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Physics

1966

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Abstract

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UDC 536.759.091

Physics

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STATISTICAL DISTRIBUTIONS IN MEDIA PERTURBED BY FOREIGN PARTICLES

(Presented by Academician N. N. Bogolyubov, 28 I 1966)

For the solution of many problems arising in the general theory of solutions (thermodynamics of solvation, thermodynamic activity of components in concentrated solutions, osmotic theory of solutions, the influence of the medium on the course of physicochemical processes), it is necessary to have an idea of the changes occurring in the solvent when foreign particles are introduced into it. Dissolved molecules may be regarded as force centers that create an external field in which the particles of the medium move. In the last 2-3 years the statistical thermodynamics of inhomogeneous systems (in an external field) has been developing especially owing to the use of powerful functional methods (1-3). The functional approach finds effective application in the thermodynamics of surface phenomena (4), in the osmotic theory of solutions (5), and also in the derivation of integral equations for distribution functions of homogeneous liquids (6, 7). In the present work this approach is applied to the study of the statistical distribution in a medium perturbed by dissolved molecules.

Functional expansions in the case of a weak external field were considered in detail by Kuni (3). He constructed a functional Taylor series with respect to the functional argument $\exp\{-\beta\psi(r)\} - 1$, where $\beta = 1/kT$, and ψ is the external field. However, it is not known how rapidly such series converge. Difficulties arise in connection with the singular behavior of intermolecular potentials at small distances between molecules. On the other hand, the case is especially interesting and occurs more frequently in which the potential energy of interaction of a dissolved molecule with the particles of the medium* $u_{\alpha s}$ consists of two parts:

$$u_{\alpha s}(r) = u_{\alpha s}^{\delta}(r) + u_{\alpha s}^{\text{d}}(r). \quad (1)$$

Here $u_{\alpha s}^{\delta}(r)$ describes the hard core of the dissolved molecule that is impenetrable for particles. The potential $u_{\alpha s}^{\text{d}}$ describes the field of attractive forces and decreases relatively slowly with distance. At large distances from the dissolved molecule $u_{\alpha s}^{\delta} \ll u_{\alpha s}^{\text{d}}$. The potential $u_{\alpha s}^{\text{d}}$, in turn, is assumed to be weak and admits functional expansions in the function $\varphi_{\alpha s}^{\text{d}} - 1$, where

$\varphi_{\alpha s}^d(r^s r^\alpha) = \exp\{-\beta u_{\alpha s}^d(r^\alpha r^s)\} \rightarrow 1$ as $|r^s - r^\alpha| \rightarrow \infty$. But at small distances the situation changes. Here strong repulsion predominates. Therefore, despite the fact that near the dissolved particle the forces of attraction to it cannot be regarded as weak, the inequality $u_{\alpha s}^\delta \gg u_{\alpha s}^d$ holds. In this region the statistical distribution of the particles of the medium is governed by the external field $u_{\alpha s}^\delta$.

In finding the distribution functions in a medium around dissolved molecules strongly interacting with the particles of the solvent, one may proceed in different ways, considering the solvent in a strong external field as an almost ideal gas or using approximations of the superposition type. The purpose of the present work is to isolate in

* The index s refers to the solvent, and the index α to the solute.

contributions to the distribution functions that depend on the long-range “tail” of the intermolecular potential. It should be noted that, in general form, the question of the relation between distribution functions in different external fields was considered by Kuni⁽³⁾. Here it is shown that, with the special choice of the function $u_{\alpha s}$ described above, it is possible to obtain functional expansions that converge rapidly both at large and at small distances from the dissolved molecule.

Let us introduce, as in⁽⁷⁾, the generating functional

$$Q_{N_s}(\varphi_{\alpha s}) = \int_V \dots \int_V \exp\{-\beta U_s(\mathbf{r}_{N_s}^s)\} \prod_{j=1}^{N_s} \varphi_{\alpha s}(r_j^s r^\alpha) \frac{d^{N_s} r^s}{V^{N_s}}, \quad (2)$$

where

$$U_s(\mathbf{r}_{N_s}^s) = \sum_{i,j}^{N_s} u_s(r_i^s r_j^s)$$

is the potential energy of N_s solvent molecules* placed in the volume V . The functional $Q_{N_s}(\varphi_{\alpha s})$, as is readily seen, is the statistical integral over the configurational space of N_s solvent molecules located in the field created by an extraneous molecule at the point r^α . The generating functional contains complete information on the structure and physical properties of the medium perturbed by the dissolved molecules. In particular, the solvation free energy at infinite dilution, defined as the difference between the free energies of the perturbed medium and the pure solvent, is equal to

$$G_{\alpha s} = -kT \ln[Q_{N_s}(\varphi_{\alpha s})/Q_{N_s}(\varphi_{\alpha s} = 1)]. \quad (3)$$

The pair distribution function $F_1(r_1^s/r^\alpha)$ of the medium perturbed by a dissolved molecule at the point r^α can be found from (2) by means of functional differentiation (7)

$$\varphi_{\alpha s}(r_1^s r^\alpha) \delta \ln Q_{N_s}(\varphi_{\alpha s}) / \delta \varphi_{\alpha s}(r_1^s r^\alpha) = c_s F_1(r_1^s/r^\alpha), \quad (4)$$

where $c_s = N_s/V$ is the solvent density. The following conditional distribution functions are calculated with the aid of the functional equation (7):

$$\begin{aligned} c_s^{-1} \varphi_{\alpha s}(r_{k+1}^s r^\alpha) \delta F_k(r_k^s/r^\alpha) / \delta \varphi_{\alpha s}(r_{k+1}^s r^\alpha) = F_{k+1}(r_{k+1}^s/r^\alpha) - \\ - F_1(r_{k+1}^s/r^\alpha) F_1(r_k^s/r^\alpha). \end{aligned} \quad (5)$$

Equations (4) and (5) together make it possible to find expressions for the higher functional derivatives of the generating functional

$$\begin{aligned} c_s^{-2} \varphi_{\alpha s}(r_1^s r^\alpha) \varphi_{\alpha s}(r_2^s r^\alpha) \delta^2 \ln Q_{N_s}(\varphi_{\alpha s}) / \delta \varphi_{\alpha s}(r_1^s r^\alpha) \delta \varphi_{\alpha s}(r_2^s r^\alpha) = \\ = F_2(r_1^s r_2^s/r^\alpha) - F_1(r_1^s/r^\alpha) F_1(r_2^s/r^\alpha), \end{aligned} \quad (6)$$

and further

$$\begin{aligned} c_s^{-3} \varphi_{\alpha s}(r_1^s r^\alpha) \varphi_{\alpha s}(r_2^s r^\alpha) \varphi_{\alpha s}(r_3^s r^\alpha) \delta^3 \ln Q_{N_s}(\varphi_{\alpha s}) / \delta \varphi_{\alpha s}(r_1^s r^\alpha) \delta \varphi_{\alpha s}(r_2^s r^\alpha) \delta \varphi_{\alpha s}(r_3^s r^\alpha) = \\ = F_3(r_1^s r_2^s r_3^s/r^\alpha) - F_2(r_1^s r_2^s/r^\alpha) F_1(r_3^s/r^\alpha) - F_2(r_2^s r_3^s/r^\alpha) F_1(r_1^s/r^\alpha) - \\ - F_2(r_1^s r_3^s/r^\alpha) F_1(r_2^s/r^\alpha) + 2F_1(r_1^s/r^\alpha) F_1(r_2^s/r^\alpha) F_1(r_3^s/r^\alpha). \end{aligned} \quad (7)$$

Let us note that (6) and (7) are analogues of relations found by F. M. Kuni (3) for an inhomogeneous system within the framework of the grand canonical ensemble.

We shall now use the apparatus described to construct expansions of the distribution functions and of the solvation free energy in functional—

* The symbol r_i^s denotes the radius vector of the i -th solvent molecule. By r_k^s is meant the set of coordinates of a group of k molecules $r_1^s, r_2^s, \dots, r_k^s$.

to the argument $\varphi_{\alpha s}^d - 1$. Taking (3) into account, we write for the solvation free energy the expansion

$$-\frac{G_{as} - G_{as}^b}{kT} = c_s \int \Phi_1(r_1^s/r^\alpha) [\varphi_{as}^d(r_1^s r^\alpha) - 1] dr_1^s + \frac{1}{2!} c_s^2 \iint \Phi_2(r_1^s r_2^s/r^\alpha) [\varphi_{as}^d(r_1^s r^\alpha) - 1] [\varphi_{as}^d(r_2^s r^\alpha) - 1] dr_1^s dr_2^s + \dots \quad (8)$$

where G_{as}^b is the solvation free energy for the short-range potential u_{as}^b . The coefficients of the series are expressed in terms of functional derivatives of the generating functional,

$$c_s \Phi_1(r_1^s/r^\alpha) = \varphi_{as}^b(r_1^s r^\alpha) \delta \ln Q_{N_s}(\varphi_{as}) / \delta \varphi_{as}(r_1^s r^\alpha) \Big|_{\varphi_{as} = \varphi_{as}^b} \quad (9)$$

and, analogously,

$$c_s^2 \Phi_2(r_1^s r_2^s/r^\alpha) = \varphi_{as}^b(r_1^s r^\alpha) \varphi_{as}^b(r_2^s r^\alpha) \delta^2 \ln Q_{N_s}(\varphi_{as}) / \delta \varphi_{as}(r_1^s r^\alpha) \delta \varphi_{as}(r_2^s r^\alpha) \Big|_{\varphi_{as} = \varphi_{as}^b}. \quad (10)$$

Comparing (9) and (10) with equations (4) and (6), we find

$$\Phi_1(r_1^s/r^\alpha) = F_1^b(r_1^s/r^\alpha),$$

$$\Phi_2(r_1^s r_2^s/r^\alpha) = F_2^b(r_1^s r_2^s/r^\alpha) - F_1^b(r_1^s/r^\alpha) F_1^b(r_2^s/r^\alpha), \quad (11)$$

and so on, where F_1^b, F_2^b, \dots are the conditional distribution functions of the medium, calculated with the potential u_{as}^b . Expression (8), together with relations (11), gives the solution of the problem under consideration, relating the solvation free energy to the long-range “tail” of the potential u_{as}^d and to distribution functions calculated with the potential u_{as}^b .

In the strong-solvation approximation, the molecules of the medium should be considered statistically independent, and one may write

$$F_k^b(r_k^s/r^\alpha) = \prod_{j=1}^k F_1^b(r_j^s/r^\alpha). \quad (12)$$

Hence $\Phi_2(r_1^s r_2^s/r^\alpha) = 0$, $\Phi_3(r_1^s r_2^s r_3^s/r^\alpha) = 0$, and so on. It is easy to see that all coefficients of the series (8) vanish when the variables of integration fall within the region of strong solvation of the dissolved molecule. Thus, the integrands of all terms of the expansion (8) are small both at large and at small distances from the dissolved molecule, ensuring rapid convergence of the series (almost) everywhere.

Fig. 1

Figure 1: Fig. 1

Treating G_{as} as a generating functional, by functional differentiation with respect to φ_{as}^d one can construct expansions of the conditional distribution functions that converge in the region of strong solvation.

Variation of (8) at fixed potential u_{as}^b gives the required result

$$F_1(r_1^s/r^\alpha) = \exp\{-\beta u_{as}^d(r_1^s r^\alpha)\} \{F_1^b(r_1^s/r^\alpha) + \\ + c_s \int [F_2^b(r_1^s r_2^s/r^\alpha) - F_1^b(r_1^s/r^\alpha)F_1^b(r_2^s/r^\alpha)] [\varphi_{as}^d(r_2^s r^\alpha) - 1] dr_2^s + \dots\}. \quad (13)$$

Higher distribution functions of the perturbed medium can be obtained from F_1 by means of the functional relation (5).

In the strong-solvation approximation (12), equation (8) gives

$$G_{as} = G_{as}^b - kTc_s \int F_1^b(r_1^s/r^\alpha) [\exp\{-\beta u_{as}^d(r_1^s r^\alpha)\} - 1] dr_1^s.$$

The unary distribution function in the region of strong solvation is equal to

$$F_1(r_1^s/r^\alpha) = \exp\{-\beta u_{\alpha s}(r_1^s r^\alpha)\} F_1(r_1^s/r^\alpha). \quad (14)$$

It should be kept in mind that, despite the known crudeness of approximation (12) outside the region of strong solvation, the accuracy of the expressions given is not reduced. Indeed, the maximum contribution to the free energy of solvation comes from the region where the interactions of the dissolved particle with the molecules of the medium are strongest, i.e., precisely from the region of strong solvation.

Fig. 1

Of course, at large distances from the dissolved molecule, where perturbations of the solvent are weak, it is necessary to take into account the intrinsic ordering of the molecules of the medium and to proceed from approximations of the superposition type

$$F_2(r_1^s r_2^s/r^\alpha) = F_1(r_1^s/r^\alpha)F_1(r_2^s/r^\alpha) \times F_2^s(r_1^s r_2^s), \quad (15)$$

where F_2^s is the binary distribution function of the pure solvent.

Again putting $\Phi_3 = 0$ and introducing (15) into expansion (13), we obtain

$$F_1(r_1^s/r^\alpha) = \exp\{-\beta u_{\alpha s}(r_1^s r^\alpha)\} F_1(r_1^s/r^\alpha) \times \\ \times \left\{ 1 + c_s \int [F_2^s(r_1^s r_2^s) - 1] F_1(r_2^s/r^\alpha) [\exp\{-\beta u_{\alpha s}(r_2^s r^\alpha)\} - 1] dr_2^s \right\}. \quad (16)$$

This representation of the unary distribution function is more exact than (14). It makes it possible to reveal the asymptotic behavior of $F_1(r_1^s/r^\alpha)$ when the distance $|r_1^s - r^\alpha|$ becomes very large. As the distance $|r_2^s - r^\alpha|$ increases, the function $\varphi_{\alpha s}(r_2^s r^\alpha)$ rapidly tends to unity, so that $\varphi_{\alpha s}(r_2^s r^\alpha) = 1$ as soon as the integration variable r_2^s in (16) leaves some solvation region of radius $R_{\alpha s}$. If the distance $|r_1^s - r^\alpha|$ is so large that $|r_1^s - r^\alpha| > R_{\alpha s}$, then in the integrand the distance $|r_2^s - r_1^s|$ may be replaced by the distance $|r_1^s - r^\alpha|$ (see Fig. 1). Since as $|r_1^s - r^\alpha| \rightarrow \infty$, $F_1(r_1^s/r^\alpha) \rightarrow 1$, and the region in which $F_1 \neq 1$ is contained within the solvation region of the dissolved molecule because of the short-range character of the potential $u_{\alpha s}$, we shall write, according to (16),

$$F_1(r_1^s/r^\alpha) \approx 1 + c_s B_{\alpha s} [F_2^s(r_1^s r^\alpha) - 1], \quad (17)$$

where

$$B_{\alpha s} = \int F_1(r_2^s/r^\alpha) [\exp\{-\beta u_{\alpha s}(r_2^s r^\alpha)\} - 1] dr_2^s$$

is a constant. Expression (17) is valid if the correlation radius in the medium exceeds the dimensions of the solvation region $R_{\alpha s}$.

Thus, far from the dissolved molecule, deviations of the density of the medium from the mean density of the pure solvent are governed by the binary distribution function of the pure solvent.

I express my deep gratitude to F. M. Kuni for valuable advice and comments.

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Received
30 VII 1965

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