

## OSMOTIC EQUILIBRIUM TREATMENT OF THE PHASE SEPARATION IN COLLOIDAL DISPERSIONS CONTAINING NON-ADSORBING POLYMER MOLECULES

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### I. Introduction

Hans Lyklema has made significant contributions to the physical chemistry of colloidal dispersions and macromolecular systems. He also has a vivid interest in the teaching of the fundamental aspects of these subjects. I felt it therefore appropriate to contribute to this volume dedicated to him on the occasion of his 60th birthday a paper which deals both with colloids and polymers and which is largely of a didactic nature. It concerns systems containing colloidal particles and non-adsorbing polymer molecules in a good solvent. As is well known the non-adsorbing polymer gives rise to an attractive potential of mean force between the colloidal particles.<sup>1-4</sup> At sufficiently high concentration of colloidal particles and polymer molecules this attractive interaction induces a phase separation in a colloid-rich phase and a polymer-rich phase.<sup>5-11</sup>

Although undoubtedly the depletion mechanism that has been put forward to explain the attractive potential of mean force is essentially correct, a number of treatments of the accompanying phase separation<sup>10,12</sup> are in my opinion not entirely consistent from a thermodynamic point of view. A great deal of attention has been lavished on the calculation of the dependence of the potential of mean force and the thermodynamic functions on the concentration and molecular weight of the free polymer. However, in the subsequent calculation of the phase separation using these thermodynamic functions little or no attention has been given to the obvious fact that after the phase separation the polymer concentration in the two coexisting phases is different and definitely not equal to the overall polymer concentration. Clearly it is not consistent to use the overall polymer concentration in the calculation of the colloid thermodynamic functions if one wants to describe the phase separation in a colloid-rich and a polymer-rich phase. Of course this criticism does not apply to the calculation of the spinodal<sup>7</sup> which indicates the limit of stability of an one-phase system.

If one wants to formulate the phase separation problem in terms of an effective one-component colloid system, one must use as an independent thermodynamic variable the chemical potential of the polymer molecules and not their concentration, since the chemical potential is the same in the two coexisting phases whereas the concentration is not. In this note I want to show that it is indeed possible to formulate the problem in this way using the method of

osmotic equilibrium systems.<sup>13,14</sup> To give an explicit example of this approach the colloid polymer dispersion will be modeled as a mixture of hard spheres and interpenetrating spheres. For this model system explicit expressions for the chemical potentials and the osmotic pressure can be obtained. As an illustration these expressions will be used to calculate the critical point of the system.

## II. Colloid polymer dispersions treated with osmotic equilibrium systems

As indicated above we wish to obtain a thermodynamic description of a system containing colloidal particles and non-adsorbing polymer molecules in a good solvent with the chemical potential of the polymer molecules as an independent thermodynamic variable. For this purpose we consider the osmotic equilibrium system illustrated in Fig. 1. It consists of three compartments separated by two semi-permeable membranes, with solvent in I, polymer solution in II and a colloid-polymer dispersion in III. The solvent, denoted by the subscript o, has a chemical potential  $\mu_o$  throughout. Membrane II/III is permeable to polymer, denoted by the subscript p, with concentration (number density)  $n_p^*$  in II and  $n_p$  in III. Finally the colloid, denoted by the subscript 1, has a concentration  $n_1$  in III. The relevant osmotic pressure  $\Pi$  in the present case is the pressure difference between III and II

$$\Pi = P_{\text{III}} - P_{\text{II}} \quad (1)$$

This osmotic pressure  $\Pi$  and the chemical potential  $\mu_1$  of the colloidal component are now functions of the temperature  $T$ , the colloid concentration  $n_1$  and the chemical potentials  $\mu_o$  and  $\mu_p$  of the solvent and of the polymer

$$\Pi = \Pi(T, \mu_o, \mu_p, n_1)$$

$$\mu_1 = \mu_1(T, \mu_o, \mu_p, n_1)$$

To calculate these thermodynamic functions one has to start from a specific model for the system. A simple example of such a model will be given in the next section. Here we wish to emphasize that once appropriate formulations for  $\Pi$  and  $\mu_1$  in terms of the above indicated thermodynamic variables have been obtained the phase separation problem can be treated in exactly the same way as for an one-component system. For example the coexistence conditions take the form

$$\begin{aligned} \Pi^\alpha(T, \mu_o, \mu_p, n_1^\alpha) &= \Pi^\beta(T, \mu_o, \mu_p, n_1^\beta) \\ \mu_1^\alpha(T, \mu_o, \mu_p, n_1^\alpha) &= \mu_1^\beta(T, \mu_o, \mu_p, n_1^\beta) \end{aligned} \quad (2)$$

where  $\alpha$  and  $\beta$  denote the coexisting phases.

Although for the explicit calculation of  $\Pi$  and  $\mu_1$  one has to start from a specific model for the system, these quantities must obviously obey the standard thermodynamic relationships such as the Gibbs Duhem relation which here takes the form

$$\left(\frac{\partial \Pi}{\partial n_1}\right)_{T, \mu_o, \mu_p} = n_1 \left(\frac{\partial \mu_1}{\partial n_1}\right)_{T, \mu_o, \mu_p} \quad (3)$$

In addition using the thermodynamic methods discussed by Vrij<sup>15</sup> in this volume one can derive cross relations between the dependence of  $\Pi$  on  $\mu_p$  on the one hand and the dependence of the "adsorption" of polymer molecules induced by the colloidal particles on  $n_1$  on the other hand. In the present case this relation takes the form

$$\left(\frac{\partial \Pi}{\partial \mu_p}\right)_{T, \mu_o, n_1} = (n_p - n_p^*) \cdot n_1 \left(\frac{\partial (n_p - n_p^*)}{\partial n_1}\right)_{T, \mu_o, \mu_p} \quad (4)$$

The relations (3) and (4) are useful to check whether expressions for  $\Pi$  and  $\mu_1$  are thermodynamically consistent, but of course, by themselves, do not allow one to obtain such expressions.

### III. Mixtures of colloidal particles and polymer molecules modeled as mixtures of hard spheres and interpenetrating spheres.

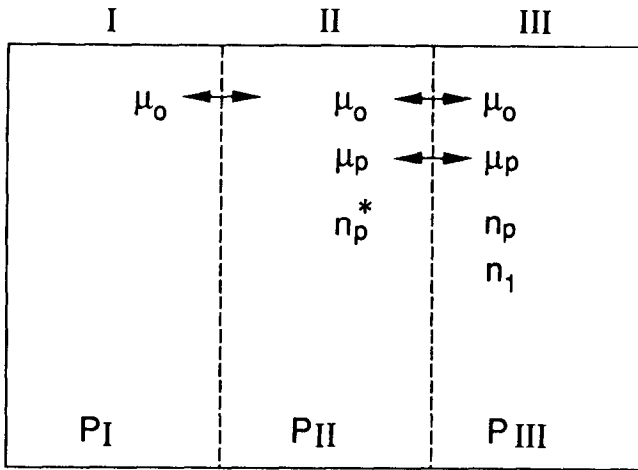
As a model for a mixture of colloidal particles and polymer molecules we depict the colloidal particles as hard spheres with diameter  $\sigma_1$  and the polymer molecules as interpenetrating spheres of diameter  $\sigma_p$ , such that the pair potentials are given by

$$\begin{aligned} u_{11}(r) &= \infty & \text{for } r < \sigma_1 \\ u_{11}(r) &= 0 & \text{for } r \geq \sigma_1 \\ u_{pp}(r) &= 0 & \text{for all } r \\ u_{1p}(r) &= \infty & \text{for } r < \bar{\sigma} \\ u_{1p}(r) &= 0 & \text{for } r \geq \bar{\sigma} \end{aligned} \quad (5)$$

where

$$\bar{\sigma} = \frac{1}{2}(\sigma_1 + \sigma_p)$$

The use of this model to describe colloidal dispersions containing non-adsorbing polymer molecules was first suggested and explored by Vrij.<sup>2</sup> In the theory of liquids this model is known as the "non-additive" hard sphere model. Widom and Rowlinson<sup>16</sup> have presented an



**figure 1**

Osmotic equilibrium system consisting of three compartments separated by two semipermeable membranes, with solvent in I, polymer solution in II and a colloid-polymer dispersion in III. The solvent is denoted by the subscript o, the polymer by the subscript p and the colloid by the subscript 1.

**Table 1**

Volume fraction of the colloidal particles and ratio of the polymer and colloid concentration at the critical point for various ratios of polymer diameter  $\sigma_p$  and colloid diameter  $\sigma_1$ .

$\frac{\sigma_p}{\sigma_1}$	$\phi_{1,crit}$	$\left(\frac{n_p}{n_1}\right)_{crit}$
0.1	0.56	140
0.2	0.41	33
0.3	0.32	15
0.4	0.26	8.7
0.5	0.22	6.0
0.6	0.18	4.4
0.7	0.16	3.6
0.8	0.14	2.9
0.9	0.12	2.5
1.0	0.10	2.2

elegant method to obtain approximate expressions for the relevant thermodynamic functions. The pressure and chemical potential of the polymer in compartment II are given by

$$P_{II} = P_I + n_p^* kT \quad (6)$$

$$\mu_p = \mu_p^{\circ}(T, \mu_o) + kT \ln n_p^* \quad (7)$$

the dependence on  $n_p^*$  of the pressure and the chemical potential reflects the fact that in the model used here the polymer molecules in the absence of colloidal particles behave as an ideal gas of point particles. For the pressure and chemical potentials in compartment III one obtains

$$P_{III} = P_I + \Pi^{\circ}(T, \mu_o, n_1) + n_p kT \left( 1 - n_1 \frac{d \ln f}{d n_1} \right) \quad (8)$$

$$\mu_p = \mu_p^{\ominus}(T, \mu_o) + kT \ln n_p - kT \ln f \quad (9)$$

$$\mu_1 = \mu_1^{\circ}(T, \mu_o, n_1) - n_p kT \frac{d \ln f}{d n_1} \quad (10)$$

Here  $\Pi^{\circ}$  and  $\mu_1^{\circ}$  are the osmotic pressure and chemical potential of a pure hard sphere system<sup>17</sup>

$$\frac{\Pi^{\circ}}{n_1 kT} = \frac{1 + \phi_1 + \phi_1^2}{(1 - \phi_1)^3} \quad (11)$$

$$\frac{\mu_1^{\circ}}{kT} = \frac{\mu_1^{\ominus}(T, \mu_o)}{kT} + \ln n_1 - \ln(1 - \phi_1) + 7 \frac{\phi_1}{1 - \phi_1} + \frac{15}{2} \left( \frac{\phi_1}{1 - \phi_1} \right)^2 + 3 \left( \frac{\phi_1}{1 - \phi_1} \right)^3 \quad (12)$$

where  $\phi_1$  is the volume fraction of the hard spheres

$$\phi_1 = \frac{\pi}{6} \sigma_1^3 n_1 \quad (13)$$

Further  $f$  is fraction of the total volume available to an interpenetrable sphere. For low concentrations of hard spheres a simple geometrical calculation yields the following expression

$$f = 1 - n_1 \frac{4\pi}{3} \sigma_1^3 + \frac{1}{2} n_1^2 \frac{4\pi}{3} \sigma_1^3 \int_{\sigma_1}^{2\sigma_1} \left( 1 - \frac{3}{4} \frac{r}{\sigma_1} + \frac{1}{16} \frac{r^3}{\sigma_1^3} \right) 4\pi r^2 dr \quad (14)$$

The term proportional to  $n_1$  accounts for the excluded volume of a hard sphere and an interpenetrating sphere and the term proportional to  $n_1^2$  corrects for the overlap of two such excluded volumes. The calculation of higher order terms rapidly becomes extremely cumbersome. However, an approximate expression for  $f$  can be obtained by realizing that according Widom's "particle-insertion" method<sup>18</sup> the chemical potential of a test hard sphere species  $p'$  with diameter  $\sigma_{p'}$  and concentration  $n_{p'} \rightarrow 0$  in a sea of hard spheres with diameter  $\sigma_1$  and number density  $n_1$  can be written as

$$\mu_p = \mu_p^*(T) + kT \ln n_p - kT \ln f \quad (15)$$

where  $f$  has exactly the same meaning as before. Comparing this expression with the well-known scaled particle expression<sup>19</sup> (or equivalently the Percus-Yevick compressibility expression<sup>20</sup>) for the chemical potentials of a mixture of hard spheres of the kind indicated one obtains

$$f = (1 - \phi_1) \exp \left[ - \left\{ A \left( \frac{\phi_1}{1 - \phi_1} \right) + B \left( \frac{\phi_1}{1 - \phi_1} \right)^2 + C \left( \frac{\phi_1}{1 - \phi_1} \right)^3 \right\} \right] \quad (16)$$

with

$$\begin{aligned} A &= 3q + 3q^2 + q^3 \\ B &= \frac{9}{2} q^2 + 3q^3 \\ C &= 3q^3 \end{aligned} \quad (17)$$

and

$$q = \frac{\sigma_p}{\sigma_1}$$

Expanding  $f$  given by eq. (16) in powers of  $n_1$  one finds that up to terms of order  $n_1^2$  this expansion agrees exactly with eq. (14). This of course is as it should be since the scaled particle expression for the chemical potential, upon which  $f$  given by eq. (16) is based, is exact up to terms of order  $n_1^2$ . From eqs. (7) and (9) it follows that

$$n_p = f n_p^* \quad (18)$$

and thus we can write eq. (10) in the form

$$\mu_1 = \mu_1^*(T, \mu_o, n_1) - kT n_p^* \frac{df}{dn_1} \quad (19)$$

and from eqs. (6) and (8) we obtain

$$\Pi = \Pi^*(T, \mu_o, n_1) - kT n_p^* \left( 1 - f + n_1 \frac{df}{dn_1} \right) \quad (20)$$

These are the desired expressions for  $\Pi$  and  $\mu_1$  in terms of the variables  $T, \mu_o, \mu_p$  (here represented in terms of the variable  $n_p^*$ ) and  $n_1$ . One easily verifies that  $\Pi$  and  $\mu_1$  satisfy the Gibbs-Duhem relation (3) and the cross relation (4). The expressions for  $\Pi$  and  $\mu_1$  have a

simple and transparent structure i.e. they consist of a hard sphere part and a part that is due to the presence of the polymer. This structure is reminiscent of the form of the pressure and the chemical potential in the Van der Waals model of a fluid where one also has a separation in a hard sphere part and a part due to attractive interactions. Like in the case of the Van der Waals fluid the additional terms compared to the hard sphere fluid are responsible for the "gas" - "liquid" phase separation.

Just to illustrate the use of the expressions for  $\Pi$  and  $\mu_1$  obtained here we determine the dependence of the location of the critical point on the ratio of  $\sigma_p$  and  $\sigma$ . The critical point in the present case is defined by

$$\left(\frac{\partial \Pi}{\partial n_1}\right)_{T, \mu_o, \mu_p} = 0 \quad \left(\frac{\partial^2 \Pi}{\partial n_1^2}\right)_{T, \mu_o, \mu_p} = 0$$

The results for the critical volume fraction of colloid and the ratio of the polymer and colloid concentration at the critical point are given in Table 1. As one intuitively expects for polymer molecules that are small compared to the colloidal particles one needs high concentrations of colloid and polymer to reach the critical point. Actually for  $q \leq 0.14$  the critical volume fraction of colloid is larger than 0.50 and for such size ratios the colloidal gas-colloidal liquid transition will most likely be preempted by a colloidal fluid-colloidal solid transition as was earlier suggested by Gast, Hall and Russel<sup>12</sup> and Vincent and coworkers<sup>10</sup>. The latter authors have found experimental indications for a critical point in colloid polymer dispersions. For a system consisting of stearyl coated silica particles (radius  $a = 6.5$  nm) and polydimethyl siloxane (molecular weight  $M = 31,000$ , radius of gyration  $r_g = 0.027 \cdot M^{1/2} \cdot \text{nm} = 4.8$  nm) the experimental critical volume fraction of colloid is about 0.08. Comparing this with the results of the model used here we find for  $q = 4.8/6.5 = 0.74$  a critical volume fraction of colloid of 0.15. For the critical polymer concentration we find for the case under consideration a theoretical value of about 20 g/l which is roughly a factor 5 too high. This seems to indicate that the present "toy" model in its unadulterated form does not give quantitative reliable estimates for the phase separation concentration. Nevertheless the model is useful from the point of view of its intended function namely to illustrate how to set up a thermodynamic consistent theory for phase separation in a mixture of colloidal particles and polymer molecules.

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### Note

After completion of this work I received a preprint of Groot and Agterof<sup>21</sup> in which the stability of colloid-polymer dispersions is also treated using the osmotic equilibrium point of view. The details of their approach however differ considerably from the work presented here.

### References

1. S. Asakura and F. Oosawa, *J. Chem. Phys.* **22** (1954) 1255; *J. Polym. Sci.* **23** (1958) 183.
2. A. Vrij, *Pure Appl. Chem.*, **48** (1976) 471.
3. J.F. Joanny, L. Leibler and P.G. de Gennes, *J. Polym. Sci. Polym. Phys. Ed.*, **17** (1979) 1073.
4. G. Fleer, J.H.M.H. Scheutjes and B. Vincent, *ACS Symp. Ser.*, **240** (1984) 245.
5. C.F. Vester, *Kolloid-Z.*, **84** (1938) 63.
6. C.L. Sieglaff, *J. Polym. Sci.*, **41** (1959) 319.
7. H. de Hek and A. Vrij, *J. Colloid Interface Sci.*, **70** (1979) 592; **84** (1981) 409.
8. B. Vincent, P.F. Luckham and F.A. Waite, *J. Colloid Interface Sci.* **73** (1980) 508.
9. P.R. Sperry, H.B. Hopfenberg and N.L. Thomas, *J. Colloid Interface Sci.*, **82** (1981) 62.
10. B. Vincent, J. Edwards, S. Emmett and R. Croot, *Colloids Surfaces*, **31** (1988) 267.
11. P.D. Patel and W.B. Russel, *J. Colloid Interface Sci.*, **131** (1989) 192.
12. A.P. Gast, C.K. Hall and W.B. Russel, *J. Colloid Interface Sci.*, **96** (1983) 251; *Faraday Disc. Chem. Soc.*, **76** (1983) 189.
13. A. Vrij, *Proc. KNAW Series B*, **88** (1985) 221.
14. D. Stigter, *Cell Biophysics*, **11** (1987) 139.
15. A. Vrij, *Cross Relation in Membrane Equilibria*. This volume.
16. B. Widom and J.S. Rowlinson, *J. Chem. Phys.*, **52** (1970) 1670.
17. J.P. Hansen and I.R. McDonald, *Theory of Simple Liquids* (Academic Press, New York, 1976).
18. B. Widom, *J. Chem. Phys.*, **39** (1963) 2809.
19. J.L. Lebowitz, E. Helfand and E. Praestgaard, *J. Chem. Phys.*, **43** (1965) 774.
20. J.L. Lebowitz and J.S. Rowlinson, *J. Chem. Phys.*, **41** (1964) 133.
21. R.D. Groot and W.G. Agterof, preprint *Faraday Disc. Chem. Soc.*, **90** (1990) 0000