

A van der Waals free energy in electrolytes revisited

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Abstract. A system of three electrolytes separated by two parallel planes is considered. Each region is described by a dielectric constant and a Coulomb fluid in the Debye-Hückel regime. In their book *Dispersion Forces*, Mahanty and Ninham have given the van der Waals free energy of this system. We rederive this free energy by a different method, using linear response theory and the electrostatic Maxwell stress tensor for obtaining the dispersion force.

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1 Introduction

The modest aim of the present paper is to give another derivation for the van der Waals free energy (generating a dispersion force) in a macroscopic arrangement of electrolytes. The considered arrangement is as follows: space is divided into three regions $i = 1, 2, 3$ by two parallel planes distant by l from each other; with the Cartesian coordinate system chosen such that the x axis is normal to the planes, we define region $i = 1$ by $x < -(l/2)$, region $i = 2$ by $-(l/2) < x < (l/2)$, and region $i = 3$ by $x > (l/2)$. Each region may be filled by an electrolyte. The solvent is macroscopically described by a continuous dielectric medium with a given dielectric constant ϵ_i and a dissolved salt microscopically modelled by a Coulomb fluid in the Debye-Hückel regime with a given Debye wavenumber κ_i . In their book [1], Mahanty and Ninham write, for this arrangement, a free energy, per unit area of one plane, of the form

$$F(l) = \frac{k_B T}{2} \int_0^\infty \frac{2\pi k dk}{(2\pi)^2} \ln[1 - \Delta_{12}\Delta_{13} \exp(-2s_2 l)], \quad (1)$$

where k_B is Boltzmann's constant, T the temperature, $s_i^2 = \kappa_i^2 + k^2$, and $\Delta_{ij} = (\epsilon_i s_i - \epsilon_j s_j)/(\epsilon_i s_i + \epsilon_j s_j)$. If $\kappa_2 = 0$, $F(l)$ is long-ranged; if $\kappa_2 \neq 0$, $F(l)$ is “screened” into a short-range expression. The result (1) has many applications in electrochemistry, biology, etc.

In reference [1] (see also [2]), the authors start with a quantum system. They work out a quantum elaborate formalism, in which the l -dependent part of the free energy is written as a sum on Matsubara frequencies

$\xi_n = 2\pi n k_B T / \hbar$, where \hbar is Planck's constant (divided by 2π). Actually, equation (1) is the $\xi_n = 0$ term of that sum. In the high-temperature regime, the quantum free energy should go to the classical one, and only the $\xi_n = 0$ term (1) should survive. Therefore, a derivation of (1), using from the start equilibrium classical (*i.e.* non-quantum) statistical mechanics, should be possible. Such a derivation has been given by Netz in a field-theoretical formalism [3]. Here, we present another purely classical derivation, based on the use of linear response theory and the Maxwell stress tensor, generalizing a method already used in a special case [4]; in this way, we obtain the dispersion force corresponding to (1).

In classical statistical mechanics, there is no coupling between charges and electromagnetic radiation (Bohr-van Leeuwen theorem) [5–7]. Therefore, we have to consider only charges interacting by the static Coulomb law.

We model each electrolyte as a system of M_i species $\alpha_i = 1, 2, \dots, M_i$ of particles, each of them carrying a charge q_{α_i} . The fugacity of species α_i is given as z_{α_i} . If each electrolyte occupied the whole space, the number density of species α_i would be n_{α_i} . The Debye wavenumber κ_i in region i is defined by

$$\kappa_i^2 = \frac{4\pi\beta \sum_{\alpha_i} n_{\alpha_i} q_{\alpha_i}^2}{\epsilon_i}, \quad (2)$$

where $\beta = 1/(k_B T)$.

The paper is organized as follows. In Section 2, we compute the electric potential created by an unit charge. In Section 3, we use the linear response theory for computing the Maxwell electrostatic stress tensor. In Section 4, we compute the kinetic part of the stress tensor. Finally, in

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Section 5, we obtain the total stress, and, by integration, recover the Mahanty-Ninham free energy (1).

2 A Green function

In the following, we shall need the electric potential at \mathbf{r}_1 knowing that there is a unit charge at \mathbf{r}_2 . In the Debye-Hückel regime (which describes the small- β case) this potential $G(\mathbf{r}_1, \mathbf{r}_2)$ is the Green function obeying

$$(\Delta_1 - \kappa_i^2)G(\mathbf{r}_1, \mathbf{r}_2) = -(4\pi/\epsilon_j)\delta(\mathbf{r}_1 - \mathbf{r}_2), \quad (3)$$

where the index i denotes the region where is \mathbf{r}_1 and j denotes the region where is \mathbf{r}_2 . At the lowest relevant order in β , the densities can be replaced by the bulk ones, this is why the bulk κ_i are used in (3). This equation is supplemented by the continuity conditions at the interfaces of G and $\epsilon(\partial G/\partial x_1)$, and by the condition that G should vanish when $|x_1| \rightarrow \infty$ (this last condition means that we assume that there is no bulk potential difference between regions 1 and 3, and these potentials have been chosen as zero without loss of generality).

Equation (3) can be replaced by a simpler one for the transverse Fourier transform of G . Let \mathbf{r}^\perp be the two-dimensional vector which describes the components of \mathbf{r} normal to the x axis. Since G depends on \mathbf{r}_1^\perp and \mathbf{r}_2^\perp only through their difference, we can define their transverse Fourier transform by

$$\tilde{G}(x_1, x_2, k) = \int d(\mathbf{r}_1^\perp - \mathbf{r}_2^\perp) \times \exp[-i\mathbf{k} \cdot (\mathbf{r}_1^\perp - \mathbf{r}_2^\perp)] G(\mathbf{r}_1, \mathbf{r}_2), \quad (4)$$

where $k = |\mathbf{k}|$ is the modulus of a two-dimensional wavenumber normal to the x -axis. Equation (3) becomes a simpler differential equation. We shall only need the case when x_2 is in region 2. Then, this equation is

$$\left(\frac{\partial^2}{\partial x_1^2} - k^2 - \kappa_i^2 \right) \tilde{G}(x_1, x_2, k) = -(4\pi/\epsilon_2)\delta(x_1 - x_2). \quad (5)$$

The solution of this equation which vanishes when $|x_1| \rightarrow \infty$ is of the form

$$\begin{aligned} \tilde{G} &= \frac{2\pi}{\epsilon_2 s_2} \exp(-s_2|x_1 - x_2|) + A(x_2) \exp(-s_2 x_1) \\ &\quad + B(x_2) \exp(s_2 x_1) \text{ when } -(l/2) < x_1 < (l/2), \\ \tilde{G} &= C(x_2) \exp(s_1 x_1) \text{ when } x_1 < -(l/2), \\ \tilde{G} &= D(x_2) \exp(-s_3 x_1) \text{ when } x_1 > (l/2), \end{aligned} \quad (6)$$

where $s_i^2 = \kappa_i^2 + k^2$. The coefficients A, B, C, D are to be determined by the continuity conditions at the interfaces. One finds, when both x_1 and x_2 are in region 2, $\tilde{G} = \tilde{G}_{\text{bulk}} + \tilde{G}_1$, where $\tilde{G}_{\text{bulk}}(x_1, x_2, k) = (2\pi/\epsilon_2 s_2) \exp(-s_2|x_1 - x_2|)$ is the Fourier transform of the bulk Debye screened potential $G_{\text{bulk}}(\mathbf{r}_1, \mathbf{r}_2) =$

$(\exp(-\kappa_2|\mathbf{r}_1 - \mathbf{r}_2|)/(\epsilon_2|\mathbf{r}_1 - \mathbf{r}_2|))$ and \tilde{G}_1 , the Fourier transform of G_1 , is

$$\begin{aligned} \tilde{G}_1(x_1, x_2, k) &= \\ &= \frac{2\pi}{\epsilon_2 s_2} \frac{2\Delta_{12}\Delta_{32} \exp(-2s_2 l) \cosh[s_2(x_1 - x_2)]}{1 - \Delta_{12}\Delta_{32} \exp(-2s_2 l)} - \frac{2\pi}{\epsilon_2 s_2} \\ &\times \frac{\exp(-s_2 l) \{ \Delta_{12} \exp[-s_2(x_1 + x_2)] + \Delta_{32} \exp[s_2(x_1 + x_2)] \}}{1 - \Delta_{12}\Delta_{32} \exp(-2s_2 l)}. \end{aligned} \quad (7)$$

3 Maxwell stress tensor

In statistical mechanics $qG(\mathbf{r}_1, \mathbf{r}_2)$ means the statistical average of the total electric potential at \mathbf{r}_1 when an additional charge q is placed at \mathbf{r}_2 . Therefore, in terms of the microscopic electric potential $\hat{\phi}(\mathbf{r})$ created by the system (dielectrics plus electrolytes, NOT q),

$$\langle \hat{\phi}(\mathbf{r}_1) \rangle_q = qG(\mathbf{r}_1, \mathbf{r}_2) - \frac{q}{|\mathbf{r}_1 - \mathbf{r}_2|}, \quad (8)$$

where $\langle \dots \rangle_q$ is a statistical average taken when q is present. The presence of q adds to the Hamiltonian the term $\hat{H}' = q\hat{\phi}(\mathbf{r}_2)$. In the classical regime, assumed to be valid for both the charged particles and the dielectrics, linear response theory says that, when q is infinitesimal

$$\langle \hat{\phi}(\mathbf{r}_1) \rangle_q = -\beta \langle \hat{H}' \hat{\phi}(\mathbf{r}_1) \rangle, \quad (9)$$

where $\langle \dots \rangle$ is a statistical average taken without \hat{H}' in the statistical weight. In writing (9), we have taken into account that $\langle \hat{\phi}(\mathbf{r}_1) \rangle = 0$ at the lowest relevant order in β ; indeed, if the rhs of equation (3) is replaced by zero, its solution vanishing at infinity is identically zero. We shall use (8) and (9) for computing the l -dependent part of the Maxwell stress tensor. We define a l -dependent part by the condition that it vanishes when $l \rightarrow \infty$. For obtaining that l -dependent part, it can be checked that it is sufficient to replace the rhs of (8) by its part $qG_1(\mathbf{r}_1, \mathbf{r}_2)$. From now on, all quantities refer to their l -dependent part. (8) and (9) give

$$\beta \langle \hat{\phi}(\mathbf{r}_1) \hat{\phi}(\mathbf{r}_2) \rangle = -G_1(\mathbf{r}_1, \mathbf{r}_2). \quad (10)$$

The xx component of the Maxwell stress tensor¹ in region 2 is [8]

$$T_{xx}(x_1) = \frac{\epsilon_2}{4\pi} \left(\frac{\partial^2}{\partial x_1 \partial x_2} - \frac{1}{2} \nabla_1 \cdot \nabla_2 \right) \langle \hat{\phi}(\mathbf{r}_1) \hat{\phi}(\mathbf{r}_2) \rangle_{\mathbf{r}_2 = \mathbf{r}_1}, \quad (11)$$

¹ Since here the electric potential is the microscopic one due to the charged particles of the system, not the macroscopic one due to some external charges, the simple Minkowski expression of the stress tensor is appropriate.

or, in terms of the Fourier transform of (10),

$$\begin{aligned} \beta T_{xx}(x) = & -\frac{\epsilon_2}{8\pi} \int \frac{d\mathbf{k}}{(2\pi)^2} \left(\frac{\partial^2}{\partial x_1 \partial x_2} - k^2 \right) \\ & \times \tilde{G}_1(x_1, x_2, k)_{x_1=x_2=x} = \frac{1}{4} \int \frac{d\mathbf{k}}{(2\pi)^2 s_2} \\ & \left[\frac{(\kappa_2^2 + 2k^2) 2\Delta_{12}\Delta_{32} \exp(-2s_2 l)}{1 - \Delta_{12}\Delta_{32} \exp(-2s_2 l)} \right. \\ & \left. + \frac{\kappa_2^2 \exp(-s_2 l) [\Delta_{12} \exp(-2s_2 x) + \Delta_{32} \exp(2s_2 x)]}{1 - \Delta_{12}\Delta_{32} \exp(-2s_2 l)} \right]. \quad (12) \end{aligned}$$

4 Kinetic part of the stress tensor

The xx component of the stress tensor has, in addition to its Maxwell part, a kinetic part, which is, in region 2, $-k_B T n_2(x)$ where $n_2(x)$ is the total number density of the electrolyte at x . It happens that the departure of $n_2(x)$ from its bulk value $n_2 = \sum_{\alpha_2} n_{\alpha_2}$ gives to the l -dependent part of the stress tensor a contribution of the same order than the Maxwell part, although the Maxwell part can be and has been computed, at the lowest order in β , by using the bulk densities in (3).

For computing $n_2(x)$, a natural idea is to use the first equation of the YBG hierarchy which gives $dn_2(x)/dx$; however, it is not easy to find the integration constant for getting $n_2(x)$. We resort to a slightly more complicated method relying on the diagrammatic renormalized Mayer expansion reviewed in reference [9]. The Debye-Hückel regime is described by writing for the excess free energy F_{exc} only the diagrams

$$-\beta F_{\text{exc}} = \bullet - - - \bullet + \text{ring diagrams}, \quad (13)$$

where a black circle stands for the density of some species of particles at some position (to be summed and integrated on), a bond stands for $-\beta$ times the Coulomb interaction between the particles at its ends, and the ring diagrams are rings made of n ($n \geq 2$) black circles and n bonds. Taking the functional derivative of (13) with respect to $n_{\alpha_2}(\mathbf{r})$ gives

$$\begin{aligned} \ln \left[\frac{n_{\alpha_2}(x)}{z_{\alpha_2}} \right] = & \circ - - - \bullet + \\ & \frac{1}{2} (\circ - - - \bullet - - - \circ + \circ - - - \bullet - - - \bullet - - - \circ + \dots), \quad (14) \end{aligned}$$

where all white circles refer to the same fixed particle of species α_2 at some point \mathbf{r} in region 2 (actually the densities depend only on the x -component of \mathbf{r}). In the rhs of (14), the first diagram is $-\beta q_{\alpha_2} \langle \hat{\phi}(x) \rangle$. The other diagrams are the sum of chain diagrams minus the first one $\circ - - - \circ$; $-\beta$ times the screened potential $q_{\alpha_2}^2 G$ is known to be given by this sum of chain diagrams (taking into account the position-dependence of the densities in the

calculation of G would give corrections of higher order in β). Therefore,

$$\begin{aligned} \ln \left[\frac{n_{\alpha_2}(x)}{z_{\alpha_2}} \right] = & -\beta q_{\alpha_2} \langle \hat{\phi}(x) \rangle \\ & - \frac{\beta q_{\alpha_2}^2}{2} \lim_{\mathbf{r}' \rightarrow \mathbf{r}} \left[G(\mathbf{r}, \mathbf{r}') - \frac{1}{\epsilon_2 |\mathbf{r} - \mathbf{r}'|} \right]. \quad (15) \end{aligned}$$

For the bulk values, a similar equation is obtained, by replacing in (15) $n_{\alpha_2}(x)$ by n_{α_2} , $\langle \hat{\phi}(x) \rangle$ by $\langle \hat{\phi}_{\text{bulk}} \rangle$, and G by G_{bulk} . Combining these two equations, we obtain

$$\begin{aligned} n_{\alpha_2}(x) = & n_{\alpha_2} \exp \left[-\beta q_{\alpha_2} \left[\langle \hat{\phi}(x) \rangle - \langle \hat{\phi}_{\text{bulk}} \rangle \right] - \frac{\beta q_{\alpha_2}^2}{2} G_1(\mathbf{r}, \mathbf{r}) \right]. \quad (16) \end{aligned}$$

Linearizing the exponential in (15), summing on α_2 , taking into account the bulk neutrality condition $\sum_{\alpha_2} q_{\alpha_2} n_{\alpha_2} = 0$ which suppresses the term containing $\langle \hat{\phi}(x) \rangle - \langle \hat{\phi}_{\text{bulk}} \rangle$, and using (7), we obtain

$$\begin{aligned} n_2(x) - n_2 = & -\frac{\kappa_2^2}{4} \int \frac{d\mathbf{k}}{(2\pi)^2 s_2} \left[\frac{2\Delta_{12}\Delta_{32} \exp(-2s_2 l)}{1 - \Delta_{12}\Delta_{32} \exp(-2s_2 l)} \right. \\ & \left. - \frac{\exp(-s_2 l) [\Delta_{12} \exp(-2s_2 x) + \Delta_{32} \exp(2s_2 l)]}{1 - \Delta_{12}\Delta_{32} \exp(-2s_2 l)} \right]. \quad (17) \end{aligned}$$

Since $n_2(x) - n_2 \rightarrow 0$ as $l \rightarrow \infty$, the l -dependent part of $n_2(x)$ is $n_2(x) - n_2$.

5 Final result

Finally, by adding the Maxwell and kinetic contributions in region 2, one finds, for the l -dependent part of the force per unit area acting on the region on the right of x , $f = -T_{xx}(x) + k_B T [n_2(x) - n_2]$. Thus,

$$f = -\frac{k_B T}{2} \int_0^\infty \frac{d\mathbf{k}}{(2\pi)^2} \frac{2s_2 \Delta_{12} \Delta_{32} \exp(-2s_2 l)}{1 - \Delta_{12} \Delta_{32} \exp(-2s_2 l)}. \quad (18)$$

This force is, as it should be, independent of x . This general expression has been rederived in special cases, sometimes by different methods, see for instance reference [4, 10]. Since $f = -\partial F(l)/\partial l$, integration of f with respect to l , with the integration constant determined by the condition that F vanishes as $l \rightarrow \infty$, gives (1).

In the formalism used by Netz [3], (1) has been obtained in a ‘‘one-loop’’ approximation; a ‘‘two-loop’’ correction has been computed in a special case. An alternative approach for obtaining corrections would be to extend the calculation in the present paper by taking into account higher-order terms in the renormalized Mayer expansion. We do not know which approach is the simplest one.

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