

Neutron scattering of colloidal particle dispersions; contrast variation with homogeneous and granular solvents

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This paper is dedicated to Kees de Kruif for his 60th birthday.

Abstract

The well known method of contrast variation is based on the assumption that the low-molecular solvent may be considered as a homogeneous background. The colloidal dispersion is described as a quasi- one component system. In this paper this assumption is analyzed in detail. The system is described as a two-component one and use has been made of our recently derived new equation for the scattering of mixtures. It is found that when solvents are condensed liquids, this assumption is accurate when the colloid particles are not too small, say larger than 3 nm. In this limiting case the partial structure factors colloid–solvent, S_{12} , and solvent–solvent, S_{22} , are dependent on the partial structure factor of the colloid, S_{11} . When the solvent compressibility is not negligible, or when extra components—such as depletion agents are present, deviations occur. This last situation is considered in detail for a special type of depletion agent of which the size may be comparable to that of the colloid particles. It is found that the usual contrast variation procedure cannot be applied unless the depletion agent is fully matched with the low-molecular solvent. When this is not the case the procedure must be adapted with the bonus that the (often negative) adsorption of the depletion agent by the colloid can be obtained. Two examples from the literature are given of light scattering from mixtures of colloids and polymers, where both components contribute to the scattering. This case, however, is in fact limited to low K . For higher K , SANS or SAXS experiments are needed. As a special feature it is revealed how the thermodynamics-of-mixing properties obtained from scattering can be exactly expressed in the *total*- and the *osmotic* compressibilities.

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1. Introduction

In this paper, I would like to discuss some questions about small angle neutron scattering, a popular technique to study the structure of colloidal

dispersions and used by Kees in many of his experimental studies (see e.g. [1]).

In scattering studies of colloidal suspensions, the solvent is usually considered a ‘continuous background’, with a scattering amplitude, which can in many instances be changed without changing the solubilizing power of the solvent like in small-

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angle neutron scattering by varying the isotopic composition of the solvent molecules (so-called contrast variation method). The scattering intensity per unit volume of the dispersion, is commonly described by:

$$I(K) = \rho_p f_p^2 B_p^2(K) S_p(K) + I_{\text{residual}}(K) \quad (1)$$

Here ρ_p is the number of particles per unit volume; f_p , the effective scattering amplitude (at $K=0$) per particle; $B_p(K)$, the particle scattering amplitude function ($B_p(K=0)=1$), and $S_p(K)$ is the structure factor of the particles in the dispersion. To compare $I(K)$ with experimentally determined intensities the latter ones must first be corrected for the residual scattering of the solvent, $I_{\text{residual}}(K)$, and a couple of other background corrections for which we refer to the literature; see e.g. [2]. The above equation is a ‘quasi’ one-component formula.

One may, however, consider the system also as a two-component fluid in which particles and solvent molecules are discussed on the same footing, albeit that the particle component 1 is much larger in size than the solvent component 2. Thus:

$$I(K) = \rho_1 f_1^2 B_1^2(K) S_{11}(K) + \rho_2 f_2^2 B_2^2(K) S_{22}(K) + 2[\rho_1 \rho_2]^{1/2} f_1 f_2 B_1(K) B_2(K) S_{12}(K) \quad (2)$$

Here ρ_i , f_i and $B_i(K)$ are the number density, the scattering amplitude and the amplitude function of component i and $S_{ij}(K)$ is the partial structure factor of the pair i, j . In our system i and j run over the values 1 and 2.

There exists, however, still another two-component expression equivalent to Eq. (2), i.e.:

$$I(K) = A_1^2(K) S_{11} \rho_1 + \frac{f_2^2 B_2^2(K) \rho_2}{1 - \tilde{C}_{22}(K)} \quad (3)$$

with

$$A_1(K) = f_1 B_1(K) + f_2 B_2(K) \frac{\rho_2^{1/2} S_{12}(K)}{\rho_2^{1/2} S_{11}(K)} \quad (4)$$

The function $A_1(K)$ appearing in Eq. (4) is a new *apparent* amplitude of the particles. It contains as a first term the amplitude of particles 1, and as a second term a contribution of the amplitude of particles 2. Further, Eq. (3) shows the presence of

a new function, $\tilde{C}_{22}(K)$, containing the so-called direct correlation function $c_{22}(r)$. In contrast to the total correlation function $h_{ij}(r) = g_{ij}(r) - 1$, present in the formulation of $S_{ij}(K)$, the direct correlation functions $c_{ij}(r)$ have a (often) short range. This is further elaborated in the next section.

The (exact) Eq. (3) was derived by us recently [3], and is a special two-component case of a p -component formula. Note that Eq. (3) contains only two (positive) terms, in contrast to Eq. (2) that contains three terms. One of them i.e. the cross term with the subscripts 1, 2 can also attain negative values.

Now the first purpose of this paper is to compare the quasi one-component formula, Eq. (1), with the two-component formulas Eqs. (2) and (3) in order to find out under which conditions the former is accurate. Further we want to find out what kind of deviations emerge when these conditions are not met, e.g. when solvent molecules become comparable in size to the colloidal particles. We will observe that Eq. (3) is the natural extension of Eq. (1) when the conditions for which this last equation is valid are not obeyed any more.

2. Total and direct correlation functions

It is useful not only to characterize the system with total correlation functions, i.e. $h_{ik}(r)$ but also by what are called ‘direct correlation functions’, written as $c_{ik}(r)$. The latter usually are the ‘output’ of theoretical calculations and have a much simpler mathematical structure than the former. Also the range of the direct correlation functions is (sometimes much) smaller than the range of the total correlation functions and comparable to the range of the pair potentials. This last property is of importance in discussing the contribution of the ‘solvent term’, i.e. the second term in Eq. (3).

For scattering properties one needs the Fourier Transforms of these correlation functions:

$$\tilde{H}_{ik}(K) = (\rho_1 \rho_2)^{1/2} \int h_{ik}(r) e^{-K \cdot r} d^3 r \quad (5)$$

$$\tilde{C}_{ik}(K) = (\rho_1 \rho_2)^{1/2} \int c_{ik}(r) e^{-K \cdot r} d^3 r \quad (6)$$

The integrals are taken over all space. The two

types of correlation functions are related by the so-called Ornstein-Zernike relations (see e.g. [3] for details):

$$\tilde{H}_{ik}(K) = \tilde{C}_{ik}(K) + \sum_{m=1}^p \tilde{H}_{im}(K) \tilde{C}_{mk}(K) \quad (7)$$

The number of components is p . In our case $p = 2$, and the equations can be written down explicitly.

$$S_{11}(K) \equiv 1 + \tilde{H}_{11}(K) = \frac{1 - \tilde{C}_{22}(K)}{\Delta(K)} \quad (8)$$

$$S_{22}(K) \equiv 1 + \tilde{H}_{22}(K) = \frac{1 - \tilde{C}_{11}(K)}{\Delta(K)} \quad (9)$$

$$S_{12}(K) \equiv \tilde{H}_{12}(K) = \frac{\tilde{C}_{12}(K)}{\Delta(K)} \quad (10)$$

where,

$$\Delta(K) = [1 - \tilde{C}_{11}(K)][1 - \tilde{C}_{22}(K)] - \tilde{C}_{12}^2(K) \quad (11)$$

$$\Delta^{-1}(K) = [1 + \tilde{H}_{11}(K)][1 + \tilde{H}_{22}(K)] - \tilde{H}_{12}^2(K) \quad (12)$$

3. The limiting case of a continuous solvent background

The idea behind Eq. (1) is that the scattering amplitude of the particles may be found by considering the background solvent as a continuous medium. What this implies may best be adstruced by the case of light scattering, where the relevant optical property is the refractive index of particles and solvent. The refractive index of the solvent is considered constant. For neutron scattering the equivalent property is the scattering amplitude per unit volume. For the further discussion we assume that our particles are spherical and homogeneously filled with material with a constant amplitude per volume unit. This choice is made here out of convenience because more complex inhomogeneous particles may be treated as well.

Now we ask ourselves how the above sketched situation may be approached from a two-component formula as described by Eq. (2). A continuous

background implies a solvent fluid, which is structureless and incompressible. A compressible fluid cannot be homogeneous, because of thermal density fluctuations, and will scatter radiation.

One way to approach the properties of a homogeneous fluid is choosing (as thought-experiment) the solvent particles smaller and smaller and increasing their number density in such a way that their volume fraction stays constant. Because the compressibility is proportional to the reciprocal number density one may make it thus as small as desired by decreasing the solvent particle size.

The intensity according to Eq. (1) then becomes in the limit of zero compressibility, (i.e. $I_{\text{residual}} = 0$):

$$I(K) = \rho_1 f_p^2 B_1^2(K) S_{11}(K) \quad (13)$$

with,

$$f_p = f_1 - \rho_2^\dagger V_1 f_2 \quad (14)$$

Here V_1 is the volume of a particle of component 1, $\rho_p = \rho_1$, and $B_p(K) = B_1(K)$, and $\rho_2^\dagger V_1 f_2$ is the scattering amplitude of an amount of particles 2 having the same volume as the particles 1. Here $\rho_2^\dagger = \rho_2 / (1 - \phi_1)$ is the number density of the pure fluid 2, and $\phi_1 = V_1 \rho_1$. Now we equate the Eqs. (13) and (2). Working out the square in the equation for f_p , dividing by f_2 and taking $B_2(K) = 1$ which is the limiting value for small solvent particles—one finds the following relation:

$$\begin{aligned} \rho_1 (\rho_2^\dagger)^2 V_1^2 f_2^2 B_1^2(K) S_{11}(K) - 2 \rho_1 \rho_2^\dagger V_1 f_1 B_1^2(K) S_{11}(K) \\ = \rho_2 f_2 S_{22}(K) + 2(\rho_1 \rho_2)^{1/2} f_1 B_1(K) S_{12}(K) \end{aligned} \quad (15)$$

This relation must be valid for any value of f_1 and f_2 . Taking f_1 , and subsequently f_2 equal to zero yields:

$$S_{12}(K) = - \left[\frac{(\rho_1 \rho_2)^{1/2}}{(1 - \phi_1)} \right] V_1 B_1(K) S_{11}(K) \quad (16)$$

$$S_{22}(K) = - \left[\frac{(\rho_1 \rho_2)^{1/2}}{(1 - \phi_1)} \right] V_1 B_1(K) S_{12}(K) \quad (17)$$

$$S_{22}(K) = \left[\frac{\rho_1 \rho_2}{(1 - \phi_1)^2} \right] V_1^2 B_1^2(K) S_{11}(K) \quad (18)$$

Let us discuss these $S_{ij}(K)$'s in the following (sub)section.

3.1. Properties of the partial structure factors for a homogeneous solvent

From the previous treatment it will be clear that only liquid structures on the scale of particles 1 are present and that structures on the scale of the solvent molecules are ignored. The ‘primary structure’ in the dispersion is dictated by the correlation function of the colloidal particles (component 1), as represented by the partial structure factor $S_{11}(K)$. The other ‘secondary structures’, $S_{12}(K)$ and $S_{22}(K)$, representing the spatial correlations of particle–solvent and solvent–solvent, follow $S_{11}(K)$ as ‘slave functions’, through the recipe given by Eqs. (16)–(18). Further it follows from these equations and Eq. (12) that the reciprocal value of the determinant Δ :

$$\Delta^{-1}(K) = S_{11}(K)S_{22}(K) - S_{12}^2(K) \quad (19)$$

is zero. This implies that the correlation functions, $\tilde{C}_{ij}(K)$ cannot be obtained in this way.

To proceed, let us assume that $S_{11}(K)$ is known (e.g. from a theory or from experiments) and that $B_1(K)$ is the form amplitude of a homogeneous sphere with diameter d_1 :

$$B_1(K) = \frac{3}{(Kd_1/2)^3} \times \left[\sin\left(\frac{Kd_1}{2}\right) - \left(\frac{Kd_1}{2}\right)\cos\left(\frac{Kd_1}{2}\right) \right] \quad (20)$$

This function shows damped oscillations around zero. Because $S_{ii}(K) > 0$, it follows from Eq. (16) that $S_{12}(K)$ is also oscillating around zero, which is what is usually observed. Let us further somewhat elaborate about the function because it occurs in the amplitude function $A_1(K)$ in Eq. (3). For small ρ_1 , $S_{11}(K)$ goes to 1, and we have from Eq. (16):

$$S_{12}^\circ(K) = -(\rho_1\rho_2)^{1/2}V_1B_1(K) \quad (21)$$

On the other hand we have from the definition in Eq. (10):

$$S_{12}(K) = (\rho_1\rho_2)^{1/2} \int_0^\infty 4\pi r^2 h_{12}(r) \frac{\sin Kr}{Kr} dr \quad (22)$$

Equating the two equations one finds that $h_{12}(r) = g_{12}(r) - 1$ must be a step function for small

ρ_1 , and that $g_{12}(r) = 0$ for $0 < r < d_1/2$ and equal to 1 for $r > d_1/2$. And this is just what one expects from a homogeneous solvent in contact with a non permeable spherical particle with diameter d_1 .

For finite ρ_1 the presence of other particles than that one centered at the origin should be taken into account. The Eq. (22) tells us that $h_{12}(r)$ will be a convolution of $\tilde{B}_1(r)$ and $h_{11}(r)$. We will not elaborate on this matter in this paper.

3.1.1. Consequences for the second two-component expression, Eq. (3) Eq. (4)

Let us substitute the previously obtained expressions for the $S_{ij}(K)$ for the two-component system into our second equations Eqs. (3) and (4). We observe from Eq. (16) that the ratio S_{12}/S_{11} becomes equal to:

$$\frac{S_{12}(K)}{S_{11}} = -\frac{(\rho_1\rho_2)^{1/2}}{1 - \phi_1} V_1 B_1(K) \quad (23)$$

Substituting this into Eq. (4) gives:

$$A_1(K) = B_1(K) \left[f_1 - \frac{\rho_2 f_2 V_1}{1 - \phi_1} \right] \quad (24)$$

Observe that the expression between the brackets is just equal to f_p , see Eq. (14).

The second term in Eq. (3) contains $1 - \tilde{C}_{22}(K)$ in the denominator. According to Eq. (8) it is equal to $S_{11}(K)\Delta(K)$, and because we found that $\Delta(K)$ becomes ∞ for a continuous solvent, it follows that the second term in Eq. (3) becomes zero. This result should not come as a surprise because both Eqs. (2) and (3) are exact. It, however, suggests that Eq. (3) is a good candidate to discuss deviations from the ideal case of a homogeneous solvent.

4. Non-ideal solvents

In this section we want to leave the ideal case of a homogeneous solvent and direct our attention to two non-ideal cases. The first one is a solvent with a finite compressibility and thus—due to density fluctuations—not homogeneous. The size of the solvent molecules is, however, still (very) small with respect to the colloidal particle size of

component 1. Further the case of a ‘granular’ solvent in which the solvent particles have a larger size, which may become comparable to the size of the colloid particles. The last case is not so relevant for a single-component solvent, but in ‘complex’ solvents where next to the low-molecular solvent component an extra macromolecular component is present, e.g. micelles or polymeric chains, this case is certainly relevant [4–8].

4.1. Solvents with a finite compressibility

Solvents with a finite compressibility undergo—because of thermal motion—density fluctuations and, therefore, refractive index fluctuations, which give rise to scattering of waves. This scattering must be subtracted—when it is not negligible—to obtain the colloid contribution from the scattering of the two-component system.

To consider this solvent scattering in more detail, let us take the scattering amplitude of the colloid particles equal to zero, i.e. $f_1 = 0$. This gives, after substitution into Eq. (3) and some rearrangement, using the Eq. (4):

$$I(K) = \rho_2 f_2^2 B_2^2(K) \left[\frac{1}{1 - \tilde{C}_{22}(K)} + \frac{S_{12}^2(K)}{S_{11}(K)} \right] \quad (25)$$

Observe that the expression between the brackets is just equal to $S_{22}(K)$. This equation clearly shows that there are two contributions from the scattering solvent. The first contribution, proportional to $1/(1 - \tilde{C}_{22}(K))$ is also present in the pure solvent, where it is equal to $1/(1 - \tilde{C}_{22}^+(K))$. This contribution is clearly due to the density fluctuations of the solvent ‘between the colloid particles’. The second contribution, i.e. $S_{12}^2(K)/S_{11}(K)$ is apparently related to the presence of the colloid particles, component 1. It can thus be considered as spatial density variations due to regions where no solvent is allowed, i.e. the space occupied by colloid material. For the idealized solvent this was equal to $V_1 \rho_1$. For a real solvent, V_1 must be replaced by $\bar{v}_1 \equiv (\partial V / \partial N_1)_{P, N_2}$ the so-called partial molecular volume of 1; a measurable quantity.

For the subtraction of the solvent scattering in Eq. (3) we need the second term in this equation. Now the range of the direct correlation function,

$c_{22}(r)$, is comparable to the solvent diameter. Because $d_2 \ll d_1$ we may use in this limit $B_2(K = 0) = 1$. Further $\tilde{C}_{22}(K)$ at $K = 0$, follows from the following relation with thermodynamic quantities [3]:

$$\left[\frac{\partial \mu_k}{\partial \rho_i} \right]_{\rho'} = \frac{kT}{(\rho_i \rho_k)^{1/2}} [\delta_{ik} - \tilde{C}_{ik}(K = 0)] \quad (26)$$

where, μ_k is the chemical potential of component k and the subscript ρ' implies that all $\rho_j \neq \rho_i$ are kept constant in the differentiation. Then one obtains:

$$\begin{aligned} I_{\text{residual}}(K = 0) &= \frac{f_2^2 \rho_2}{1 - \tilde{C}_{22}(K = 0)} \\ &= \frac{f_2^2}{(1/kT) [\partial \mu_2 / \partial \rho_2]_{\rho_1}} \end{aligned} \quad (27)$$

It is shown in Appendix A that:

$$\left[\frac{\partial \mu_2}{\partial \rho_2} \right]_{\rho_1} = \bar{v}_2^2 \left[\frac{1}{\chi} + \frac{1}{\chi_{\Pi} - \chi} \right] \quad (28)$$

where, $\bar{v}_2 \equiv (\partial V / \partial N_2)_{N_1, P}$ is the partial molecular volume of particles 2, and where, $\chi \equiv (-1/V)(\partial V / \partial P)_{N_1, N_2}$, and $\chi_{\Pi} \equiv (-1/V)(\partial V / \partial \Pi)_{N_1, \mu_2}$ are, respectively, the total—and the osmotic compressibility. Here Π is the osmotic pressure of a system, which is in (membrane) equilibrium with a reservoir with constant μ_2 (see also Fig. 1). Then:

$$I_{\text{residual}} = \frac{f_2^2 kT \chi}{\bar{v}_2^2} \left[1 - \frac{\chi}{\chi_{\Pi}} \right] \quad (29)$$

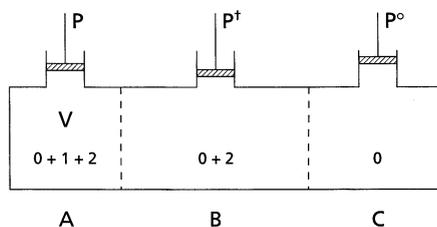


Fig. 1. Osmotic device to make manipulations at constant chemical potential. Left is ‘the system’ A with volume V and pressure P with the components 0, 1, 2, separated from the (very large) reservoir B with a membrane that is only permeable to the complex solvent (component 0 plus component 2). Right is the reservoir C which contains pure solvent and is separated from reservoir B with a membrane that is only permeable to the solvent component 0. The pressure is P^f in B and P^o in C.

For condensed liquid solvents it is found (see Appendix B) that χ/χ_{II} has values of 10^{-6} – 10^{-3} for particles 1 with a diameter of $d_1 = 3.1$ nm (e.g. a protein molecule with molar mass of 10^4), when ϕ_1 is 0.1 and 0.4, respectively. This ratio χ/χ_{II} will even become smaller for larger particles 1 (it scales as $(d_2/d_1)^3$). This implies that we may drop the expression between brackets in Eq. (29). Further we will assume incompressible colloid particles 1. One then finds, $\chi = (-1/V)(\partial V/\partial P) = (1 - \phi_1)\chi_2^\dagger$, where χ_2^\dagger is the compressibility of pure solvent 2. Then:

$$I_{\text{residual}} = \frac{f_2^2 k T \chi_2^\dagger (1 - \phi_1)}{(\bar{v}_2^\dagger)^2} \quad (30)$$

And this is a simple, plausible result because it implies that the residual scattering intensity is equal to that of the pure solvent ‘between the colloid particles’.

For so-called ‘super critical solvents’ which are becoming in vogue for industrial processes, see e.g. [9], χ may be appreciably larger and the expression between the brackets in Eq. (29) may not be neglected any more.

4.2. The case of a ‘granular solvent’

In contrast to the previous case, where $d_2/d_1 \ll 1$, we will consider in this section a solvent containing larger particles having dimensions up to that of the colloid particles 1. Because one-component solvents with large molecules are not common in connection with colloidal suspensions, we will in this section convey our attention to a ‘quasi two-component’ system, defined as follows. It is a three-component system with a low-molecular weight solvent component 0, a colloidal component 1, and an (extra) solvent component 2. Thus we have in fact a ‘complex’ solvent of two components. For component 2 we may think of ‘depletion agents’ like polymer molecules [4–6,8], microemulsion particles [7] and also of dendrimers, micelles and proteins as well. The role of the solvent component 0 is reduced to that of a continuous background having the sole function of a contrast variable. This is sufficient in this discussion because the scattering of the complex

solvent alone (component 2 and 0) will be mainly due to the scattering contribution of component 2.

The granular component of the (complex) solvent is thus component 2. It cannot in general be considered as a ‘condensed fluid’ as in the previous section because its concentration can be varied. This is just one of the interesting properties as a depletion agent determining the (effective) interactions between the colloid particles 1 (depletion force). In such a case it is convenient to describe the dilution properties with an *osmotic* system (see Fig. 1). The left membrane in this figure is only permeable to the components 0 and 2 and the right membrane to component 0. The left compartment, A, is the ‘system’ having a volume V_3 a pressure P and number densities ρ_i . The middle compartment, B, is a reservoir containing component 0 and 2 only. The reservoir is chosen very large to insure that its composition is not changed upon changing the composition of the ‘system’. The pressure in the middle compartment is P^\dagger and the densities are designated as ρ_i^\dagger . The right compartment, C, is pure component 0 at a pressure P° . Because only pressure differences are relevant in our discussion, we take for convenience $P^\circ \equiv 0$. Then the pressures P and P^\dagger are equal to the osmotic pressures with respect to the right reservoir, C.

Further, to make connection with the two-component system in the previous section we call $P - P^\dagger = \Pi$, the (Donnan) osmotic pressure of our ‘quasi’ two-component system. Then we may use the equations of the previous section for χ and χ_{II} . The temperature is always kept constant.

4.2.1. Simple mixture of colloid particles and macromolecules

We will restrict ourselves to systems, which are dilute in the colloid component 1 but not necessarily in component 2. We will further restrict to a very simple type of particles 2, mimicking a polymer molecule at the theta state and having the following properties. The interaction potentials are spherically symmetric and given by (see also Fig. 2):

$$u_{12}(r) = \infty; \quad r < \frac{d_1 + d_2}{2}$$

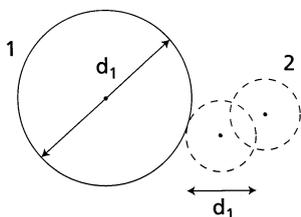


Fig. 2. Colloidal hard sphere 1 with diameter d_1 and macromolecules 2 with diameter d_2 . The molecules 2 have a hard sphere type interaction with colloid 1 but have no interaction among themselves.

$$u_{12}(r) = 0; \quad r > \frac{d_1 + d_2}{2}$$

$$u_{22}(r) = 0; \quad 0 < r < \infty \quad (31)$$

Around each particle 1 there is a zone where no centers of particles 2 can come. At $r > (d_1 + d_2)/2$ the average number density of particles 2 is constant. The volume of the empty zone (see Fig. 3) is:

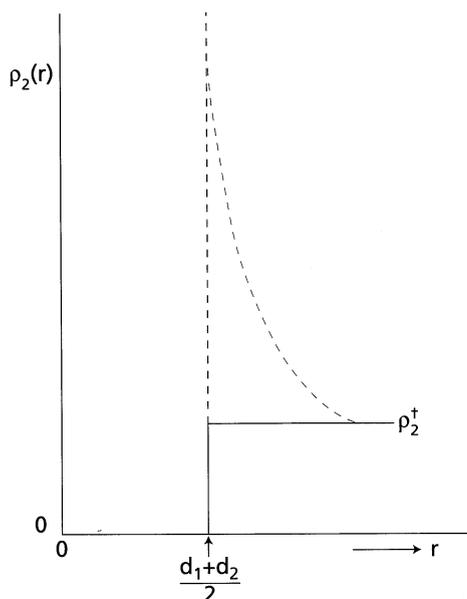


Fig. 3. Number density of macromolecules 2, $\rho_2(r)$, around a colloid particle 1. Solid line, step function in the case of a hard sphere interaction between colloid 1 and macromolecule 2 (see also Fig. 2). Dashed line, the macromolecule 2 feels an attractive force of colloid 1.

$$V_{12}^{\text{ex}} = \frac{\pi}{6}(d_1 + d_2)^3 \quad (32)$$

The volume available to the particles 2 is then equal to $(V - N_1 V_{12}^{\text{ex}})$. When $\rho_1 = 0$, $\rho_2 = \rho_2^\dagger$ because of equilibrium, and for small ρ_1 we have:

$$\rho_2 = \frac{N_2}{V} = \rho_2^\dagger [1 - \rho_1 V_{12}^{\text{ex}}] \quad (33)$$

up to and including linear terms in ρ_1 . The pressure P in A is equal to the sum of $\rho_1 kT$ due to the particles 1 (van't Hoff's law) and the pressure due to N_2 point particles (see e.g. [10]), thus:

$$\frac{P}{kT} = \rho_1 + \rho_2(1 + \rho_1 V_{12}^{\text{ex}}) \quad (34)$$

up to and including linear terms in ρ_1 . The second term on the RHS of Eq. (34) is the number density of particles 2 'between the particles 1' and is equal to ρ_2^\dagger .

Let us now turn our attention to the scattering properties of our quasi two-component system.

4.2.2. Scattering properties of a quasi two-component system

From Eqs. (3) and (4) one obtains up to and including terms linear in ρ_1 :

$$I(K) = [A_1^\circ(K)]^2 \rho_1 + I_{\text{residual}} \quad (35)$$

because $S_{11}(K) \rightarrow 1$ for $\rho_1 \rightarrow 0$. Here:

$$A_1^\circ(K) = f_1 B_1(K) + f_2 \left(\frac{\rho_2}{\rho_1}\right)^{1/2} B_2(K) S_{12}^\circ(K) \quad (36)$$

is the limiting form for $\rho_1 \rightarrow 0$, and:

$$S_{12}^\circ(K) = (\rho_1 \rho_2)^{1/2} \int_0^\infty 4\pi r^2 h_{12}^\circ(r) \frac{\sin Kr}{Kr} dr \quad (37)$$

where, $h_{12}^\circ(r)$ the total correlation function for the pair 1,2 for $\rho_1 \rightarrow 0$.

4.2.3. The residual intensity

We start the discussion for $K = 0$. Then we can invoke Eq. (29):

$$I_{\text{residual}} = \frac{f_2^2 k T \chi}{\bar{v}_2^2} \left[1 - \frac{\chi}{\chi_{II}} \right] \quad (38)$$

The compressibilities are (see Appendix C):

$$\frac{\chi^{-1}}{kT} = \rho_1 + \rho_2 + 2\rho_1\rho_2 V_{12}^{\text{ex}} \quad (39)$$

$$\frac{\chi_{II}^{-1}}{kT} = \rho_1 \quad (40)$$

Further we need \bar{v}_2 the partial molecular volume of particles 2. Note that this is not (nearly) a constant as for condensed phases, but varies with ρ_2 . In Appendix C we find:

$$\bar{v}_2 = \frac{1}{\rho_1 + \rho_2 + \rho_1\rho_2 V_{12}^{\text{ex}}} \quad (41)$$

Substituting the above obtained three equations into Eq. (38) gives:

$$I_{\text{residual}}(K=0) = \rho_2 f_2^2 \quad (42)$$

which is (again) the scattering from the particles 2 between the particles 1.

In experimental situations it is often necessary to adjust ρ_2 in a dilution procedure of component 1 in order to keep ρ_2^\dagger constant, for which an experimental value of V_{12}^{ex} is needed which may, however, be obtained from an experimental value of A_1° .

Let us now look at the general case $K=0$. Invoking the result of Eq. (42), implies that $\tilde{C}_{22}(K=0)=0$. But it seems natural to assume that $\tilde{C}_{22}(K)=0$ for all K because the core size of the particles 2 is zero in this model fluid. Thus one obtains:

$$I_{\text{residual}}(K) = \rho_2 f_2^2 B_2^2(K) \quad (43)$$

Let us now turn our attention to the effective amplitude $A_1^\circ(K)$.

4.2.4. The effective amplitude of particles 1

For our simple mixture $h_{12}^\circ(r)$ is known (see also Fig. 3).

$$h_{12}^\circ(r) = -1 \quad \text{for } r < \frac{d_1 + d_2}{2}$$

$$h_{12}^\circ(r) = 0 \quad \text{for } r > \frac{d_1 + d_2}{2} \quad (44)$$

So one obtains from Eq. (37):

$$S_{12}^\circ(K) = -(\rho_1\rho_2)^{1/2} V_{12}^{\text{ex}} B_{12}(K) \quad (45)$$

where

$$B_{12}(K) = \frac{24}{K^3(d_1 + d_2)^3} \times \left[\sin K \left[\frac{d_1 + d_2}{2} \right] - K \left[\frac{d_1 + d_2}{2} \right] \cos K \left[\frac{d_1 + d_2}{2} \right] \right] \quad (46)$$

or

$$A_1^\circ(K) = f_1 B_1(K) - \rho_2^\dagger f_2 B_2(K) V_{12}^{\text{ex}} B_{12}(K) \quad (47)$$

Note that the limiting value $\rho_2 = \rho_2^\dagger$.

4.3. Effective amplitude for $K=0$; contrast variation

For $K=0$, Eq. (47) reduces to:

$$A_1^\circ(K=0) = f_1 - \rho_2^\dagger f_2 V_{12}^{\text{ex}} \quad (48)$$

This can be described as a scattering entity as depicted in Fig. 4, where the scattering amplitude

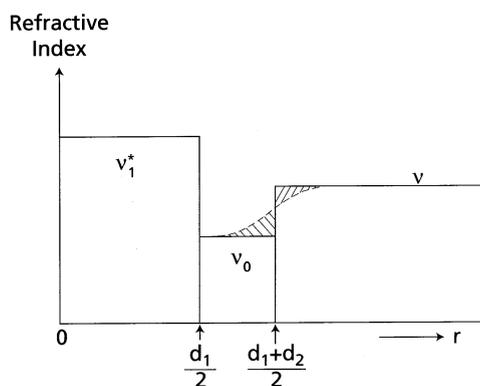


Fig. 4. Refractive index profile around a colloid particle: v_1^* is the refractive index of particle 1; v_0 is the refractive index of pure solvent 0; v is the refractive index of the solution containing the components 0 and 2. Solid lines, refractive material is (artificially) concentrated at the center of particle 2. Dashed line, refractive material is evenly distributed over a sphere with diameter d_2 (schematic).

per unit volume, v , is given. We call this a (rescaled) refractive index. Near the matching point it is connected with the common optical refractive index, n , as $v = (2\pi/\lambda^2 n_0)n$, with n_0 the refractive index of pure solvent 0 and λ the wavelength of the light in the solvent medium.

For $r < d_1/2$ the particle interior has a refractive index v_1^* . When the scattering material in particles 2 is assumed to be concentrated at the particle center, the refractive index v of the complex solvent—i.e. the solution of 2 in 0—is found for $r > (d_1 + d_2)/2$. In the region $d_1/2 < r < (d_1 + d_2)/2$ there is pure solvent 0 with a refractive index v_0 . Of course it is not realistic to concentrate the scattering material of 2 at the particle center; a more realistic spatial distribution around the center of 2 makes the transition of v_0 to v more gradual, e.g. as sketched with the dashed line in Fig. 4. (The excess amount of material in the 2 shaded areas must be the same, however).

Thus we obtain the following relations for the scattering amplitudes:

$$f_1 = V_1(v_1^* - v_0) \quad (49)$$

$$f_2 = V_2(v_2^* - v_0) \quad (50)$$

where $V_1 = (\pi/6)d_1^3$ and $V_2 = (\pi/6)d_2^3$, and v_i^* is the refractive index of particle i , and v_0 that of pure solvent 0.

Further we have for the refractive index of a solution of particles 2 in solvent 0:

$$v = v_0 + (v_2^* - v_0)\rho_2 V_2 \quad (51)$$

Now let us first look at the case where $V_{12}^{\text{ex}} \approx V_1$, i.e. $d_2 \ll d_1$. Then one obtains from Eqs. (48) and (51):

$$\begin{aligned} A_1^\circ(K=0) &= V_1(v_1^* - v_0) - \rho_2^\dagger V_1 V_2 (v_2^* - v_0) \\ &= V_1(v_1^* - v) \end{aligned} \quad (52)$$

and this is just the result of the contrast variation equation, where the refractive index of the background medium is now equal to the refractive index of the solution of 2 in 0.

But in general $V_{12}^{\text{ex}} > V_1$ and one finds:

$$A_1^\circ(K=0) = V_1(v_1^* - v) - (V_{12}^{\text{ex}} - V_1)(v - v_0) \quad (53)$$

The first term in this equation is the same as in Eq. (52), and would be the result of a simplistic contrast variation procedure. The presence of the

second term implies that this is not the whole story, and shows the effect of an annulus around particle 1 with a volume $V_{12}^{\text{ex}} - V_1 = (\pi/6)[(d_1 + d_2)^3 - d_1^3]$. When $v - v_0 = 0$, i.e. when the particles 2 are matched away, this term is zero. This is often done in experiments where component 2 is a depletion agent [6]. However, when $v \neq v_0$ and $V_{12}^{\text{ex}} > V_1$ a simplistic contrast variation procedure is incorrect but opens the opportunity to obtain information about the value of V_{12}^{ex} . Then one can perform two experiments; a first one with $v = v_0$, from which V_1 can be found. Then a second one in which one can determine $A_1^\circ(K=0) - V_1(v_1^* - v)$, which is equal to V_{12}^{ex} (see next section).

The depletion of polymer as described so far is a special case. In general it is conceivable that polymer molecules are attracted by the colloid particle surface. Then the function $h_{12}^\circ(r)$ as given in Eq. (22) is not a step function any more, but has an upswing at $r = (d_1 + d_2)/2$, as sketched in Fig. 3 with a dashed line. For $K=0$ the integral in Eq. (22) describes the ‘adsorbed’ amount of polymer, Γ° , by the colloid particle. This quantity was considered in more detail in our previous paper [3], where we have found that Γ can also be defined in thermodynamic terms in our osmotic device (see Fig. 1) ($\Gamma = (\partial\rho_2/\partial\rho_1)_{\mu}$). Further discussion of this point is, however, beyond the scope of this paper.

4.4. Intensities; numerical example

Let us now consider briefly what our model predicts about the conditions under which there is a possibility to measure the depletion of solvent component 2. Clearly, two opposing trends play a role here. The first one is that the depletion (adsorption) contribution to the effective amplitude A_1° increases with f_2 (for $f_2 = 0$ no depletion can be measured). The second one is that the residual scattering must be kept as modest as feasible, which asks for small values of f_2 . Obviously there is a trade-off here.

Let us assume first that the intensity scattered by the colloid component 1 alone (without component 2) is large enough to allow a study at low volume fractions, say, smaller than 3%, in order to obtain a linear relation between intensity and

colloid concentration. Then, let us consider for the first criterion the amplitude A_1° and assume that a decrease of 30% is measurable with sufficient accuracy (this implies a decrease in intensity of 51%). Thus we obtain from Eq. (48): $\rho_2 f_2 V_{12}^{\text{ex}} = 0.30 f_1$ or with the help of the Eqs. (49) and (50): $\phi_2 = 0.30(V_1/V_{12}^{\text{ex}})(v_1^* - v_0)/(v_2^* - v_0)$; where $\phi_i = \rho_i V_i$. When, e.g. $v_1^* = v_2^*$, and $d_2/d_1 = 0.3$, this gives: $\phi_2 = 0.30/2.20 = 0.136$.

For the second criterion we will take that the intensity of the colloid plus corona: $(1 - 0.30)f_1^2 \rho_1$ is five times larger than the residual scattering. This gives: $0.49f_1^2 \rho_1 = 5f_2^2 \rho_2$, and leads to the following relation: $\phi_1/\phi_2 = 10.2(V_2/V_1)(v_2^* - v_0)^2/(v_1^* - v_0)^2$. For $v_1^* = v_2^*$ and $d_2/d_1 = 0.3$ we obtain: $\phi_1 = 0.275\phi_2$, and with $\phi_2 = 0.136$: $\phi_1 = 0.037$. Both values are quite acceptable.

We may take other values for v_1^* and v_2^* but then it turns out that the product of ϕ_1 and ϕ_2 stays constant. This follows when we take the expressions of the two criteria and eliminate the ratio $(v_1^* - v_0)/(v_2^* - v_0)$. This leads to the expression: $\phi_1 \phi_2 = (\alpha^2 \beta / (1 - \alpha^2)) (V_1 V_2 / (V_{12}^{\text{ex}})^2)$. Here α takes the place of the number 0.30 and β takes the place of the number 5 used above.

The term $I_{\text{residual}}(0) = \rho_2 f_2^2$ is in many practical situations an upper bound for the scattering at $K = 0$, i.e. when there are repulsive forces working between the particles 2, making the osmotic compressibility (much) smaller than the ideal value given by van't Hoff's law. Then the value of β may be given a smaller number.

For the special case that both the colloid particles 1 and the solvent particles 2 are described as 'Hard Spheres', we refer to our previous paper [3] (Fig. 6 and 7) where some results are shown for $K \neq 0$.

The above considerations could help the experimentalist to judge if his system can be used to detect and measure the adsorption (depletion) of solvent component 2 by the colloid 1.

5. Experimental and discussion

In many reported scattering experiments of mixtures of colloidal particles and macromolecules, the contribution of the macromolecules is

very small [7,8] or minimized by contrast variation [6]. We only know of a few papers where attempts have been made to disentangle the contributions of both components to the scattering. One is an early paper of de Hek et al. [4] on lightscattering of a mixture of colloidal Silica particles ($d = 92$ nm) and Polystyrene ($M = 700\,000$ g mol⁻¹; $R_g = 24$ nm) in cyclohexane. The (lyophilized) Silica particles behave as 'hard spheres'. The polystyrene-cyclohexane mixture at 34.5 °C is at the theta state (which implies that the second virial coefficient is zero) and is mimicked by our overlapping sphere model used above. The theoretical analysis was based on an analogous theory as given above but was strictly thermodynamic of origin and, therefore, valid for $K = 0$ only.

Using the f 's for silica and polystyrene it was possible to estimate V_{12}^{ex} as having the value 3.6 ± 0.2 cm³ g⁻¹ leading to a value $d_2 = 24 \pm 4$ nm. This is indeed comparable to the radius of gyration of the polymer. It was also found that the apparent radius of gyration of the silica particles decreased when polystyrene was added to the suspension. This was also found to be in qualitative agreement with an optical model of the depletion layer.

Another paper is that of Tong et al. [5] in which lyophilized colloidal calcium carbonate particles ($d_1 = 10$ nm) plus hydrogenated polyisoprene ($M = 86\,000$ and $26\,000$ g mol⁻¹) in the 'good' solvent decane. These particles are appreciably smaller than the previous ones but the experimental results are similar. The theory they used is restricted to dilute mixtures, also for the polymer, whereas our treatment is not restricted to low polymer concentrations. Further both components are described as 'hard sphere' components (for which explicit formulas are known), which, however, limits the scope of the analysis.

We are not aware of other scattering (SANS or SAXS) experiments that disentangle colloid and polymer contributions. It would be of appreciable interest if such experiments could be undertaken because the previous experimental results are in fact restricted to small K .

There are theoretical investigations [11–13] and also recent simulations of local polymer chain densities around a sphere [12], which would make such measurements on well defined materials very

timely. They can be used to interpret the experimental data with the help of our equations.

Appendix A: Derivation of a relation between partial derivatives of the chemical potentials and the osmotic- and total compressibilities

Derivation of a relation between partial derivatives of the chemical potentials and compressibilities.

We want a relation between the derivative $(\partial\mu_2/\partial\rho_2)_{\rho_1}$ and the total- and osmotic compressibilities χ and χ_{II} .

$$\chi_{II}^{-1} \equiv \rho_1 \left[\frac{\partial P}{\partial \rho_1} \right]_{\mu_2} = \rho_1^2 \left[\frac{\partial \mu_1}{\partial \rho_1} \right]_{\mu_2} \quad (54)$$

The RHS of this equation follows from the Gibbs–Duhem relation at constant T :

$$dP = \rho_1 d\mu_1 + \rho_2 d\mu_2 \quad (55)$$

We start with writing:

$$\left[\frac{\partial \mu_2}{\partial \rho_2} \right]_{\rho_1} = V \left[\frac{\partial \mu_2}{\partial N_2} \right]_{VN_1} = VF_{22} \quad (56)$$

where $F_{ij} = (\partial^2 F / \partial N_i \partial N_j)_{VN'}$ = $(\partial\mu_i / \partial N_j)_{VN'}$, and F is the Helmholtz free energy. Here the subscript N' means that the N 's not present in the derivative are kept constant. $F_{ij} = F_{ji}$.

We also need $G_{ij} = \partial^2 G / \partial N_i \partial N_j)_{PN'}$ = $(\partial\mu_i / \partial N_j)_{PN'}$ where G is the Gibbs free energy. They are related as follows [14]:

$$F_{ij} = G_{ij} + \frac{\bar{v}_i \bar{v}_j}{\chi V} \quad (57)$$

Here $\bar{v}_i = (\partial V / \partial N_i)_{PN'}$ is the partial molecular volume of component i , and $\chi = -(1/V)(\partial V / \partial P)_N$ is the total (isothermal) compressibility of the system. $G_{ij} = G_{ji}$.

Further one has:

$$\sum_{i=1}^p N_i G_{ij} = 0 \quad (58)$$

To derive the relation between $(\partial\mu_1 / \partial N_1)_{\mu_2 V}$ and F_{22} , we will apply a standard method (see [15] (Jacobian determinants)) that is straightforward

and relatively easy to apply, also in multicomponent systems.

Thus we write:

$$\left[\frac{\partial \mu_1}{\partial N_1} \right]_{\mu_2 V} = \frac{\partial \mu_1 \mu_2 V}{\partial N_1 \mu_2 V} = \frac{\mathcal{A}}{\mathcal{B}} \quad (59)$$

with

$$\mathcal{A} = \frac{\partial \mu_1 \mu_2 V}{\partial N_1 N_2 P} \equiv \begin{vmatrix} G_{11} & G_{12} & \bar{v}_1 \\ G_{21} & G_{22} & \bar{v}_2 \\ \bar{v}_1 & \bar{v}_2 & -\chi V \end{vmatrix} \quad (60)$$

$$\mathcal{B} = \frac{\partial N_1 \mu_2 V}{\partial N_1 N_2 P} \equiv \begin{vmatrix} 1 & 0 & 0 \\ G_{21} & G_{22} & \bar{v}_2 \\ \bar{v}_1 & \bar{v}_2 & -\chi V \end{vmatrix} \quad (61)$$

where we have used the relation $\bar{v}_i = (\partial\mu_i / \partial P)_N$. Working out the determinants and using the relations in Eq. (58) leads to the result:

$$\left[\frac{\partial \mu_1}{\partial \rho_1} \right]_{\mu_2} = V \left[\frac{\partial \mu_1}{\partial N_1} \right]_{\mu_2 V} = \frac{VG_{11}}{\bar{v}_2^2 \rho_2^2 + \chi V \rho_2^1 G_{11}} \quad (62)$$

Combining this with Eqs. (54) and (58) then leads to the relatively simple expression:

$$VG_{22} = \frac{\bar{v}_2^2}{\chi_{II} - \chi} \quad (63)$$

Then invoking Eq. (57)—which one can easily derive with the same type of Jacobians—gives the desired result:

$$\left[\frac{\partial \mu_2}{\partial \rho_2} \right]_{\rho_1} = \bar{v}_2^2 \left[\frac{1}{\chi_{II} - \chi} + \frac{1}{\chi} \right] \quad (64)$$

The same method can be used to derive the following two partial derivatives:

$$\bar{v}_2 = \left[\frac{\partial V}{\partial N_2} \right]_{N_1 P} = \left[\frac{\partial P}{\partial \rho_2} \right]_{\rho_1} \chi \quad (65)$$

and:

$$\Gamma \equiv \left[\frac{\partial N_2}{\partial N_1} \right]_{\mu_2 V} = \left[\frac{\partial \rho_2}{\partial \rho_1} \right]_{\mu_2} = -\frac{\bar{v}_1}{\bar{v}_2} \left[1 - \frac{\chi}{\chi_{II} \rho_1 \bar{v}_1} \right] \quad (66)$$

Appendix B: Numerical evaluation of χ and χ_{II} for some mixtures of colloid 1 plus low-molecular solvent 2

I: dilute systems

For small ρ_1 , $S_{11}(K) = 1$ and Π the osmotic pressure follows van't Hoff's law:

$$\Pi = kT\rho_1 = kT \frac{N_1}{V} \quad (67)$$

Thus the osmotic compressibility:

$$\chi_{II} = -\frac{1}{V} \left[\frac{\partial V}{\partial P} \right]_{N_1, \mu_2} = -\frac{1}{V} \left[\frac{\partial V}{\partial \Pi} \right]_{N_1, \mu_2} \quad (68)$$

using the Eq. (67) becomes:

$$\chi_{II}^{-1} = \Pi = kT\rho_1 \quad (69)$$

For χ_2^\dagger choose, e.g. the isothermal compressibility of pure water at 25 °C [16]: $\chi_{H_2O}^{25} = 0.46 \times 10^{-10} \text{ cm}^3 \text{ erg}^{-1} = 0.46 \times 10^{-9} \text{ Pa}^{-1}$.

We calculate Π for a 1% solution of a spherical macromolecule with a molar mass of 10^4 g mol^{-1} (say a small protein) with a mass density of 1 g cm^{-3} . This leads to $d_1 = 3.17 \text{ nm}$ and $\Pi = 2470 \text{ Pa}$ (this corresponds with a hydrostatic pressure head of 24.7 cm in an osmometer). Then $\chi_{II}^{-1} = 2470 \text{ Pa}$, and thus $\chi/\chi_{II} = 1.14 \times 10^{-6}$; a very low value.

II: Concentrated systems

Let us take a concentration which is 40 times the previous dilute one, i.e. a volume fraction of colloid particles equal to $\phi_1 = \rho_1 V_1 = 0.40$. Then, $\chi = (1 - \phi_1)\chi_{H_2O}^\dagger$, when we assume that the colloid particles are incompressible. Further:

$$\chi_{II} = \frac{1}{\rho_1} \frac{\partial \rho_1}{\partial \Pi} = \frac{1}{\rho_1 kT} \frac{(1 - \phi_1)^4}{(1 + 2\phi_1)^2} \quad (70)$$

The formula stems from the Percus–Yevick theory and is a good approximation valid for colloidal particles with ‘hard-sphere’ interactions. Taking $\phi_1 = 0.4$, one finds: $\chi/\chi_{II} = 0.69 \times 10^{-3}$, still very small.

Further it follows from Eq. (66) in Appendix A, that under the same conditions:

$$\Gamma = \left[\frac{\partial \rho_2}{\partial \rho_1} \right]_{\mu_2} = -\frac{\bar{v}_1}{\bar{v}_2} \quad (71)$$

is a good approximation.

Appendix C: Evaluation of χ and χ_{II} for some mixtures of colloid 1 plus macromolecule 2 in a low molecular solvent 0

We start from Eq. (34) for the pressure of our quasi- two-component system (remember that P is an osmotic pressure and that the chemical potential μ_0 of the ‘background’ low molecular component 0 is kept constant in a reservoir C at a pressure P equal to zero).

$$\frac{P}{kT} = \frac{N_1}{V} + \frac{N_2}{V} \left[1 + \frac{N_1}{V} V_{12}^{\text{ex}} \right] \quad (72)$$

Using the definition $\chi = (-1/V)(\partial V/\partial P)_{N_1, N_2, \mu_0}$ one finds:

$$\frac{\chi^{-1}}{kT} = \rho_1 + \rho_2 + 2\rho_1\rho_2 V_{12}^{\text{ex}} \quad (73)$$

The (Donnan) osmotic compressibility follows from van't Hoff's law:

$$\frac{\chi_{II}}{kT} = \rho_1 \quad (74)$$

Further one finds from Eq. (65) up to and including terms linear in ρ_1 :

$$\frac{1}{\bar{v}_2} = \rho_1 + \rho_2 + \rho_1\rho_2 V_{12}^{\text{ex}} \quad (75)$$

and for the limit $\rho_1 \rightarrow 0$:

$$\Gamma^\circ \equiv \left[\frac{\partial \rho_2}{\partial \rho_1} \right]_{\mu_2}^\circ = -\rho_2^\dagger V_{12}^{\text{ex}} \quad (76)$$

The last equation does not come as a surprise because it also follows from our earlier Eq. (33): $\rho_2 = \rho_2^\dagger(1 - \rho_1 V_{12}^{\text{ex}})$.

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