FREE ENERGY OF NONREGULAR CONDENSED SYSTEMS WITH IMPURITIES

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Abstract
In the study of nonregular condensed systems with impurity particles, one of the necessary and complex problems is the calculation of the characteristics of the system itself, and, first and foremost, the free energy of the system [1-8]. The aim of this work is precisely the theoretical calculation of the thermodynamic characteristics of complex nonregular condensed systems with polyatomic impurity particles, taking into account the intramolecular vibrations of the impurities. Temperature-dependent Green's functions are a convenient tool for calculating the thermodynamic characteristics of such systems. Theoretical calculations using temperature-dependent Green's functions allow for consideration of both the effects of frequency and spatial dispersion in condensed systems, as well as the specific interactions between polyatomic impurity particles and the medium.

Keywords: free energy, Green functions, condensed medium, nonregular systems, impurity particles

Free energy of the system

The electrostatic part of the change in the free energy of the system upon introduction of a polyatomic polarizable particle into a condensed medium can be represented as:

$$\delta\Omega = \delta\Omega_0 + \delta F^m + \delta\Omega_1 + \delta\Omega_2 \quad (1)$$

where $\delta\Omega_0$ is the free energy of solvation calculated at the equilibrium values of the intramolecular coordinates of the impurity vibrations, δF^m is the solvation energy of the medium caused by a charged impurity particle, $\delta\Omega_1$ is the change in the free energy of the system caused by the interaction of the polarization fluctuations of the medium with the static field of the impurity, $\delta\Omega_2$ is the change in the free energy of the system associated with the interaction of the polarization fluctuations of the medium with the intramolecular vibrations of the impurity.

When polyatomic charged impurity particles dissolve in a condensed medium, the main contribution to the change in the free energy of the system will be made by $\delta\Omega_1$.

To calculate the value of $\delta\Omega_1$, one can use the relationship between the change in free energy and the corresponding *S*-matrix, which has the form

$\delta\Omega_1 = -kTln\langle S_{(1)}\rangle_0$ (2)

And $S_{(1)}$ matrix has the form:

$$S_{(1)}(\beta) = T_\tau exp\left[\int_0^\beta d\tau \int d\vec{r}\delta\vec{P}(\vec{r},\tau)\Delta\vec{E}(\vec{r})\right] \ \beta = 1/kT \quad (3)$$

In the last formula, $\delta\vec{P}$ is the polarization fluctuation of the system, and $\Delta\vec{E}$ is the change in the electric field strength of the reactants during the charge transfer process, *T* – temperature.

If the exponential function in the *S*-matrix is represented as a series, then

$$\langle S_{(1)}\rangle_0 = \sum_{n=0}^{\infty}\frac{1}{(2n)!}\int d\overrightarrow{r_1}\ldots\int d\overrightarrow{r_{2n}}\int_0^\beta d\tau_1\ldots\int_0^\beta d\tau_{2n}E^0_{i_1}(\overrightarrow{r_1})\ldots E^0_{i_{2n}}(\overrightarrow{r_{2n}})\cdot\langle T_\tau\delta P_{i_1}(\vec{r}_1\tau_1)\ldots\delta P_{i_{2n}}(\overrightarrow{r_{2n}},\tau_{2n})\rangle_0 \quad (4)$$

Here, quantum-statistical averaging is performed over the states of the Hamiltonian of the medium H^m.

In the approximation of decoupling of quantum-statistical averages for operators $\delta\vec{P}$, we obtain

$$\langle S_{(1)}\rangle_0 = exp\left[-\frac{1}{2}\int d\vec{r}d\overrightarrow{r'}\int_0^\beta d\tau\int_0^\beta d\tau' E^0_i(\vec{r})E^0_k\left(\overrightarrow{r'}\right)G^0_{\delta P_i\delta P_k}(\vec{r},\vec{r}';\tau-\tau')\right] \quad (5)$$

Passing to the Fourier representation in imaginary time and integrating over τ and τ', we obtain:

$$\langle S_{(1)}\rangle_0 = exp\left[-\frac{1}{2}\int d\vec{r}d\overrightarrow{r'}E^0_i(\vec{r})E^0_k\left(\overrightarrow{r'}\right)G^0_{\delta P_i\delta P_k}(\vec{r},\vec{r}';\ \omega=0)\right] \quad (6)$$

Since at $\omega = 0$, $G(\omega_n = 0) = G^R(\omega = 0)$, then

$$\delta\Omega_1 = \frac{1}{2}\int d\vec{r}d\overrightarrow{r'}E^0_i(\vec{r})E^0_k\left(\overrightarrow{r'}\right)G^0_{\delta P\delta P}(\vec{r},\vec{r}';\ \omega=0) \quad (7)$$

For the change of the free energy of a system when charged particles are introduced into a condensed medium, the following form of writing can be used:

$$\delta\Omega_1 = \frac{1}{2}\int d\vec{r}d\overrightarrow{r'}G_{\rho\rho}(\vec{r},\vec{r}')\varphi^{ex}(\vec{r},)\,\varphi^{ex}\left(\overrightarrow{r'},\right)\frac{1}{2}G_{\varphi\varphi}\rho^{ex}\rho^{ex} \quad (8)$$

where φ^{ex} and ρ^{ex} are the scalar potential and charge density of the impurity particle, respectively

When determining the Green function $G_{\varphi\varphi}(\vec{r},\vec{r}')$, it can be taken into account that, with an accuracy of up to the electron charge, the Green function $G_{\varphi\varphi}(\vec{r},\vec{r}')$ coincides with the magnitude of the electrostatic potential of the system at the point $\vec{r}$ when a unit charge is placed at the point $\vec{r}'$.

Effects of spatial dispersion of the medium

The effects of spatial dispersion of the medium when calculating the change in the free energy of the system upon the introduction of impurity particles into a condensed medium can be taken into account if some model functions are used as the Green function operators of the polarization fluctuations of the medium, or the charge density, or the scalar potential of the medium. In this case, for Green function can be used a function of the type:

$$G_{\varphi\varphi}(\vec{r},\vec{r}') = f(\vec{r})\frac{1}{|\vec{r}-\vec{r}'|} \quad (9)$$

where $f(\vec{r})$ is some function of the coordinate r.

In this case, the behavior of the Green function will be of the type:

$$G_{\varphi\varphi}(\vec{r},\vec{r}') = G_{\rho\varphi}(\vec{r},\vec{r}') = -f(\vec{r})\delta(\vec{r}-\vec{r}') \quad (10)$$

The Fourier component of the function $f(\vec{r})$ can be expressed through the longitudinal component of the dielectric constant of the medium $\varepsilon^l(k)$:

$$f(\vec{k}) = [1 - 1/\varepsilon^l(k)]\,{}^1\!/_{4\pi} \quad (11)$$

As a result for Green function we have:

$$G_{\varphi\varphi}(\vec{k},\vec{k}') = -{}^1\!/_{4\pi}\left[1 - {}^1\!/_{\varepsilon^l(k)}\right]\delta_{\vec{k}\vec{k}'} \quad (12)$$

For homogeneous isotropic local media we have

$$G_{\varphi\varphi}(\vec{k},\vec{k}') = -{}^1\!/_{4\pi}\left[1 - {}^1\!/_{\varepsilon^l(k)}\right]\delta_{\vec{k}\vec{k}'} \equiv -\left({}^{C_0}\!/_{4\pi}\right)\delta_{\vec{k}\vec{k}'} \quad (13)$$

Accordingly, in $\vec{r}$-space the Green function has the form:

$$G_{\varphi\varphi}(\vec{r},\vec{r}') = -\left({}^{C_0}\!/_{4\pi}\right)\delta(\vec{r}-\vec{r}') \quad (14)$$

If the impurity particle is a spherically symmetric particle of radius r_0 and has a charge z, then for the change in free energy we obtain

$$\delta\Omega_1 = -{}^{C_0 z^2}\!/_{8\pi r_0} = -\left({}^{z^2}\!/_{8\pi r_0}\right)\left(1 - {}^1\!/_{\varepsilon}\right) \quad (15)$$

To take into account the effects of spatial dispersion of the medium, the function $G_{\varphi\varphi}$ in formula (14) is "blurred." We introduce the function

$$G_{\varphi\rho}(\vec{r},\vec{r}') = -\left({}^{C_0}\!/_{4\pi}\right)\Delta_\lambda(|\vec{r}-\vec{r}'|) \quad (16)$$

where, as function, we choose an exponentially decaying function normalized to unity of the form

$$\Delta_\lambda(|\vec{r}-\vec{r}'|) = \left({}^1\!/_{8\pi\lambda^3}\right)exp\left({}^{|\vec{r}-\vec{r}'|}\!/_{\lambda}\right) \quad (17)$$

If we use the classical approximation for ρ^{ex} and assume that the charge localization point coincides with the origin of the coordinate system, then

$$\rho^{ex}(\vec{r}) = z\delta(\vec{r}) \quad (18)$$

where z is the charge of the impurity particle.

In this case, for $\delta\Omega_1$ we have:

$$\delta\Omega_1 = -{}^{C_0 z^2}\!/_{16\pi\lambda} = \left(-{}^{C_0 z^2}\!/_{16\pi\lambda}\right)\left(1 - {}^1\!/_{\varepsilon}\right) \quad (19)$$

Similarly, one can calculate the change in the free energy of a system in which the spatial dispersion effect has a complex form. For example, for a system with oscillations and damping, the function Δ_λ can be calculated as:

$$\Delta_{\bar{\lambda}}(|\vec{r}-\vec{r}'|) = \left[{}^{\nu\left(\nu^2 - 3\bar{\lambda}^2\right)}\!/_{8\pi}\right]e^{-\nu|\vec{r}-\vec{r}'|}cos\left(\bar{\lambda}|\vec{r}-\vec{r}'|\right) \quad (20)$$

In this case, for the change of the system's free energy, we obtain:

$$\delta\Omega_1 = -\left({}^{C_0}\!/_{8\pi}\right)\left[{}^{\nu\left(\nu^2 - 3\bar{\lambda}^2\right)}\!/_{\left(\left(\nu^2 - \bar{\lambda}^2\right)^2 - 4\bar{\lambda}^2\nu^2\right)}\right] \quad (21)$$

The parameter $1 / \bar{\lambda}$ will be approximately equal to the diameter of the solvent molecule.

For the quantum approximation, the charge density ρ^{ex} can be expressed as follows:

$\rho^{ex}(\vec{r}) = e|\Psi(\vec{r})|^2$ (22)

Here $\Psi(\vec{r})$ is the wave function.

The normalized function can be used as the wave function:

$$\Psi(\vec{r}) = \left[{}^{\alpha^{3/2}}\!/_{(8\pi)^{1/2}}\right]e^{-\alpha r/2} \quad (23)$$

For this case, for the change in the free energy of the system $\delta\Omega_1$, we obtain:

$$\delta\Omega_1 = -\left({}^{C_0 e^2}\!/_{32\pi^2}\right)\int d\vec{r}d\vec{r'}\,d\vec{r''}\Delta_\lambda(|\vec{r}-\vec{r}'|)\left[{}^{|\Psi(\vec{r})|^2\left|\Psi\left(\vec{r''}\right)\right|^2}\!/_{|\vec{r}-\vec{r}''|}\right] \quad (24)$$

Considering the form of the function $\Delta_\lambda(|\vec{r}-\vec{r}'|)$ (17) and taking the wave function as shown in (23), we have

$$\delta\Omega_1 = -\left({}^{C_0 e^2\alpha^6}\!/_{(8\pi)^4\lambda^3}\right)\int d\vec{r}d\vec{r'}\,d\vec{r''}exp\left(-\frac{|\vec{r}-\vec{r}'|}{\lambda}\right)\exp\left[-\alpha(r+r'')\frac{1}{|\vec{r}'-\vec{r}''|}\right] \quad (25)$$

After integrating over coordinates $\vec{r}$, $\vec{r'}$, and $\vec{r''}$, we obtain

$$\delta\Omega_1 = -\left(C_0 e^2 (\alpha/2)^4 / 8\pi\lambda^2\right)\left(32\alpha^7 - 4\alpha^9\lambda^2 + 4\alpha^6/\lambda - 55\alpha^5/\lambda^2 - 21\alpha^4/\lambda^3 + 38\alpha^3/\lambda^4 + 26\alpha^2/\lambda^5 - 20\alpha/\lambda^6 - 12/\lambda^7\right) \quad (26)$$

If we use a function $\Delta_\lambda(|\vec{r} - \vec{r}'|)$ in the form (20), then for $\delta\Omega_1$ we obtain:

$$\delta\Omega_1 = -\left[C_0 e^2 (\alpha/2)^4 \nu(\nu^2 - 3\bar{\lambda}^2)/8\pi\right] Re\left\{32\alpha^7\left[1/(\nu - i\bar{\lambda})\right] - 4\alpha^9/(\nu - i\bar{\lambda})^3 + 4\alpha^6 - 55\alpha^5(\nu - i\bar{\lambda}) - 21\alpha^4(\nu - i\bar{\lambda})^2 + 38\alpha^3(\nu - i\bar{\lambda})^3 + 26\alpha^2(\nu - i\bar{\lambda})^4 - 20\alpha(\nu - i\bar{\lambda})^5 - 12(\nu - i\bar{\lambda})^6\right\} \quad (27)$$

To describe the effects of spatial dispersion of the medium, we can also use a function of the form

$$\Delta_\lambda(|\vec{r} - \vec{r}'|) = \left(1/\lambda^3\lambda^{-3/2}\right) exp\left(-|\vec{r} - \vec{r}'|^2/\lambda^2\right) \quad (28)$$

In this case, if for the wave function we use the form (23), then for $\delta\Omega_1$we obtain:

$$\delta\Omega_1 = -C_0 e^2\alpha^3/4 \int_0^\infty dr r e^{-\alpha r}\Phi\left(r/\lambda\right) \quad (29)$$

where $\Phi\left(r/\lambda\right)$ is the error integral

$$\Phi\left(r/\lambda\right) = 1/\sqrt{\pi}\int_0^{r/\lambda} e^{-t^2}dt \quad (30)$$

During numerical calculations, for the error integral, we can use the following approximation:

$$\Phi\left(r/\lambda\right) = 1 - \sqrt{\frac{2}{\pi}}e^{-(r/\lambda)^2}[b_1 t + b_2 t^2 + b_3 t^3 + b_4 t^4 + b_5 t^5] \quad (31)$$

where

$t = 1/\left(1 + P\sqrt{2}\frac{r}{\lambda}\right)$; P=0.2316; $b_1 = 0.3195$; $b_2 = -0.3566$; $b_3 = 1.7815$; $b_4 = -1.8213$; $b_5 = 1.3303$ (32)

For the charge density in the quantum case, one can also use expression

$$\rho(\vec{r}) = \left(e\alpha^3/56\pi\right)\left(1 + \alpha r/2\right)^2 e^{-\alpha r} \quad (33)$$

If we use expression (28) for function Δ_λ, then for $\delta\Omega_1$ we have:

$$\delta\Omega_1 = -\left(9C_0 e^2\alpha/56\right) + \left(C_0 e^2\alpha^3/14\sqrt{2\pi}\right)\int_0^\infty dr\left\{r\left(1 + \frac{\alpha r}{2}\right)^2[b_1 t + b_2 t^2 + b_3 t^3 + b_4 t^4 + b_5 t^5]e^{-\left(\alpha r + r^2/\lambda^2\right)}\right\} \quad (34)$$

For the change of the free energy of a system when a polyatomic polarizable dipole charged particle is introduced into a condensed medium, calculations can be carried out with one or another degree of accuracy, taking into account various effects: the quantum or classical nature of the impurity characteristics, the effects of spatial dispersion of the medium, which can be described by various model functions; the interaction of intramolecular vibrations of the impurity with polarization fluctuations of the medium.

Conclusion

Charge transfer processes in complex condensed systems were studied. Free energies of solvation were calculated for the complex nonregular condensed systems with polyatomic impurity particles. To calculate the free energies of solvation of particles in condensed systems, the apparatus of temperature Green functions for nonregular condensed systems was used, allowing for the effects of frequency and spatial dispersion of the system and the specific interactions of impurity particles with the medium to be taken into account. The characteristics of the system were obtained taking into account the electrostatic interaction of the impurity particle with the medium. In particular, the theoretical results obtained allow us to calculate the solvation energies of impurity particles in nonregular condensed medium, in which spatial dispersion effects are described by various functions.

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