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STATISTICAL DESCRIPTION OF EXCESS PROPERTIES OF MANY-PARTICLE BINARY SYSTEMS

Excess properties of almost ideal many-particle binary mixtures have been studied theoretically in the framework of the Kirkwood–Buff approach based on the calculation of statistical correlation integrals. With the help of the Percus–Yevick approximation for distribution functions and the superposition approximation for partial structure factors, an expression describing the compressibility of binary system in terms of the parameters of monodisperse phases i s derived. Using generalized functions, analytical expressions for correlation integrals in terms of component packing fractions are obtained. The theoretical results for the compressibility of a system are compared with the experimental data on the sound velocity. In this case, we introduce a correction function, which depends on the packing degree and the composition content and is determined by fitting the experimental data. This allows us to describe the excess properties of binary systems.

K e y w o r d s: Kirkwood–Buff method, binary mixture, excess properties, isothermal compressibility.

1. Introduction

Studying the physical properties of simple binary mixtures with the help of statistical mechanics methods is one of the traditionally challenging and, at the same time, complicated problems of the statistical physics of solutions. A well-known theoretical approach in this domain, which has a statistical substantiation, is the Kirkwood–Buff (KB) one [1], which allows the basic thermodynamic quantities to be written in terms of correlation integrals.

In the framework of the KB approach, the application of the superposition approximation for the structure factor $S_{12}(0)$ made it possible to obtain an expression for the isothermal compressibility $\beta_T^{(12)}$ in terms of the partial parameters of monodisperse phases. The introduction of a correction functions defined at the phenomenological level (data on experimental measurements of the sound velocity and its relation to the isothermal compressibility are used as a phenomenological basis) allowed experimental data on the measurement of the excess compressibility of a binary solution (the liquid mixture $CHCl_3/CCl_4$ is used as an example) to be interpreted theoretically.

The application of an invariant model proposed in works [2, 3] for the Percus–Yevick distribution function (PYDF), which is based on the apparatus of generalized functions, made it possible to obtain analytical expressions for the corresponding correlation integrals, which contain information on the component packing fractions and make allowance for a phenomenological information about the stereologic parameters of a local structure. The obtained relations explicitly demonstrate the influence of the local structure morphology on the excess properties of binary systems. The application of the proposed model approach to the description of the corresponding parameters in bimodal systems with a local structure developed at the meso- and macroscale levels, in particular, for granular materials, and some other soft-matter objects, will be carried out elsewhere.

2. Kirkwood–Buff Method and Its Application to Finding the Isothermal Compressibility

Following work [1], let us consider a many-particle binary (particles of sorts α and β) system in volume V. The one- ($\rho_\alpha^{(1)}(r_1)$) and two-particle ($\rho_{\alpha\beta}^{(2)}(r_1, r_2)$) distribution functions are defined by means of the transformation

$$\int_V dr_1 \int_V dr_2 \left[\rho_{\alpha\beta}^{(2)}(r_1, r_2) - \rho_\alpha^{(1)}(r_1) \right] = \langle N_\alpha N_\beta \rangle - \langle N_\alpha \rangle \langle N_\beta \rangle - \delta_{\beta\alpha} \langle N_\alpha \rangle, \qquad (1)$$

where N_α is the number of α-th particles in the volume V, $\langle...\rangle$ means the averaging over the configuration ensemble, and $\delta_{\alpha\beta}$ is the Kronecker delta-symbol. With the use of Eq. ([1]), we can determine partial quantities of the type

$$\rho_\alpha^{(1)}(r_1) = c_\alpha, \quad \rho_{\alpha\beta}^{(2)}(r_1, r_2) = c_\alpha c_\beta g_{\alpha\beta}(r_{12}), \qquad (2)$$

where $c_\alpha = \frac{N_\alpha}{V}$ is the particle concentration, and $g_{\alpha\beta}(r_{12})$ is the partial pair distribution function. Accordingly, the correlation integral is defined by the relation

$$G_{\alpha\beta}^V = \frac{1}{V} \int_V \int_V (g_{\alpha\beta}(r_{12}) - 1)\, dr_1 dr_2 =$$
$$= V \frac{\langle N_\alpha N_\beta \rangle - \langle N_\alpha \rangle \langle N_\beta \rangle}{\langle N_\alpha \rangle \langle N_\beta \rangle} - \frac{\delta_{\alpha\beta}}{c_\alpha}. \qquad (3)$$

The complicated character of the KB approach consists in the information incompleteness of partial distribution functions. For both simple liquids and complex many-particle systems, the experimental measurements of static structure factors together with the self-consistent solution of the inverse problem of reconstruction of the distribution function itself [2–6] are a recognized source of required information. The structure factor $S_{\alpha\beta}(\mathbf{k})$ of the mixture can be written in the form

$$S_{\alpha\beta}(\mathbf{k}) = x_\alpha \delta_{\alpha\beta} + x_\alpha x_\beta \rho \tilde{h}_{\alpha\beta}(\mathbf{k}), \qquad (4)$$

where x_α and x_β are the partial concentrations of the components in the solution, and $\tilde{h}_{\alpha\beta}(\mathbf{k})$ is the Fourier transform of the direct correlation function

$$h_{\alpha\beta}(r_{12}) = g_{\alpha\beta}(r_{12}) - 1. \qquad (5)$$

The relation between the isothermal compressibility of a binary mixture and the structure factors can be established with the help of the KB formula [4]

$$\rho k_{\rm B} T \beta_T^{(12)} =$$
$$= \frac{S_{11}(0)S_{22}(0) - S_{12}^2(0)}{x^2 S_{22}(0) - x(1-x)S_{12}(0) + (1-x)^2 S_{11}(0)}. \qquad (6)$$

The partial structure factors of monodisperse phases, $S_{11}(0)$ and $S_{22}(0)$, are connected with the corresponding isothermal compressibilities $\beta_T^{(1)}$ and $\beta_T^{(2)}$ by means of the relations

$$S_{11}(0) = \rho_1 k_{\rm B} T \beta_T^{(1)}, \quad S_{22}(0) = \rho_2 k_{\rm B} T \beta_T^{(2)}. \qquad (7)$$

Let us take advantage of the superposition approximation for the partial structure factor $S_{12}(0)$ in the form

$$S_{12}(0) = S_{11}(0)S_{22}(0) + \epsilon, \qquad (8)$$

where ϵ is the correction function, which is determined phenomenologically. Substituting Eq. (8) into Eq. (6) and holding the terms linear in ϵ, we obtain

$$\rho k_{\rm B} T \beta_T^{(12)} =$$
$$= \frac{1 - S_{11}(0)S_{22}(0)}{x^2 (S_{11}(0))^{-1} + (1-x)^2 (S_{22}(0))^{-1} - x(1-x)} +$$
$$+ \Omega(x, S_{ii}(0))\,\epsilon. \qquad (9)$$

In formula (9), the term with $\Omega(x, S_{ii}(0))$ depends only on the parameters of monodisperse phases.

3. Analytical Model for Pair Distribution Function

To simplify the further analysis, let us consider a model expression for the distribution function, which involves only some of the structural morphology features and looks like

$$g_{ij}(r) = \Theta(r - d_0^{(ij)}) + A_{ij}\delta(r - d_1^{(ij)}), \qquad (10)$$

where $r = |\mathbf{r}_1 - \mathbf{r}_2|$; $\mathbf{r}_1$ and $\mathbf{r}_2$ are the coordinates of the selected pair of particles; Θ and δ are the generalized Heaviside and Dirac, respectively, functions; and the quantities $d_0^{(ij)}$, $d_1^{(ij)}$, and A_{ij} will be defined below. A detailed consideration of this model was made in works [2, 3].

As was already mentioned above, functions of type (10) describe the simplest structural features, e.g., the zero probability for the particles in any selected pair to approach each other to a relative distance less than $d_0^{(ij)}$. In this case, $d_0^{(ij)}$ can be regarded as the diameter of a hard sphere (the superscripts i and j denote the kinds of molecules).

Hence, the model expression (10) approximately describes the short-range ordering of particles in a given vicinity of the selected particle. If $d_0^{(ij)}$ determines the particle "diameter", then the parameter $d_1^{(ij)}$ can be determined with the help of ordering-scale parameters, e.g., the radii of coordination spheres b, i.e. $d_1^{(ij)} = b d_0^{(ij)}$.

Using Eq. (10) and calculating the correlation integrals (3), we obtain

$$G_{ij} = \frac{4}{3}\pi \left(d_0^{(ij)3} - d_1^{(ij)3} + 3A_{ij} d_1^{(ij)2} \right). \qquad (11)$$
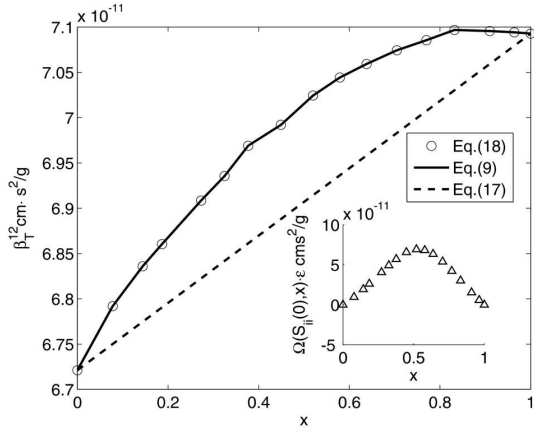
Fig. 1. Results of calculations of the quantity β_m by relation (9). Circles denote the experimental results used to determine the correction function. The dashed curve is the isothermal compressibility of an ideal system. The function $\epsilon\Omega(x, S_{ii}(0))$ corresponding to Eq. (9) is shown in the inset
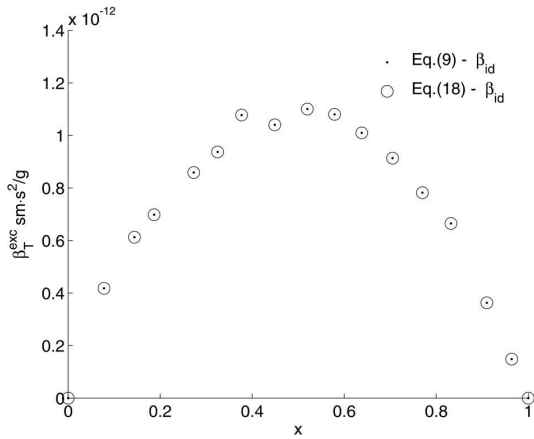

Fig. 2. Dependence of the excess isothermal compressibility β_{exc} on the component concentration x for the $CCl_4/CHCl_3$. Calculations are carried by formula (16), in which the quantity β_m was determined from Eq. (9) and the phenomenological relation (18)

The coefficient A_{ij} can be determined with the help of the normalization condition for the PYDF,

$$\frac{1}{\tilde{V}} \int_{\tilde{V}} g_{ij}(r)dr = 1, \quad A_{ij} = \frac{\tilde{V} - 8V_{ij}N_{ij}}{4\pi N_{ij}b^2 d_0^{(ij)2}}, \tag{12}$$

where $\tilde{V}$ is the size of the examined region, N_{ij} the number of the ij-th particles in the region $\tilde{V}$, V_{ij} the volume of the ij-th particle, and $d_0^{(ij)} = \frac{d_0^{(1)} + d_0^{(2)}}{2}$. Substituting Eq. (11) into Eq. (12), we obtain

$$G_{ij} = V_{ij}\left(2 - \eta_{ij} - 8b_{ij}^3\right), \tag{13}$$

where η_{ij} is the packing parameter in the monodisperse and binary phases.

The isothermal compressibility in the framework of the KB approach [1] for monodisperse systems is connected with the correlation integral as follows:

$$\beta_T = \frac{\rho G + 1}{k_B T \rho}. \tag{14}$$

A generalization of formula (17) to the case of a binary mixture looks like

$$\beta_T = \frac{1}{k_B T} \frac{1 + \rho_1 G_1 + \rho_2 G_2 + \rho_1 \rho_2 \left(G_1 G_2 - G_{12}^2\right)}{\rho_1 + \rho_2 + \rho_1 \rho_2 \left(G_1 + G_2 - 2G_{12}\right)}. \tag{15}$$

Relations (13), (14), and (15) explicitly demonstrate the dependence of β_T on the morphology of a local structure, in particular, the packing parameter η. Other parameters, which determine the local stereology and, in turn, depend on the partial concentrations and the solution asymmetry degree, can be determined either experimentally or from the results of numerical simulation.

4. Excess Isothermal Compressibility

The research of excess thermodynamic properties of molecular systems is a potential source of information on the character of the intermolecular interaction. For instance, the physical origin of excess properties is explained in work [7] by the intermolecular interaction between the solution components. A key concept in this way is the so-called excess property of a macroscopic quantity. The excess property is defined as a deviation of the experimentally measured (or theoretically calculated) parameter from the ideal one, with the determination of the latter being a separate problem. In particular, the excess isothermal compressibility β_{exc} of the binary solution can be determined as follows:

$$\beta_{\mathrm{exc}} = \beta_m - \beta_{id}, \tag{16}$$

where β_m is determined from experimental measurements or theoretical simulations, and β_{id} is given, e.g., by the equation

$$\beta_{id} = (1 - x)\beta_1 + x\beta_2. \tag{17}$$

In order to apply phenomenological data to the verification of the obtained model relations, let us use

the results of work [7] dealing with the experimental measurements of a sound velocity in a $CCl_4/CHCl_3$ solution. In work [8], the following phenomenological relation between the sound velocity u and the isothermal compressibility β_T was proposed:

$$\beta_T = \frac{1.38 \times 10^{-8}}{\left(6.3 \times 10^{-4} u^{1.5} n\right)^{1.5}}, \tag{18}$$

where n is the density. Formula (18) agrees well with the data of isothermal compressibility measurements for a wide class of systems, including binary mixtures.

In Fig. 1, the results of calculations of the quantity β_m by formula (9) are plotted. Circles correspond to experimental data used for the determination of the function $\epsilon\Omega(x, S_{ii}(0))$. In Fig. 2, the results of calculations of the excess compressibility for the system defined above with the use of the approach described in Section 2 are exhibited. It is evident that the results of theoretical calculation, after making a correction, agree well with the experimental data.

5. Conclusions

The excess properties of many-particle binary systems have been studied theoretically. In the framework of the KB approach with the use of the superposition approximation for the structure factor, an expression for the isothermal compressibility in terms of partial parameters of monodisperse phases is derived. On the basis of the proposed approach, the theoretical description of the excess properties of a binary solution is made. The solution $CCl_4/CHCl_3$ was taken as an example. The results obtained agree well with the data of experimental measurements.

The application of the analytical PYDF model in terms of generalized functions allowed analytical expressions for correlation integrals to be obtained. It is found that, owing to the properties of the PYDF, the model expressions for the correlation integrals appreciably depend on the packing degree in a certain vicinity of the particle. The applied approach, being formally scale-invariant, is also based on the phenomenological information concerning the local structure obtained from alternative sources.

Taking the aforesaid into account, the proposed approach can be used for the description of macroscopic parameters not only in molecular multicomponent systems, but also polydisperse soft-matter objects with a complicated morphology at the mesoscale level.

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СТАТИСТИЧНИЙ ОПИС НАДЛИШКОВИХ
ВЛАСТИВОСТЕЙ БІКОМПОНЕНТНИХ СИСТЕМ

Р е з ю м е

Проведено теоретичне дослідження надлишкових властивостей майже ідеальних бікомпонентних багаточастинкових сумішей. На цьому шляху використовується підхід Кірквуда–Баффа, який ґрунтується на визначенні статистичних кореляційних інтегралів. За допомогою апроксимації Перкуса–Йєвіка для функцій розподілу (та суперпозиційного наближення для парціальних структурних факторів, отримано співвідношення для опису стисливості бінарної системи в термінах параметрів монодисперсних фаз. У рамках моделі, яка спирається на апарат узагальнених функцій, отримані аналітичні вирази для кореляційних інтегралів, які наочно демонструють залежність від компактизації системи. Порівняння результатів теоретичних підходів із даними експериментального визначення стисливості, яке здійснюється за допомогою вимірів швидкості звуку, після введення корегуючої функції (яка залежить від степеня впакування та від компонентного складу, і визначається шляхом порівняння теоретичних розрахунків та експериментальних даних), дозволило здійснити опис надлишкових властивостей бікомпонентних систем.