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► To cite this version:

J.M. Victor, J.P. Hansen. “ Liquid-gas ” transition in charged colloidal dispersions. Journal de Physique Lettres, 1984, 45 (7), pp.307-312. 10.1051/jphyslet:01984004507030700 . jpa-00232348

HAL Id: jpa-00232348

<https://hal.science/jpa-00232348>

Submitted on 1 Jan 1984

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Classification

Physics Abstracts

82.70K — 64.70F

« Liquid-gas » transition in charged colloidal dispersions

J. M. Victor and J. P. Hansen

Laboratoire de Physique Théorique des Liquides (*),
Université Pierre et Marie Curie, 75230 Paris Cedex 05, France

(Reçu le 8 décembre 1983, accepté le 2 février 1984)

Résumé. — Nous utilisons la théorie thermodynamique des perturbations pour délimiter le domaine de conditions physiques qui devraient permettre l'observation d'une séparation de phase « liquide-gaz » dans des suspensions aqueuses de particules colloïdales chargées.

Abstract. — We use thermodynamic perturbation theory to determine the range of physical conditions under which a « liquid-gas » phase separation should be observable in electrostatically stabilized aqueous suspensions of spherical colloidal particles.

Light and neutron scattering experiments have shown that colloidal dispersions, like charged polystyrene spheres [1], micelles [2] or microemulsions [3] can exhibit considerable, liquid-like, short-range order. Moreover when the concentration of colloidal particles is increased, a transition to an ordered (crystalline) phase is observed, under the action of the purely steric or electrostatic repulsion between the particles [4]. The electrostatic repulsion between charged colloidal particles may be weakened (screened) by the addition of an electrolyte to a point where the attractive van der Waals forces become dominant for distances beyond the particle diameter, leading to irreversible coagulation [5]. In this letter we examine the possibility of observing an intermediate behaviour, where charge-stabilized dispersions of colloidal particles undergo a reversible phase separation into a dilute « gas » phase coexisting with a concentrated « liquid » phase under the combined action of a screened electrostatic repulsion and the van der Waals attraction. The analogy with the phase diagram of simple molecular substances would then be complete, with the colloidal dispersion exhibiting the usual gas, liquid and solid phases. The possible existence of a « liquid-gas » phase separation has been suggested earlier on experimental grounds [6] and examined theoretically by Grimson [7] in a somewhat different context (i.e. for small neutral, or weakly charged colloidal particles). Here we examine the case of highly charged spherical colloids of arbitrary size and determine theoretically the range of physical parameters over which the phase transition may be observable experimentally in aqueous solutions.

Consider a monodisperse aqueous suspension of charged impenetrable colloidal particles of diameter σ ; the solvent is adequately modelled by a continuum of dielectric constant ϵ , while the counter-ions and any added electrolyte will be characterized by the Debye screening length λ_D .

(*) Equipe Associée au CNRS.

The interaction between colloidal particles is modelled by the usual DLVO potential [5], which is the sum of the screened electrostatic repulsion between their double-layers and of the van der Waals attraction :

$$v(x) = J \frac{e^{-\kappa(x-1)}}{x} - \frac{A}{12} h(x) \quad (1)$$

where $x = r/\sigma$ is the reduced distance between the centres of two particles, $\kappa = \sigma/\lambda_D$ is the reduced inverse Debye length, J is the electrostatic coupling constant related to the surface or zeta potential ψ_0 via $J = \pi\epsilon_0 \epsilon \sigma^2 \psi_0^2$, A is Hamaker's constant and the function $h(x)$ describes the van der Waals attraction between the colloidal spheres :

$$h(x) = \frac{1}{x^2 - 1} + \frac{1}{x^2} + 2 \ln \left(1 - \frac{1}{x^2} \right) \quad (2)$$

$h(x) \sim 1/3x^6$ for $x \gg 1$, while the $1/2(x-1)$ singularity of $h(x)$ at contact leads to coagulation. In the presence of a charge the suspension is charge-stabilized because the Coulomb barrier completely masks the van der Waals attraction for sufficiently large J and weak screening. As κ increases due to the addition of salt, the Coulomb barrier is gradually reduced and in the strong screening regime, the potential (1) takes, at short distances ($x-1 \ll 1$), the simplified form :

$$v(y) = J \left[e^{-y} - \frac{1}{\gamma y} \right] \equiv J\varphi(y) \quad (3)$$

where $y = \kappa(x-1)$ and $\gamma = 24 J/\kappa A$. $\varphi(y)$ exhibits a positive maximum at $y = y_M (x = x_M)$ as soon as $\gamma > 2.7$, and a subsequent minimum at $y_m > y_M (x_m > x_M)$. Coagulation will be prevented as soon as the Coulomb barrier $v(x_M) = J\varphi(y_M)$ is substantially larger than the thermal energy $k_B T$; we shall, somewhat arbitrarily, assume, that the dispersion is charge-stabilized when $\varphi(y_M) > 10 T/T_J$, where $T_J = J/k_B$, but the results are rather insensitive to the precise value of the assumed potential barrier. The situation is schematically represented in figure 1; whenever the preceding condition is fulfilled, we replace $v(x)$ by the hard sphere potential $v(x) = \infty$ for $x < x_M$, thus introducing an effective HS diameter $x_M > 1$; this is justified because the high Coulomb barrier will prevent particles from getting as close as x_M .

We now use thermodynamic perturbation theory [8] to calculate the osmotic properties of the suspension. The effective potential in figure 1 is separated into its repulsive and attractive parts, $v(x) = v_0(x) + w(x)$, where the potential of the « reference system » is :

$$\begin{aligned} v_0(x) &= \infty & x < x_M \\ &= v(x) - v(x_M) & x_M < x < x_m \\ &= 0 & x > x_m \end{aligned} \quad (4a)$$

and the perturbation is defined by

$$\begin{aligned} w(x) &= v(x_m) & x < x_m \\ &= v(x) & x > x_m \end{aligned} \quad (4b)$$

The properties of the reference system are related to the known properties of an equivalent hard sphere fluid via the « blip-function » expansion [9, 8]; for a steep potential $v_0(x)$, the equivalent hard sphere diameter σ' is given by a systematic expansion [10] in which the leading term is the

Fig. 1. — DLVO potential for $T_j = 60\,000\text{ K}$, $T_A = 1\,800\text{ K}$, $\kappa = 200$ ($\gamma = 4$). $S = 1 + 3.1/\kappa$ for $T_0 = 300\text{ K}$. (---) $v(x)$; (-·-) $v_0(x)$; (—) $w(x)$. a : true HS diameter; b : effective HS diameter x_M ; c : Barker-Henderson diameter S . Note that $w(x)$ is not defined for $x < S$.

density-independent Barker-Henderson diameter :

$$S = \frac{\sigma'}{\sigma} = x_M + \int_{x_M}^{x_M} [1 - e^{-\beta v_0(x)}] dx$$

$$= 1 + \frac{S}{\kappa} + O\left(\frac{1}{\kappa^2}\right) \quad (5)$$

where $\beta = 1/k_B T$ and all terms of order $1/\kappa^2$ and higher are neglected, which is justified in the strong screening limit where $\kappa \gg 1$. The thermodynamic properties of the reference system are those of a hard sphere fluid of packing fraction $\eta' = \pi n \sigma'^3/6 = \eta S^3$, where $n = N/V$ is the number of colloidal particles per unit volume and $\eta = \pi n \sigma^3/6$. Note that $\eta' > \eta$, but in practical calculations the difference between η' and η is generally negligible in the present context.

To first order in the attractive perturbation $w(x)$, the Helmholtz free energy per particle, $f = F/N$ is given by the « high temperature approximation » (HTA) [8] :

$$f = f_0(\eta') + 12 \eta \int_S^\infty g_0(\eta', x) w(x) x^2 dx \quad (6)$$

where $f_0(\eta')$ is the free energy of the reference fluid and $g_0(\eta'; x)$ is the corresponding hard sphere pair distribution function, which is well known for all packing fractions, e.g. from the analytic solution of the Percus-Yevick (PY) equation, which is quite accurate below $\eta' \simeq 0.4$ [8]. The osmotic pressure P and isothermal osmotic compressibility χ_T follow directly by differentiating the free energy (6) with respect to the packing fraction η . If $\hat{c}(k)$ denotes the dimensionless Fourier transform of the direct correlation function, the compressibility relation reads :

$$1 - \hat{c}(0) = \frac{\beta}{n\chi_T} = \frac{\partial}{\partial \eta} \left[\eta^2 \left(\frac{\partial \beta f}{\partial n} \right)_T \right]. \quad (7)$$

It is easily verified that (7) with f given by (6) constitutes the $k \rightarrow 0$ limit of the « mean density approximation » (MDA) of Henderson and Ashcroft [11], i.e. :

$$c(r) = c_0(r) - \frac{1}{2} \beta w(r) \frac{\partial^2}{\partial \eta^2} [\eta^2 g_0(\eta', r)]. \quad (8)$$

The spinodal decomposition curve is obtained from the equation $1 - \hat{c}(0) = 0$ (the locus of points where the compressibility diverges). The top of the spinodal curve, which coincides with the critical point of the liquid-gas phase transition, is obtained by solving the coupled equations :

$$1 - \hat{c}(0) = 0 \quad (9a)$$

$$\frac{\partial}{\partial \eta} [1 - \hat{c}(0)]_{T=T_c} = 0 \quad (9b)$$

which yield the critical temperature T_c and the critical packing fraction $\eta_c \simeq \eta'_c$. We have carried out the numerical calculations using the familiar PY equation-of-state [8] for the reference system, and the PY pair distribution functions. The calculation which we have just sketched can be further simplified by making a mean field approximation for the contribution of the perturbation to the thermodynamic properties, i.e. by replacing $g_0(\eta'; x)$ by 1 in (6). This is clearly equivalent to making the random phase approximation (RPA) :

$$c(r) = c_0(r) - \beta w(r) \quad (10)$$

in the compressibility (7); this is precisely the approximation used by Grimson [7] in his study of spinodal decomposition in weakly charged colloidal dispersions. Equation (10) carries however some ambiguity, since the perturbation $w(r)$ is not defined inside the effective hard core radius, i.e. for the physically irrelevant separations $r < \sigma'$ (i.e. $x < S$). This difficulty is clearly overcome in the MDA (Eq. (8)) and in the same spirit we have set $w(x) = 0$ for $x < S$ in the RPA, which amounts to replacing g_0 by its low density limit $\theta(x - S)$ in (6), where θ denotes the Heaviside function. The corresponding spinodal and critical point are again derived from (9), but the calculations are now practically analytic throughout; in particular $\eta'_c = 0.129$, independent of the perturbation, and the reduced spinodal curve $T(\eta)/T_c$ is universal.

For given values of the potential parameters T_A , T_J and κ , the critical coordinates (η'_c, T_c) can be determined from (9) in either of the RPA (mean field) or MDA approximations. However the resulting critical temperature may be unphysical (e.g. if T_c falls below the freezing point of the solvent !) or too high compared to the repulsive potential barrier ($10 k_B T_c > v(x_M)$), thus leading to coagulation. For that reason we have inverted the problem by asking which values of the potential parameters will lead to a prescribed, physically acceptable value of T_c and guarantee stability against coagulation. We proceed by fixing T_c at a value T_0 ($= 300$ K say), and

T_J . The minimum barrier condition reads :

$$\varphi(y_m) = 10 \frac{T_J}{T_0} \quad (11)$$

which determines the minimum value of γ , as is immediately clear from (3). Equations (9) for T_c and η'_c depend parametrically on T_A , T_J and γ . In the present context they are solved to yield T_A and η'_c for fixed values of T_0 , T_J and $\gamma = \gamma(T_0/T_J)$. The resulting $T_A(T_J)$ relationship is shown in figure 2 for $T_0 = 273$ and 300 K. The corresponding curve separates the (T_A, T_J) plane into a lower region where only coagulation occurs at the temperature T_0 , and an upper region where a « liquid-gas » transition takes place with a critical temperature $T_c > T_0$. The predictions of mean field theory are seen to differ considerably from the more accurate MDA, as might have been expected. In the following we shall restrict ourselves to the MDA results. For $T_A < 1\,000$ K, the latter predict values of $\eta'_c > 0.5$, indicating that for too weak van der Waals attractions, the « liquid » phase no longer exists, since the ordered (« solid ») phase is expected to be stable beyond an effective packing fraction $\eta' \simeq 0.5$.

Given a (T_A, T_J) point on the stability curve in figure 2, $\gamma = 24 T_J/(T_A \kappa)$, as determined from the minimum barrier condition (11), is the minimum value below which coagulation occurs at the temperature T_0 . This determines the maximum value of the screening parameter, $\kappa_{\max}$, at that temperature. If we now choose a point (T_A, T_J) above the stability curve, the corresponding critical temperature T'_c under the minimum barrier condition (11) will be higher than the temperature T_0 for which the stability curve has been drawn. As before, condition (11) determines the minimum value of γ and hence $\kappa_{\max}$, i.e. the highest concentration of added salt beyond which the suspension is expected to coagulate. For lower concentrations, such that $\kappa < \kappa_{\max}$, T'_c is expected to decrease : the situation is described in figure 3 which shows the variation of T'_c and η'_c with κ , in the range $273 \text{ K} < T'_c < T_c^{\max} = T_c(\kappa_{\max})$, as calculated from the MDA approximation for a given set (T_A, T_J) . The values of the potential parameters, for which our calculation predicts a « liquid-gas » transition above the freezing point of water, turn out to be physically quite reasonable. For colloidal particles of diameter $\sigma = 0.5 \mu$, with a surface potential $\psi_0 = 25 \text{ mV}$ and a Hamaker constant $A = 2.5 \times 10^{-20} \text{ J}$, we have $T_J = 50\,000 \text{ K}$ and $T_A = 1\,800 \text{ K}$; for a concentration 0.015 M of a monovalent salt, $\kappa = 195$, and we find $T_c = 309 \text{ K}$, $\eta'_c = 0.255$.

Fig. 2. — Separation of the (T_A, T_J) plane in the mean field (upper curves) and MDA (lower curves) theories. The stability curves are drawn for two temperatures : (—) $T_0 = 273 \text{ K}$, (---) $T_0 = 300 \text{ K}$. The regions labelled « liquid-gas transition » and « coagulation » refer only to the lower pair of curves (MDA); the corresponding regions in the mean field approximation lie similarly above and below the upper pair of curves.

Fig. 3. — Variation of T_c and η'_c with κ for fixed values of T_A and T_J . 1) $T_J = 70\,000$ K and $T_A = 4\,000$ K. $\kappa_{\min} = 115$, $\kappa_{\max} = 132$. 2) $T_J = 50\,000$ K and $T_A = 1\,800$ K. $\kappa_{\min} = 183$, $\kappa_{\max} = 204$. For $\kappa > \kappa_{\max}$, the suspension coagulates. For $\kappa_{\min} < \kappa < \kappa_{\max}$ and $T_0 < T_c(\kappa)$, a liquid and a gas phase coexist in the suspension.

In summary, using the techniques of the theory of liquids, we have shown that colloidal particles suspended in water and interacting *via* the standard DLVO potential (1), will undergo a « liquid-gas » phase separation below a salt concentration-dependent critical temperature; the transition is expected to occur for physically reasonable values of the potential parameters and should hence be observable in the laboratory. In fact this « liquid-gas » transition may be closely related to the reversible « coagulation » into the secondary minimum of the DLVO potential which has been detected experimentally [12]. An important point illustrated in figure 2 is the existence of a minimum value of T_J ($\approx 40\,000$ K) below which no phase transition can be observed at room temperature. This implies that for a fixed surface potential of, say, 25 mV, the colloidal particles must exceed a minimum size ($\sigma > 4\,000$ Å in the present example) for the « liquid-gas » transition to take place. Complete spinodal and coexistence curves based on the present theory will be published elsewhere.

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