On the Statistical Theory of Mixed Ion-Dipole Systems of Interacting Particles

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Abstract

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On the Statistical Theory of Mixed Ion-Dipole Systems of Interacting Particles

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The present work is devoted to a generalization of the method of collective variables with the transition integral function (1) to systems with noncentral interaction.

Consider a system of N ions of M species, with N_a particles in each species a, and S dipoles characterized by a constant dipole moment $\mathbf{m}(\vartheta\varphi)$. The interaction energy of this system has the form:

$$U = \frac{1}{2}\sum_{\substack{a,b\\ i\neq j}} e_a e_b r_{ij}^{-1} + \sum_{\substack{1\leq a\leq M\\ 1\leq i\leq N_a\\ 1\leq r\leq S}} \varphi_{ar}(r_{ir},\vartheta_r,\varphi_s) + \frac{1}{2}\sum_{\substack{1\leq r\leq S\\ 1\leq s\leq S}} \varphi_{rs}(r_{rs},\vartheta_r,\vartheta_s,\varphi_r,\varphi_s), \quad (1)$$

where

$$\varphi_{ar}(r_{ir},\vartheta_r,\varphi_r) = e_a \mathbf{m}_r \nabla r_{ir}^{-1}; \qquad \varphi_{rs} = \mathbf{m}_r \nabla \mathbf{m}_s \nabla r_{rs}^{-1}.$$

Introducing the "dimensionless charge"

$$\lambda_a(k) = e_a(k)\left[\sum_{1\leq a\leq M+S} e_a(k)e_a(-k)N_a\right]^{-1/2},$$

where $e_a(k) = e_a$ for $1 \leq a \leq M$, $e_a(k) = i\mathbf{k}\mathbf{m}_a$, $N_a = 1$, $M < a \leq M + S$, we define the collective variable ρ_k by the expression

$$\rho_k = \sum_{1\leq a\leq M+S} \lambda_a \sum_{i=1}^{N_a} e^{i\mathbf{k}\mathbf{r}_i}, \qquad k \neq 0. \quad (2)$$

Let us pass in (1) to the Fourier representation; then

$$U = \frac{1}{2}\sum_{k}\theta\alpha(k)\rho_k\rho_{-\mathbf{k}} - \frac{1}{2}\sum_{k}\theta\alpha(k) + U(0), \tag{3}$$

where

$$\alpha(k) = \sum_{1\le a\le M+S} e_a(k)e_a(-k)N_a v(k)(\theta V)^{-1}; \qquad v(k) = 4\pi k^{-2}, \qquad U(0) = \frac{1}{2}\sum_{a,b}\lambda_a\lambda_b\theta\alpha(k).$$

Our problem consists in finding the free energy of the equilibrium system with potential (1). In doing so, we shall omit its kinetic part.

We begin with the configurational integral Z:

$$Z = \int \exp\left\{-\frac{U}{\theta}\right\} J\left(\frac{\rho}{r}\right) \prod_{k}{}' (d\rho_k)\, d\Omega_1 \ldots d\Omega_s, \tag{4}$$

where $\theta = kT$; $d\Omega_i$ is the element of solid angle of the i-th dipole; the prime indicates that $\mathbf{k}$ varies in the upper half-sphere.

$J(\rho/r)$ is the integral transition function to collective variables:

$$J\left(\frac{\rho}{r}\right) = \int \prod_{\mathbf{k}}{}' \delta\left(\rho_{\mathbf{k}} - \sum_{1\le a\le M+S}\lambda_a \sum_{i=1}^{N_a} e^{i\mathbf{k}\mathbf{r}_i}\right) dq_1 \ldots dq_{N+S}. \tag{5}$$

For an overall neutral system of ions, the function J was calculated in work (^{1}).

In the presence of dipole forces, it is expedient to calculate J in such a way as to split the plasma factor $e^{-\rho_{\mathbf{k}}\rho_{-\mathbf{k}}}$ into two parts: an ionic and a nonionic one. For the second, instead of the product $\rho_{\mathbf{k}}\rho_{-\mathbf{k}}$, the exponent must contain the operator

$$\sum_{M<a\le M+S} D_2^a,$$

corresponding to pair groups.

Ultimately, the transition function of the mixed system has the form

$$J = V^{N+S}\prod_{\mathbf{k}}{}' \exp\left\{\sum_{1\le a\le M}\sum_{n\ge 3}(-1)^n N_a D_n^a(\mathbf{k}) + \right.$$
$$\left. + \sum_{M<a\le M+S}\sum_{n\ge 2}(-1)^n D_n^a(\mathbf{k})\right\} \exp\left[-\left\{\frac{1}{\gamma^2}\rho_{\mathbf{k}}\rho_{-\mathbf{k}} + \ln\gamma^2\pi\right\}\right], \tag{6}$$

where

$$\gamma^2 = \sum_{1\le a\le M} \lambda_a^2 N_a, \qquad D_n^a = \sum_{\mathbf{k}1+\dots+\mathbf{k}_n=0} \frac{\lambda_a(\mathbf{k}_1)\dots\lambda_a(\mathbf{k}_n)}{n!} \frac{\partial^n}{\partial\rho_{\mathbf{k}1}\dots\partial\rho_{\mathbf{k}n}}.$$

In the sums $\mathbf{k}_1 + \dots + \mathbf{k}_n = 0$, none of the sums of order lower than n must be equal to zero.

Subsequently, after substituting (6) into (4), integration over $\rho_\mathbf{k}$ is performed. It is easy to verify that a nonzero result is obtained only for even differentiations of the form $\partial^{2n}/\partial\rho_{\mathbf{k}1}\partial\rho_{-\mathbf{k}1}\dots$. As a result of this differentiation under the integral, sums of products of factors $(\rho_\mathbf{k}\rho_{-\mathbf{k}} - 1)$ arise, each of which can be obtained by parametric differentiation of Z with respect to $\alpha(k)$. Then we expand the combination of operators $\partial/\partial\alpha(k)$. Z is represented in the form of a series with sums of the type

$$\sum_{a,b} \sum_{\mathbf{k}1+\dots+\mathbf{k}_n=0} \lambda_a^n\lambda_b^n \frac{\alpha(\mathbf{k}_1)}{\alpha(\mathbf{k}_1)+1} \cdots \frac{\alpha(\mathbf{k}_n)}{\alpha(\mathbf{k}_n)+1} \tag{7}$$

The expression

$$\frac{\lambda_a\lambda_b\alpha(k)}{\gamma^2\alpha(k)+1}$$

is the Fourier transform of the self-consistent potential g_{ab}:

$$g_{ab} = -e_a e_b r^{-1} \exp[-\varkappa r] \qquad \text{for } a, b \le M; \tag{8a}$$

$$g_{ab} = -e_a \mathbf{m}_b \nabla r^{-1} \exp[-\varkappa r] \qquad \text{for } 1 \le a \le M < b \le M + S; \tag{8 }$$

$$g_{ab} = -\mathbf{m}_a \nabla \mathbf{m}_b \nabla r^{-1} \exp[-\varkappa r] \qquad \text{for } a, b > M, \tag{8 }$$

where

$$\varkappa = \left[4\pi \sum_a N_a e_a^2 (V\theta)^{-1}\right]^{1/2}.$$

Each sum (7) reduces to a group integral of g_{ab}, just as in work (^{1}). New in comparison with (^{1}) is the application of the operatortors $\prod_{a>M}\exp(D_2^0)$. Mixed products of the operators $D_2^a D_2^b$, etc., lead to double group integrals. Powers D_2^a with identical a are summed into the exponential $\exp\left[-\frac{1}{2}\sum_{\mathbf{k};\,a>M}\lambda_a^2\frac{\alpha(k)}{\alpha(k)+1}\right]$, which, together with the corresponding free term from (3), is equal to

$$\exp\left[-\left\{\frac{1}{4\pi V^2\theta}\sum_{a<M<b}\int\Phi_{ab}g_{ab}\,dq_a\,d\Omega_a\,dq_b\right\}\right]. \tag{9}$$

In the present work it is assumed that

$$U(0)=\frac{1}{2}\sum_{a,b}\lambda_a\lambda_b\theta\alpha(0)=0. \tag{10}$$

Owing to (9) and (10), in expression (4) for Z there are no common factors depending simultaneously on all Ω. Therefore, after the inverse Fourier transformation, integration over the angles is performed. Then Z can be written in the form of an exponential function with group integrals proportional to N.

For the free energy $F=-\theta\ln Z$ we finally obtain the expression*

$$\begin{aligned}F_1 ={}& -(N+S)\theta\ln V-S\theta\ln 4\pi-\frac{1}{3}\varkappa\sum_c e_c^2N_c\\&-\theta\left\{\frac{1}{2}\sum_{a,b}\frac{1}{V}N_aN_b\int\left[\exp(g_{ab})-1-g_{ab}-\frac{1}{2}g_{ab}^2\right]dq+\sum_{abc}\cdots\right\}\\&-\theta\left\{\sum_{a,r}\frac{1}{4\pi V^2}N_a\int\left[\exp(g_{ar})-1-g_{ar}-\frac{1}{2}g_{ar}\left(g_{ar}+\frac{\Phi_{ar}}{\theta}\right)\right]dq_a\,dq_r\,\Omega\,dr+\cdots\right\}\\&-\theta\left\{\frac{1}{2}\sum_{rs}(4\pi V)^{-2}\int\left[\exp(g_{rs})-1-g_{rs}\right]dq_r\,dq_s\,d\Omega_r\,d\Omega_s+\cdots\right\}+\cdots.\end{aligned} \tag{11}$$

Here

$$\int g_{ar}\,dq_a\,dq_r\,d\Omega_r=\int g_{rs}\,dq_r\,dq_s\,d\Omega_r\,d\Omega_s=0. \tag{12}$$

As is known, system (1) will not be stable without the inclusion of short-range forces, which account for attraction and repulsion effects at small distances. The integrals in (11) diverge at zero. Therefore we supplement the potential (1) by short-range forces:

$$\sum_{a,b}\varphi_{ab}(r)+\sum_{a,s}\varphi_{as}(r\Omega_s)+\sum_{s,t}\varphi_{st}(r\Omega_s\Omega_t). \tag{13}$$

The only requirement imposed here on (13) is the presence at zero of a positive pole of higher order than the order of the corresponding poles in (1).

Using the "addition" theorem ([2],[3]), we write:

$$F = F^0 - \frac{\theta}{2} \sum_{a,b;\,i,j} \frac{\delta F^0}{\delta \Phi_{ab}} f_{ab}(r_{ij})\, dq_i\, dq_j - \cdots, \tag{14}$$

where $f_{ab} = \exp(-\varphi_{ab}/\theta) - 1$.

From expressions (8) it is easy to write the variations g:

$$\delta g_{rs} = -\frac{1}{\theta}\delta\Phi_{rs} - \sum_a N_a (V\theta)^{-1} \int (\delta\Phi_{ra} g_{as} + g_{ra}\delta\Phi_{as})\, dq_a - \sum_{a,b} N_a N_b (V^2\theta)^{-1} \int g_{ra}\delta\Phi_{ab} g_{bs}\, dq_a dq_b. \tag{15}$$

Similar variations are obtained also for the other g' s.

With the aid of (12), (15) we compute the functional derivatives in (11). Then they are substituted into (14). As a result of grouping identical group integrals, we find the free energy of the mixed system of particles with allowance for short-range forces:

$$\begin{aligned} F = F_{ug} &- \frac{1}{3}\chi \sum_c e_c^2 N_c - \theta \sum_{a,b} N_a N_b (2V)^{-1} \int \left(\psi_{ab} - \frac{1}{2} g_{ab}^2\right) dq \\ &- \theta \sum_{a,b,c} (3! V^2)^{-1} N_a N_b N_c \int (\psi_{ab}\psi_{ac}\psi_{bc} + 3 g_{ab}\psi_{ac}\psi_{bc})\, dq_1 dq_2 \\ &- \theta \sum_{a,r} (4\pi V)^{-1} N_a \int \left[\psi_{ar} - {}^1\!/\!{}_2 g_{ar}\left(g_{ar} + \frac{1}{\theta}\Phi_{ar}\right)\right] dq\, d\Omega_r \\ &- \theta \sum_{a,r,s} (2V^2(4\pi)^2)^{-1} N_a \int (\psi_{ar}\psi_{as}\psi_{rs} - g_{ar}g_{as}\psi_{rs}) dq\, dq_1 d\Omega_r d\Omega_s \\ &- \theta \sum_{r,s} (2V(4\pi)^2)^{-1} \int \psi_{rs} dq\, d\Omega_r d\Omega_s \\ &- \theta \sum_{r,s,t} (3!(4\pi)^3 V^2)^{-1} \int \psi_{rs}\psi_{rt}\psi_{st} dq\, dq'\, d\Omega_r d\Omega_s d\Omega_t. \end{aligned} \tag{16}$$

Here

$$\psi_{ab} = \exp\{-\varphi_{ab}/\theta + g_{ab}\} - 1 - g_{ab}; \quad \psi_{ar} = \exp\{-\varphi_{ar}/\theta + g_{ar}\} - 1,$$

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* The notation for species is as follows: a, b, c, d for ions; r, s, t, u for dipoles.

$$\psi_{rs} = \exp\{-\varphi_{rs}/\theta + g_{rs}\} - 1.$$

The last two terms of the third and fourth lines can be reduced to the integral

$$\sum_{a,b,c,t} (8\pi\theta V^3)^{-1} N_a N_b N_c \int g_{at} g_{tb} \Phi_{ac} g_{cb}\, dq_1 dq_2 dq_3 d\Omega_t,$$

which enters into the fourth-order correlation integrals.

The free energy (16) is not only an initial function for thermodynamic calculations. With its aid one can also compute the distribution functions. The functional derivative with respect to $-\varphi$ or to $-\Phi$ leads to the binary distribution function.

Various limiting transitions give already known results of the theory of systems of ions, dipoles, and neutral particles.

Expression (16) is generalized to the case of induced dipoles and multipoles. It can serve as the starting point for calculating the effects of formation of Bjerrum pairs and other associations in ionic systems.

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Note: Figure translations are in progress. See original paper for figures.