interest.

VH arbitrarily classify the dispersion as thermodynamically stable when the Coulomb barrier in  $\varphi(r)$  is larger than a certain value which is substantially higher than the thermal energy  $k_B T$  that must be later correlated with experiment.

In this work we discuss whether by the introduction of the deep minimum in the model potential—the sticky hard sphere (SHS)—criteria for irreversible change can be formulated. This would indicate the suitability of the arbitrary criteria introduced by VH to separate the stable system from one which has undergone irreversible coagulation.

In order to analyse the problem of stability within the one-component description of the colloidal dispersion, one needs to study the competition between the Coulomb barrier and the deep narrow primary minimum in the DLVO potential.

The importance of the role played by the first minimum of the DLVO potential in obtaining a rich variety of phase behaviour has been recognized in the recent paper by Kendrick *et al* (1988). However, in their work, an approximate form was used for the van der Waals attraction which gives a primary minimum that differs from that of the conventional DLVO potential in being of finite depth and greater width.

More recently Hemmer and Stell (1990) have studied the effect of strong short-range attractions on the phase transition in a one-dimensional fluid by using a model potential which contains both a long-range and short-range attractive part.

For the present studies a thermodynamic perturbation theory is employed, the calculations being carried out within the RPA, with a SHS reference system plus a DLVO perturbation potential. As pointed out by VH, using the RPA results in only qualitative accuracy.

The SHS was first introduced by Baxter (1968), within the Percus–Yevick (PY) approximation, as an exactly soluble pathological model. Its main virtue appeared to be that it was the simplest non-trivial model—within the pair distribution function theories of liquids—that exhibits a liquid–vapour transition and a critical point (for a recent discussion see Juanos i Timoneda and Haymet (1989)) as well as, within the framework of density functional theory, a freezing transition (Smithline and Haymet 1985). The interest in this system has recently led to careful Monte Carlo studies by Seaton and Glandt (1986, 1987a, b) and by Kranendonk and Frenkel (1988).

The suitability of the SHS as a reference system to study colloidal dispersions has been the subject of careful scrutiny in recent work by Regnaut and Ravey (1989). However, to our knowledge, this is the first work actually to make use of the SHS in calculations based on thermodynamic perturbation theory.

In section 2 the effects of the separation of the DLVO potential between a HS reference system and the potential tail at points other than the maximum of the Coulomb barrier are discussed. These calculations indicate the role played by the Coulomb barrier. In section 3 the SHS reference system is now placed at the first zero of the DLVO potential in order to study the effects due to the presence of the primary minimum. The SHS is basically characterized by two parameters: the packing fraction  $\eta$ , and the ‘stickiness parameter’  $\tau^{-1}$ . The latter parameter, or more precisely  $\tau$ , is related in some way to the temperature  $T$  of the system under study; the different choices for this relationship are discussed below and the most appropriate choice for the present calculations is indicated.

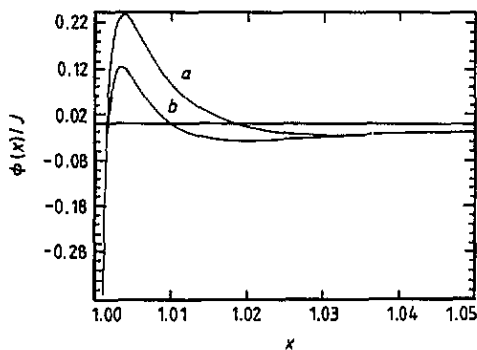


Figure 1. DLVO potential for two values of  $K$  at  $T^* = 0.067$ : curve  $a$ , 160.26; curve  $b$ , 221.01.

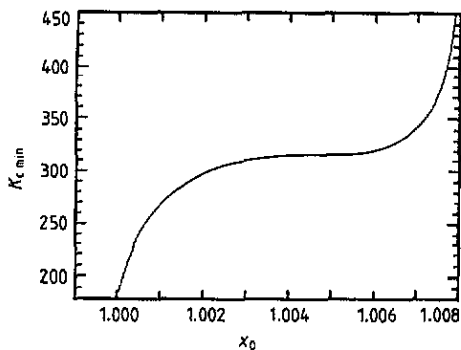


Figure 2. RPA with a HS reference system. Plot of the minimum critical parameter  $K_{c,min}$  (see text) as a function of the cut-off distance  $x_0$  at  $T^* = 0.111$ .

2. The DLVO potential and the RPA with a HS reference system

As indicated in the preceding section the potential energy of interaction used between two colloidal particles is the DLVO potential which, following VH, is written

$$\varphi(r) = \varphi_{es}(r) + \varphi_{vw}(r) \tag{2.1}$$

where the electrostatic repulsion  $\varphi_{es}(r)$  is approximately given by

$$\varphi_{es}(r) = J\sigma_0 \exp[-k_D(r - \sigma_0)]/r = J \exp[-K(x - 1)]/x \tag{2.2}$$

where  $\sigma_0$  is the effective diameter of the macroions,  $J = \pi\epsilon_0\epsilon_r\sigma_0\psi_0^2$  is the electrostatic coupling constant,  $\epsilon = \epsilon_0\epsilon_r$  denotes the dielectric constant of the solvent,  $\psi_0$  is the surface potential of the colloidal particles and  $k_D$  is the inverse of the Debye screening length. Hence the reduced length  $x = r/\sigma_0$ , and reduced Debye wavenumber  $K = k_D\sigma_0$ . In all the calculations reported here the value  $\sigma_0 = 0.6 \mu\text{m}$  is used.

The van der Waals contribution to  $\varphi(r)$  may be written as

$$\varphi_{vw}(r) = -(A/12)h(x) \tag{2.3}$$

where  $A$  is the Hamaker constant, and

$$h(x) = 1/(x^2 - 1) + 1/x^2 + 2 \ln(1 - 1/x^2). \tag{2.4}$$

The thermodynamic perturbation theory used in this work is the RPA for the Ornstein-Zernike direct correlation function  $c(r)$  of the monodisperse colloidal system.

The RPA consists of writing

$$\tilde{c}(q) = \tilde{c}_0(q) - \tilde{\varphi}(q) \tag{2.5}$$

where  $\tilde{c}(q)$  is the Fourier transform (FT) of  $c(r)$  and  $\beta = (k_B T)^{-1}$ . In equation (2.5),  $\tilde{c}_0(q)$  denotes the FT of the direct correlation function  $c_0(r)$  of the reference system, and  $\tilde{\varphi}(q)$  the FT of the potential given by equation (2.1) for values  $x > x_0$ . Here  $x_0$  denotes the position of the cut-off for the reference system following the WCA division of the potential as discussed by Grimson (1983a).

In all calculations the reduced value  $T_J = J/k_B = 60000 \text{ K}$  is used, the regime studied by VH, and the reduced temperature  $T^* = T_A/T$ , where  $T_A = A/k_B$ . In figure 1,  $\varphi(x)$  is

shown for two values of  $K$  at  $T^* = 0.067$ . It should be noted that in the calculations the change in shape of  $\varphi(x)$  with  $K$  must be taken into account. In the examples chosen for figure 1, note that there is not much change in the value of the first zero of  $\varphi(x)$ , say  $x_1$ , whereas the position of the second zero, say  $x_2$ , changes substantially with  $K$ .

As stated in section 1, the first set of calculations were carried out using a HS reference system. For the calculations presented here, only the value of  $\bar{c}(q)$  in its long-wavelength limit  $\bar{c}(q = 0)$  is required. For  $\bar{c}_0(0) = \bar{c}_{\text{HS}}(0)$  the closed algebraic form is provided by the PY approximation (Grimson 1983a).

The spinodal curve in the RPA is given by

$$1 - \rho\bar{c}(0) = 0 \quad (2.6)$$

and the critical point

$$(\partial/\partial\rho)[1 - \rho\bar{c}(0)] = 0 \quad (2.7)$$

where  $\rho$  denotes the bulk number density of the dispersed phase for different values of the cut-off positions  $x_0$ , such that  $x_1 < x_0 < x_2$ , and different temperatures.

Within the RPA, and using the PY approximation, equation (2.6) reads (Grimson 1983a)

$$(1 + 2\eta)^2/(1 - \eta)^4 + (24\beta/x_0^3\sigma_0^3)\eta\bar{\varphi}(0; K) = 0. \quad (2.8)$$

From equation (2.7), one obtains

$$2(1 + 2\eta)/(1 - 5\eta)(1 - \eta)^3 + (12\beta/x_0^3\sigma_0^3)\bar{\varphi}(0; K) = 0. \quad (2.9)$$

From equations (2.8) and (2.9) the critical packing fraction  $\eta_c = 0.1287$  (Grimson 1983a) irrespective of the value of  $T^*$  is obtained. Rewriting equation (2.8) as

$$T^* = -24\bar{\varphi}(0; K)\eta(1 - \eta)^4/x_0^3\sigma_0^3A(1 + 2\eta)^2 \quad (2.10)$$

with the value  $A = 6.07 \times 10^{-20}J$  for the Hamaker constant is used in all the calculations below.

For each value of  $x_0$  and  $T^*$ , using equation (2.10), the spinodal curve for the charged colloidal dispersion is calculated as a function of electrolyte concentration as measured by the reduced inverse Debye screening length  $K$  and the packing fraction  $\eta$ . At each  $T^*$ , equation (2.9) yields a critical value for  $K$ , say  $K_c$ , at  $\eta_c$ .

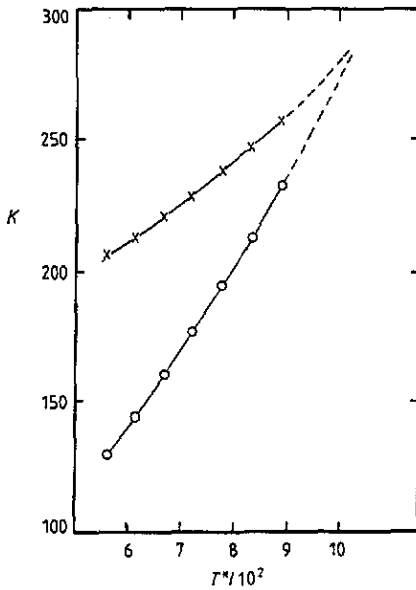
Once the spinodal curve is obtained, the coexistence curve may be evaluated by the usual procedure of requiring, at the temperature  $T^*$ , mechanical equilibrium (i.e. equality of the osmotic pressures of the two phases) and chemical equilibrium (i.e. equality of the chemical potentials) as discussed by Grimson (1983a). This curve bounds the two-phase region: one vapour like and the other liquid like.

For each value of  $T^*$  the value of  $x_0$  which leads to the minimum value of  $K_c$ , say  $K_{c\text{min}}$ , is calculated and also that value which leads to the maximum value of  $K_c$ , say  $K_{c\text{max}}$ . The results are summarized in table 1. It can be seen that, as a rule,  $K_{c\text{max}}$  occurs at a value very near the first zero,  $x_1$  of the DLVO potential, whereas  $K_{c\text{min}}$  occurs just before the value of  $x_0$  reaches the second zero,  $x_2$ .

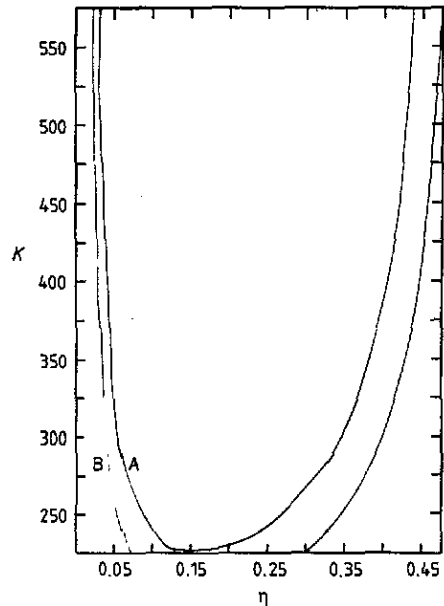
In figure 2,  $K_{c\text{min}}$  is plotted as a function of cut-off distance  $x_0$  for the value of  $T^* = 0.111$ . It is seen that  $K_{c\text{min}}$  remains constant over a wide range of values of  $x_0$ . In fact, for this value of  $K_{c\text{min}}$ , and the parametrization used in our calculations, the height of the Coulomb barrier has already taken on negative values. This means that at this value of  $K_{c\text{min}}$  ( $\approx 350$ ) the system energetically prefers to coagulate irreversibly.

**Table 1.** Critical parameters  $K_{c,max}$  and  $K_{c,min}$  as functions of the reduced temperature  $T^*$ , and the cut-off position  $x_0$  at which these are found.  $x_1$  and  $x_2$  denote the first and second zeros, respectively, of the DLVO potential.

$T^*$	$K_{0,max}$	$x_{c,max}$	$x_1$	$K_{c,min}$	$x_{0,min}$	$x_2$
0.056	206.55	1.0020	1.0020	129.70	1.0240	1.0250
0.061	213.52	1.0020	—	144.51	1.0205	—
0.067	221.01	1.0020	—	160.26	1.0170	1.0180
0.072	229.09	1.0020	—	176.98	1.0145	—
0.078	237.83	1.0020	—	194.72	1.0120	1.025
0.083	247.33	1.0020	—	213.43	1.0105	—
0.089	257.69	1.0020	—	232.98	1.0085	—
0.111	Neither maximum nor minimum, just level					



**Figure 3.** RPA with a HS reference system. Plot of the maximum and minimum critical parameters,  $K_{c,min}$  (x) and  $K_{c,max}$  (o) (see text), as functions of the reduced temperature  $T^*$ .



**Figure 4.** RPA with a HS reference system. Behaviour of the spinodal curve for large values of  $K$  at  $T^* = 0.067$  and two values of the cut-off distance: curve A denotes  $x_0 = 1.00225$ ; curve B denotes  $x_0 = 1.0005$ .

In figure 3,  $K_{c,max}$  and  $K_{c,min}$  appear to converge to the same value ( $\approx 285$ ). At this value, within the limitations imposed by the approximation of ignoring the strong attractive part of the DLVO potential because of the cut-off at  $x_0$ , the crossover to irreversible coagulation has occurred as the height of the Coulomb barrier is zero.

Finally, it is also worth noting that, at any temperature, as  $K$  is increased, the spinodal line tends to straighten up at the ends. This is shown in figure 4 for two values of  $x_0$  at  $T^* = 0.067$ . This behaviour is associated with phase instability as, for these values of  $K$ , the potential barrier in the DLVO potential drops below zero.

### 3. RPA results with a SHS reference system

The potential defining a SHS reference system is given by

$$\beta\varphi_{\text{SHS}}(r) = \begin{cases} \infty & r < d \\ \ln[12\tau(r_1 - d)/r_1] & d < r < r_1 \\ 0 & r > r_1 \end{cases} \quad (3.1)$$

in the limit  $d \rightarrow r_1$ , with  $r_1$  denoting the position of the first zero in the DLVO potential. SHSs are assumed to mimic the hard core and the deep narrow primary minimum of the DLVO colloids.

Henceforth we shall follow Barbooy's (1974) (see also Barbooy and Baer (1975)) notation of the SHS solution in the PY approximation. Now  $\tilde{c}_0(0) = \tilde{c}_{\text{SHS}}(0)$  and

$$1 - \rho\tilde{c}_{\text{SHS}}(0) = (1 + 2\eta - \lambda\eta)^2/(1 - \eta)^4. \quad (3.2)$$

The dimensionless parameter  $\lambda$  is related to  $\tau$  and  $\eta$  by

$$\eta\lambda^2/2(1 - \eta)^4 + [6\eta/(1 - \eta) + \tau]\lambda + (1 + \eta/2)/(1 - \eta) = 0 \quad (3.3)$$

where only one of the roots leads to a physical solution, namely that for which the values of  $\lambda$  satisfy the condition  $\lambda < 2 + \eta^{-1}$ .

Now the spinodal curve from equation (2.6) reads

$$(1 + 2\eta - \lambda\eta)^2/(1 - \eta)^4 + (24\beta/x_1^3\sigma_0^3)\tilde{\varphi}(0; K) = 0 \quad (3.4)$$

and the critical point from equation (2.7) is given by

$$(1 + 2\eta - \lambda\eta)(2 - \lambda - \lambda'\eta)/(1 - 5\eta)(1 - \eta)^3 + (12\beta/x_1^3\sigma_0^3)\tilde{\varphi}(0; K) = 0 \quad (3.5)$$

with  $\lambda' = \partial\lambda/\partial\eta$ . From (3.4) and (3.5) the following equation is obtained:

$$(2 - \lambda - \lambda'\eta)/(1 + 2\eta - \lambda\eta) = (1 - 5\eta)/2\eta(1 - \eta) \quad (3.6)$$

The equation equivalent to equation (2.10) for HS, is obtained from (3.5) and now reads

$$T^* = -24\eta\tilde{\varphi}(0; K)(1 - \eta)^4/x_1^3\sigma_0^3A(1 + 2\eta - \lambda\eta)^2 \quad (3.7)$$

but now depends on  $\tau$ .

As has been done with the HS reference system, the spinodal curve and then the coexistence curve could be calculated by, say, fixing  $T^*$  and plotting  $K$  as a function of  $\eta$ . However, now  $T^*$  also depends on  $\tau$  and the understanding of the relationship between the stickiness parameter  $\tau^{-1}$  and the temperature is crucial to the use of the SHS as a reference system. In a seminal paper on the SHS (Baxter 1968),  $\tau$  is introduced as a 'dimensionless measure of the temperature of the system', but it is in the paper of Barbooy (1974) that the relationship between  $\tau$  and  $T$  is discussed in terms akin to that used in this work. However, other avenues are possible for the choice of  $\tau$  but one has to be careful with the choice owing to the basic instability of the model itself. One method is to use the HS reference system (i.e.  $\lambda = 0$ ) to find  $K_c$  and  $\eta_c = 0.1287$ . From equation (3.7), one can now solve for  $\tau$  at fixed  $T$  and then obtain the spinodal curve. However, this is incorrect as  $\eta_c$  is not the critical value of the SHS system.

The critical SHS values (Barbooy 1974)  $\eta_c = (3\sqrt{2} - 4)/2$  and  $\tau_c = 2 - \sqrt{2}$  could also be used. However, this leads to an obviously unsuitable coexistence curve.

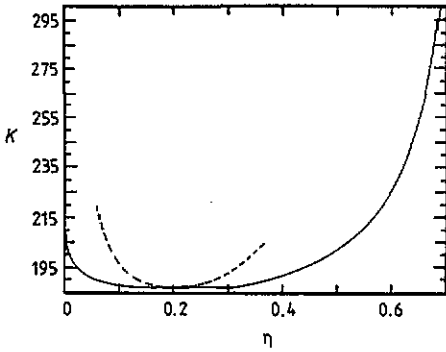


Figure 5. RPA with a SHS reference system, showing spinodal (---) and coexistence (—) curves for  $T^* = 0.067$  and  $\tau = 2.8$ . Here  $\tau$  is regarded as a free parameter.

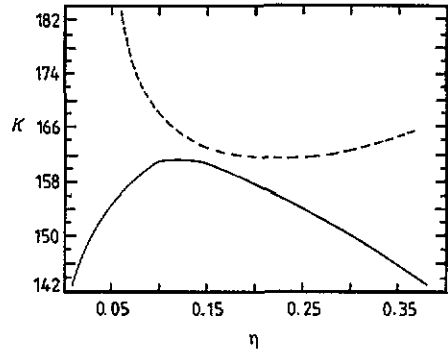


Figure 6. Same as in figure 5, but for  $\tau = 0.8$ .

Another choice is to take  $\tau$  as a free parameter to evaluate the spinodal and coexistence curves. Whilst the results obtained in figure 5 look interesting, in figure 6 the behaviour is again unsuitable.

The approach actually opted for is based on the important observation made by Barboy (1974). He noted that the second virial coefficient of the SHS, plotted as a function of  $\tau/\tau_c$ , and that for the Lennard-Jones potential, plotted as a function of  $T/T_c$  (with  $T_c$  denoting the critical temperature), are very close over a wide range of temperatures. This result suggests firstly that  $\tau$  is proportional to  $T$  and secondly that the second virial coefficient may be used as a convenient procedure to quantify this proportionality. In our case and for ease of computation it is assumed

$$B_2(\text{SHS}) = B_2(\text{DLVO}) = B_2(\text{Sutherland})$$

i.e. the DLVO potential is replaced for the suitably parametrized Sutherland potential (Hirschfelder *et al* 1954) in the calculation of the second virial coefficient. This procedure quantifies the proportionality between  $\tau$  and  $T$  which, to order  $T^{*-2}$ , reads

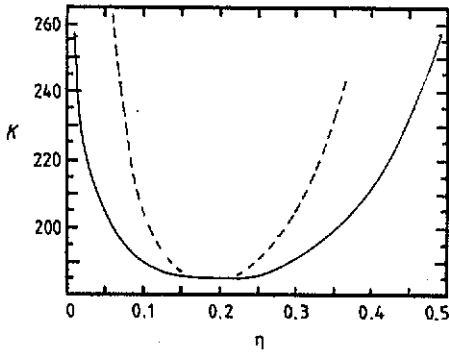
$$\tau = 54T^*[1 + (1/6^3)T^{*-1}]^{-1}. \tag{3.8}$$

With these results it is possible to evaluate the spinodal and coexistence curves. The results obtained for  $T^* = 0.067$  are shown in figure 7 with critical values  $\eta_c = 0.121$  and  $K_c = 190.33$ .

In figure 7, note the flattening of the coexistence curve around the critical point. This is also seen in figure 5. Moreover, there are already signs of the onset of this behaviour in figure 4.

VH introduced irreversible coagulation to their model by imposing a phenomenological constraint familiar from the DLVO theory of colloid stability. They assume that irreversible coagulation occurs when the height of the primary maximum in the DLVO interaction potential drops below a value that must be later correlated with experimental studies. This leads to a horizontal line partitioning off a coagulated or unstable region of the phase diagram. The flattened region of the coexistence curve obtained here bears a strong resemblance to the phenomenological line of VH.





**Figure 7.** RPA with a SHS reference system showing spinodal (----) and coexistence (—) curves for  $T^* = 0.067$ . Here  $\tau$  is obtained by equating the second virial coefficient of the SHS system to that obtained from the Sutherland potential (equation (3.8)).

#### 4. Discussion

We have studied in this work several aspects related to the phase stability of charge-stabilized colloidal dispersions. First, we have considered the changes which take place as the screened Coulomb barrier is allowed to reveal the portion of the curve that descends toward the first zero in the DLVO potential. Values of the barrier position below this zero were not considered; if included, they will lead to the type of phase behaviour already discussed by Kendrick *et al* (1988). In the work presented above, the interest has been focused on the competition between the contributions to the DLVO potential and their relationship to the criteria of phase stability.

We have been particularly interested in the role played by the primary minimum of the DLVO potential and have presented results, based on the RPA, in which this minimum has been modelled by the SHS reference system. Our results suggest that the line drawn by VH, indicating the onset of irreversible coagulation according to a phenomenological criterion, may be an approximation to the flat region which develops in the coexistence curve of the system under study.

However, we have not attempted to determine criteria to find the lowest value of  $K$  for which we have a flat region in the coexistence curve, for the following reasons. First, as stated in section 1, the RPA predicts the correct qualitative trends but it is not sufficiently reliable for quantitative calculations. In particular, the RPA predicts critical temperatures that are too high. Second, there are difficulties in the splitting of the potential with any other thermodynamic perturbation theory when we use a SHS reference system. We are currently studying ways of overcoming this problem. Finally, as referred to above, there are also difficulties with the pathological nature of the SHS, so much so that there is only a narrow window (about 10–15% of the physically allowed values of the stickiness parameter) for which we are able to obtain meaningful results.

Summing up, we have qualitatively shown that it is possible, in principle, to establish well defined criteria for the phase stability of charged colloidal dispersions within a single thermodynamic perturbation theory by appropriately choosing a reference system that mimics the gross features of the interaction potential.

#### Acknowledgment

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