Ergodic approximation in the theory of binary molecular solutions

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Abstract. An exact representation of the classical partition function of a two-component solution with interatomic potentials of a general form via a functional integral is obtained. The ergodic Weyl theorem (ergodic approximation) is used to calculate the functional integral. It is obtained an expression for the Helmholtz free energy via Fourier transforms of interatomic potentials, including renormalization in the case of their singularity. It is shown that, in order to correctly describe the separation of binary solutions into phases, it is necessary to take into account the ergodic contribution to the Helmholtz free energy. The necessary condition of the phase separation in binary solutions is established.

1. Introduction
Statistical thermodynamics is the theoretical basis for investigating the thermodynamic properties of solutions at the present time. Within statistical thermodynamics the problem of finding thermodynamic functions reduces to calculation of the configuration integral of a system of interacting particles

\[ Z_{\text{conf}} = \int \cdots \int \left[ \prod_{\alpha=1}^{M} \prod_{s=1}^{N_\alpha} \frac{dR_\alpha^s}{V} \right] \exp \left[ -\beta W(\ldots R_\gamma^s, \ldots) \right] \]  

where \( \beta = 1/T \) is reciprocal temperature \( T \) in energy units (the Boltzmann constant is equal to 1), \( W(\ldots R_\gamma^s, \ldots) \) is the energy of interactions of all particles, depending on their coordinates \( R_\gamma^s \), \( M \) is the number of components in the system, \( V \) is the system volume, index \( s \) numbers the particles, Greek indices \( \alpha, \gamma \) are components indexes, \( N_\alpha \) is total number of particles of component \( \alpha \). The configuration integral in the formula (1) is normalized to unity, i.e. in the absence of interactions it is equal to 1.

An exact analytic calculation of the configuration integral even for one-component system has by now been performed only for an extremely limited set of model potentials that are very far from "real" potentials [1]. Note that among the exactly solved models there are no three-dimensional models. Estimates of the errors of existing approximate methods for calculating configurational integrals also do not exist.
Most theoretical studies of solutions are based on phenomenological models [2, 3, 4, 5]. In these models some form of dependence of thermodynamic functions on thermodynamic variables (temperature, volume, pressure, composition of the system) is postulated. Interatomic interactions are accounted by means of appropriate empirical parameters.

The functional integration method for calculating the configuration integral of one-component systems with a central interatomic potential admitting the Fourier transform was proposed in papers [6, 7, 8, 9]. This method was further developed in [10, 11]. In particular, the equations of state of one-component systems with model potentials are derived in these papers and the equilibrium between the liquid and gas phases is investigated. A good agreement with the experimental data was obtained.

The purpose of this paper is to generalize the method of functional integration to the case of two-component systems with two-body central interatomic potentials of a general type and the construction of a microscopic theory of binary molecular solutions.

2. Model

We consider a two-component system characterized by two-body interatomic potentials $v_{\alpha\gamma}(\mathbf{R}_s^\alpha - \mathbf{R}_s^\gamma)$. The expression for the potential energy $W$ of a system of interacting particles is the following

$$W = \frac{1}{2} \sum_{\alpha,\gamma=1}^{2} \left\{ \sum_{s,s'=1}^{N_s} v_{\alpha\gamma}(\mathbf{R}_s^\alpha - \mathbf{R}_{s'}^\gamma) \right\} - \frac{1}{2} \sum_{\alpha=1}^{2} N_{\alpha} v_{\alpha\alpha}(0),$$

where the value $-\frac{1}{2} \sum_{\alpha=1}^{2} N_{\alpha} v_{\alpha\alpha}(0)$ compensates the terms of self-action, i.e. the summands with coincident indices $s = s'$ in the interaction energy of identical atoms ($\alpha = \gamma$).

Suppose that the interatomic potentials $v_{\alpha\gamma}(\mathbf{R}_s^\alpha - \mathbf{R}_s^\gamma)$ allow a representation in the form of the Fourier integral

$$v_{\alpha\gamma}(\mathbf{R}_s^\alpha - \mathbf{R}_s^\gamma) = \frac{1}{V} \sum_{\mathbf{k} \in \Omega} \tilde{v}_{\alpha\gamma}(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{R}_s^\alpha} e^{-i\mathbf{k} \cdot \mathbf{R}_s^\gamma} + \frac{1}{V} \tilde{v}_{\alpha\gamma}(0).$$

The summation over $\mathbf{k}$ in the right side of this relation is fulfilled over the set of all wave vectors $\Omega$ except for the vector $\mathbf{k} = 0$: this summand is taken into account by the last term in formula (3).

Let us note that the condition for the existence of a thermodynamic limit imposes certain restrictions on the interatomic potentials [12, 13, 14, 15]. For one-component systems with interatomic potential $v_{\alpha\alpha}(\mathbf{r})$ this condition has the form [16]

$$\tilde{v}_{\alpha\alpha}(\mathbf{k}) \geq 0,$$

where $\tilde{v}_{\alpha\alpha}(\mathbf{k})$ is the Fourier transform of the interatomic potential. For binary systems, the condition of non-negativity of the diagonal elements of the matrix $\tilde{v}_{\alpha\gamma}(\mathbf{k})$ should be supplemented by the following condition:

$$\det \tilde{v}(\mathbf{k}) \geq 0.$$ (5)

Interatomic potentials that do not satisfy conditions (4), (5) are called catastrophic or unstable, since there is no thermodynamic limit $N \to \infty$, $V \to \infty$, $N/V = n = \text{const}$ for them. Therefore, we assume that the Fourier transforms of the interatomic potentials satisfy the conditions of noncatastrophicity (4), (5).

By summation over $s$ and $s'$ in the expression contained in the curly brackets of formula (2), the sums of the following type occur after substituting relation (3)
\[ \tilde{\rho}_\alpha (k) = \sum_{i=1}^{N_k} e^{i k \cdot R_s^\alpha} = \sum_{j=1}^{N_R} \left[ \cos(\mathbf{k} \cdot \mathbf{R}_s^\alpha) + i \sin(\mathbf{k} \cdot \mathbf{R}_s^\alpha) \right] = C_\alpha (k) + i S_\alpha (k). \] (6)

These variables (collective coordinates), \( \tilde{\rho}_\alpha (k) \), as well as \( C_\alpha (k) \) and \( S_\alpha (k) \) were first introduced in [17]. They are related to the microscopic density of the number of particles by the Fourier transform and are often used in statistical mechanics since the 1950s [6, 18, 19, 20].

\[ \rho_\alpha (r) = \sum_{i=1}^{N_k} \delta (r - R_s^\alpha) \] (7)

We represent the expression in the curly brackets of the formula (2) in terms of the variables \( C_\alpha (k) \) and \( S_\alpha (k) \):

\[ \sum_{s',\gamma} \mathbb{v}_{s'\gamma} (R_s^\alpha - R_s^\gamma) = \frac{1}{V} \sum_{k \in \Omega} \mathbb{v}_{s'\gamma} (k) \left[ C_\alpha (k) + i S_\alpha (k) \right] \left[ C_\gamma (k) - i S_\gamma (k) \right] \]

\[ \mathbb{v}_{s'\gamma} (0) \frac{N_\alpha N_\gamma}{V} = \frac{1}{V} \sum_{k \in \Omega} \mathbb{v}_{s'\gamma} (k) \left( C_\alpha (k) C_\gamma (k) + S_\alpha (k) S_\gamma (k) \right) + \mathbb{v}_{s'\gamma} (0) \frac{N_\alpha N_\gamma}{V}. \] (8)

Let us note that sums of the type

\[ \sum_{k \in \Omega} \mathbb{v}_{s'\gamma} (k) C_\gamma (k) S_\gamma (k) = 0, \] (9)

by virtue of the fact that

\[ \mathbb{v}_{s'\gamma} (k) = \mathbb{v}_{s'\gamma} (-k), \quad C_\alpha (-k) = C_\alpha (k), \quad S_\alpha (-k) = -S_\alpha (k). \] (10)

We also note that the relations (10) imply the linear independence of both the set of variables \( C_\alpha (k) \), and the set of variables \( S_\gamma (k) \), defined on the space \( \Omega \) of all wave vectors \( k \in \Omega \). Therefore, in the sequel, the summation over the wave vectors \( k \in \Omega \) will be replaced by summation over the half-space \( k \in \Omega /2 \), obtained by intersection of the space \( \Omega \) by an arbitrary plane passing through the origin of coordinates \( k = 0 \):

\[ \sum_{k \in \Omega} \ldots \rightarrow 2 \sum_{k \in \Omega/2} \ldots \] (11)

As a result, we have the following expression for the potential energy of a two-component system of interacting particles via collective variables \( C_\alpha (-k) \) and \( S_\alpha (-k) \):

\[ W = -\frac{N_\alpha}{2} v_1 (0) - \frac{N_\gamma}{2} v_2 (0) + \frac{1}{2V} \sum_{a,\gamma=1}^2 \mathbb{v}_{a\gamma} (0) N_\alpha N_\gamma \]

\[ + \frac{1}{V} \sum_{a,\gamma=1}^2 \left\{ \sum_{a,\gamma=1}^2 \mathbb{v}_{a\gamma} (k) C_\alpha (k) C_\gamma (k) + \sum_{a,\gamma=1}^2 \mathbb{v}_{a\gamma} (k) S_\alpha (k) S_\gamma (k) \right\}. \] (12)

3. Representation of the partition function by means of the functional integral

To calculate the partition function, it is necessary to perform averaging of the exponent containing the potential energy of the system

\[ Z_{\text{conf}} = \int \ldots \left[ \prod_{a=1}^2 \left( \prod_{s=1}^{N_k} \frac{dR_s^\alpha}{V} \right) \right] e^{-\beta W}, \] (13)

where

\[ e^{-\beta W} = A \prod_{k \in \Omega/2} \exp \left\{ -\frac{\beta}{V} \sum_{a,\gamma=1}^2 \mathbb{v}_{a\gamma} (k) \left( C_\alpha (k) C_\gamma (k) + S_\alpha (k) S_\gamma (k) \right) \right\}. \] (14)
Atomic coordinates are contained only in the variables $C_\alpha(k)$ and $S_\alpha(k)$. Each of the factors of the product with respect to $k$ on the right-hand side of formula (14) contains exponents of quadratic forms with respect to variables $C_\alpha(k)$ and $S_\alpha(k)$.

We use the Stratonovich-Hubbard transformation, based on the well-known identity

$$\exp\left[-\frac{1}{2}(b, A b)\right] = \frac{1}{(\det A)^{1/2}} \left(2\pi\right)^{n/2} \times$$

$$\times \int \cdots \int \exp\left[-\frac{1}{2}(x, A^{-1} x) - i(b, x)\right] [dx],$$

where $A$ is arbitrary positive definite square matrix $n \times n$, $b$ is column vector consisting of $n$ elements, $[dx] = \prod_{j=1}^{n} dx_j$.

Note that the identity (16) expresses the exponential of the quadratic form $(b, A b)$ on the left-hand side of this formula in terms of the exponent of the linear form $(b, x)$ on the right-hand side. As a result, we have the following exact representation of the quantity $e^{-\beta W}$ through the functional integral

$$e^{-\beta W} = A \int \cdots \int \left( \prod_{k \in \Omega^2} \frac{dx_1(k) dx_2(k) dy_1(k) dy_2(k)}{(2\pi)^2} \right)$$

$$\times \exp\left[-\frac{1}{2} \sum_{k \in \Omega^2} \sqrt{\det \tilde{\nu}(k)} \sum_{a, r=1}^{2} x_a(k) \{\tilde{\nu}_{a r}(k)\}^{-1} x_r(k)\right]$$

$$\times \exp\left[-\frac{1}{2} \sum_{k \in \Omega^2} \sqrt{\det \tilde{\nu}(k)} \sum_{a, r=1}^{2} y_a(k) \{\tilde{\nu}_{a r}(k)\}^{-1} y_r(k)\right]$$

$$\times \exp\left[-i \sqrt{\frac{2\beta}{V}} \sum_{k \in \Omega^2} \left(\det \tilde{\nu}(k)\right)^{1/4} \sum_{a=1}^{2} x_a(k) C_\alpha(k)\right]$$

$$\times \exp\left[-i \sqrt{\frac{2\beta}{V}} \sum_{k \in \Omega^2} \left(\det \tilde{\nu}(k)\right)^{1/4} \sum_{a=1}^{2} y_a(k) S_\alpha(k)\right] \right].$$

4. Factorization of the configuration integral with respect to atomic coordinates

To calculate the configuration integral, it is necessary to integrate expression (17) over all atomic coordinates $R_{\alpha}^{s}$. Only the factors in the last two lines of this expression depend on atomic coordinates. Integrating these lines with respect to atomic coordinates, we obtain
\[ \int \cdots \int \left( \prod_{j=1}^{N_1} \frac{dR_{1j}}{V} \right) \left( \prod_{j=2}^{N_2} \frac{dR_{2j}}{V} \right) \times \exp \left\{ -i \sum_{j=1}^{N_1} \sum_{k \in \Omega / 2} \frac{2\beta}{V} (\det \tilde{\nu}(k))^\frac{1}{2} \left[ x_j(k) \cos(kR_{1j}) + y_j(k) \sin(kR_{1j}) \right] \right\} \times \exp \left\{ -i \sum_{j=2}^{N_2} \sum_{k \in \Omega / 2} \frac{2\beta}{V} (\det \tilde{\nu}(k))^\frac{1}{2} \left[ x_j(k) \cos(kR_{2j}) + y_j(k) \sin(kR_{2j}) \right] \right\} \]

\[ = \left\{ \int \frac{dR_1}{V} \exp \left\{ -i \sum_{k \in \Omega / 2} \frac{2\beta}{V} (\det \tilde{\nu}(k))^\frac{1}{2} \left[ x_1(k) \cos(kR_{11}) + y_1(k) \sin(kR_{11}) \right] \right\} \right\}^{N_1} \times \left\{ \int \frac{dR_2}{V} \exp \left\{ -i \sum_{k \in \Omega / 2} \frac{2\beta}{V} (\det \tilde{\nu}(k))^\frac{1}{2} \left[ x_2(k) \cos(kR_{22}) + y_2(k) \sin(kR_{22}) \right] \right\} \right\}^{N_2} \]

\[ = (F_{1})^{N_1} (F_{2})^{N_2}, \]

where

\[ F_{\alpha} = \int \frac{dR_{\alpha}}{V} \exp \left\{ -i \sum_{k \in \Omega / 2} \frac{2\beta}{V} (\det \tilde{\nu}(k))^\frac{1}{2} \left[ x_{\alpha}(k) \cos(kR_{\alpha\alpha}) + y_{\alpha}(k) \sin(kR_{\alpha\alpha}) \right] \right\}. \]

The values \( F_{\alpha} \) depend on the corresponding auxiliary variables \( x_{\alpha}(k) \) and \( y_{\alpha}(k) \), as well as on the Fourier transform of the interatomic potentials \( \tilde{\nu}_{\alpha\gamma}(k) \), the volume \( V \) and the inverse temperature \( \beta \).

We single out the principal terms in the quantities \( (F_{\alpha})^{N_{\alpha}} \) in the thermodynamic limit \( N_{\alpha} \to \infty \), \( V \to \infty \), \( \frac{N_{\alpha}}{V} = n_{\alpha} = \text{const} \).

We note that the functions \( F_{\alpha} \) satisfy the inequality

\[ |F_{\alpha}| \leq 1, \]

since the modulus of the exponential in the integrand of (19) is equal to one.

Function

\[ \Phi_{\alpha}(R_{\alpha}) = \sum_{k \in \Omega / 2} \left[ (\det \tilde{\nu}(k))^\frac{1}{2} \left[ x_{\alpha}(k) \cos(kR_{\alpha\alpha}) + y_{\alpha}(k) \sin(kR_{\alpha\alpha}) \right] \right], \]

contained in the exponent of formula (19), by virtue of the Riemann-Lebesgue lemma [21], tends to zero at \( |R_{\alpha}| \to \infty \). Therefore, outside of some finite domain \( V_{0} \) the exponent in the integrand of the formula (19) tends to one. Hence it follows

\[ \lim_{V \to \infty} F_{\alpha} = 1. \]

Thus, the value \( (F_{\alpha})^{N_{\alpha}} \) represents indeterminacy of the form \( 1^{\infty} \).

5. Evaluation of one-particle integrals (19)

To calculate the integral (19) we use the Weyl theorem [22].

Theorem. Let us assume that

1. \( \psi_{\nu}(x) = a_{\nu} + b_{\nu}x \quad (\nu = 1, 2, \ldots, M) \), where the numbers \( a_{\nu} \) and \( b_{\nu} \) is the set of constants;

2. numbers \( b_{\nu} \) are rationally independent;

\[ \psi_{\nu}(x) = a_{\nu} + b_{\nu}x \quad (\nu = 1, 2, \ldots, M) \]
3. The function \( f(\psi_1, \psi_2, \ldots, \psi_M) \) is periodic in all variables \( \psi \) with the period 1 and is integrable in the cube \( 0 \leq \psi \leq 1 \).

Then the following equality holds

\[
\lim_{x \to 0} \frac{1}{x} \int f(\psi_1(x), \psi_2(x), \ldots, \psi_M(x)) \, dx = \int_{y = 0}^{1} \cdots \int_{y = 0}^{1} f(\psi_1, \psi_2, \ldots, \psi_M) \prod_{\nu = 1}^{M} d\psi_{\nu}.
\]

(23)

This theorem has an evident generalization to the case of vectorial variable \( x \).

We carry out the following transformations in the integral (19)

\[
\frac{2\beta V}{V} \left( \det (k) \right) \frac{1}{(\pi)} \left[ x_\alpha(k) \cos(kR_\alpha) + y_\alpha(k) \sin(kR_\alpha) \right]
\]

(24)

For \( V \to \infty \), the integral (19) after applying the Weyl theorem is transformed to the following form

\[
F_\alpha = \prod_{k \in \Omega} \int \frac{2\beta}{V} \left[ x_\alpha(k) + y_\alpha(k) \right] \left( \det (k) \right)^{1/2} \sin\left[ 2\pi \psi_\alpha(k) \right] \, d\psi_\alpha(k)
\]

(25)

where \( J_0(x) \) is the modified Bessel function of zero order. Hence we obtain

\[
F_{\alpha}^{\nu} = \prod_{k \in \Omega} \int J_0 \left( \frac{2\beta}{V} \left[ x_\alpha(k) + y_\alpha(k) \right] \left( \det (k) \right)^{1/2} \right)
\]

(26)

The largest value of the Bessel function \( J_0(x) \) is equal to one and this value is achieved at a single point \( x = 0 \). Using the asymptotics of the Bessel function in the neighborhood of this point, we obtain a value \( F_{\alpha}^{\nu} \) in the thermodynamic limit

\[
F_{\alpha}^{\nu} = \exp \left[ -\frac{\beta n_\alpha}{2} \sum_{k \in \Omega} \left( \det (k) \right)^{1/2} \left( x_\alpha^2(k) + y_\alpha^2(k) \right) \right]
\]

(27)

Now we turn to the calculation of the partition function and Helmholtz free energy of the solution.

6. The partition function and Helmholtz free energy of the solution

Substituting formulas (27) and (17) in (13), we obtain the following expression for the configuration integral

\[
Z_{\text{conf}} = A \prod_{k \in \Omega} \left( \frac{1}{1 + \beta n_{\tilde{V}_1}(k) + \beta n_{\tilde{V}_2}(k) + \beta^2 n_{n_1} \det (k)} \right)
\]

(28)

This implies the expression for the partition function

\[
Z = A \prod_{k \in \Omega} \left( \frac{1}{1 + \beta n_{\tilde{V}_1}(k) + \beta n_{\tilde{V}_2}(k) + \beta^2 n_{n_1} \det (k)} \right)
\]

(29)

where \( \lambda_\alpha \) is the de Broglie thermal wavelength of the \( \alpha \)-th component, \( N = N_1 + N_2 \); \( c_1 = \frac{N_1}{N} \);

\[
c_2 = \frac{N_2}{N} = 1 - c_1.
\]
The Helmholtz free energy in the thermodynamic limit $N \to \infty, V \to \infty, N/V = n = \text{const}$ has the following form
\[
F = -T \ln Z = -\frac{N}{2} (c_1 v_{11}(0) + c_2 v_{22}(0)) + \frac{N^2}{2V} \left[ c_1^2 \tilde{v}_{11}(0) + 2c_1 c_2 \tilde{v}_{12}(0) + c_2^2 \tilde{v}_{22}(0) \right] + TV \left[ c_1 \ln c_1 + c_2 \ln c_2 \right] + TN \ln \left[ n (\lambda_1)^{v_{11}} (\lambda_2)^{v_{22}} \right] \quad (30)
\]
\[
+ \frac{TV}{2} \int_{k \in \Omega} \frac{dk}{(2\pi)^3} \ln \left[ 1 + n\beta (c_1 \tilde{v}_{11}(k) + c_2 \tilde{v}_{22}(k)) + c_1 c_2 (n\beta)^2 \det \tilde{v}(k) \right] \]

The appearance of the factor $1/2$ in the last line of this formula is due to the replacement of $\Omega / 2$ of the product in (29) by $k \in \Omega$ in the integral term of formula (30).

7. Isolation of the singular part of the interatomic potentials at $r = 0$

The expression (30) for the Helmholtz free energy contains the values $v_{11}(0), v_{22}(0)$ — the values of interatomic potentials $v_{11}(r)$ and $v_{22}(r)$ at the origin of coordinates $r = 0$. As is known, actual interatomic potentials have a singularity at this point and therefore formula (30) should be improved.

We note that the potentials at the origin $v_{aa}(0)$ are related to the Fourier transforms of the potentials by the relation
\[
v(0) = \int_{k \in \Omega} \frac{dk}{(2\pi)^3} \tilde{v}(k). \quad (31)
\]

The singularity of the interatomic potentials at a point $r = 0$ means the divergence of this integral at $k = |k| \to \infty$, i.e. insufficiently rapid decrease of the function $\tilde{v}(k)$ at $k = |k| \to \infty$. By virtue of the fact that at $k \to \infty$
\[
\ln \left[ 1 + n\beta (c_1 \tilde{v}_{11}(k) + c_2 \tilde{v}_{22}(k)) + c_1 c_2 (n\beta)^2 \det \tilde{v}(k) \right] \equiv n\beta (c_1 \tilde{v}_{11}(k) + c_2 \tilde{v}_{22}(k)), \quad (32)
\]
then the singularity of the interatomic potential $v(r)$ leads to the divergence of the integral over $k$ in the formula (30). However, this divergence is completely compensated by the term
\[
-\frac{N}{2} (c_1 v_{11}(0) + c_2 v_{22}(0)) = -\frac{TV}{2} \int_{k \in \Omega} \frac{dk}{(2\pi)^3} n\beta (c_1 \tilde{v}_{11}(k) + c_2 \tilde{v}_{22}(k)) \quad (33)
\]
in this formula. Combining this expression with the integral term in (30), we obtain
\[
F = TN \left[ c_1 \ln c_1 + c_2 \ln c_2 \right] + TN \ln \left[ n (\lambda_1)^{v_{11}} (\lambda_2)^{v_{22}} \right]
\]
\[
+ \frac{N^2}{2V} \left[ c_1^2 \tilde{v}_{11}(0) + 2c_1 c_2 \tilde{v}_{12}(0) + c_2^2 \tilde{v}_{22}(0) \right] + \frac{TV}{2} \int_{k \in \Omega} \frac{dk}{(2\pi)^3} \ln \left[ 1 + n\beta (c_1 \tilde{v}_{11}(k) + c_2 \tilde{v}_{22}(k)) + c_1 c_2 (n\beta)^2 \det \tilde{v}(k) \right] \]
\[
- n\beta (c_1 \tilde{v}_{11}(k) + c_2 \tilde{v}_{22}(k)). \quad (34)
\]

This expression for the Helmholtz free energy is applicable not only for regular interatomic potentials, but also for singular potentials. In other words, the singularity of the interatomic potentials in the neighborhood of the origin of coordinates does not prevent the use of the formula (34) for calculating thermodynamic functions. This agrees with the general result of Zagrebnov and Pastur [23] that thermodynamic potentials have the property of asymptotic independence from the extension of the potential in the singularity neighborhood.

Direct use of formulas (34) and (30) for the study of the thermodynamic functions of solutions is significantly complicated by the presence of a logarithmic function in the integrand. Therefore, it is advisable to exclude the logarithmic function without loss of accuracy and generality. In the case when all the interatomic potentials are central, i.e.
the Fourier transformants of all potentials $\tilde{v}_{\alpha\gamma}(k)$ depend only on $k = |k|$. We first consider the integral term in expression (30). It has the following structure

$$W = \int_{k \in \Omega} \frac{dk}{(2\pi)^3} \ln[1 + \tilde{v}(k)],$$

where

$$\tilde{v}(k) = n\beta[c_1\tilde{v}_{11}(k) + c_2\tilde{v}_{22}(k)] + c_1c_2(n\beta)^2 \det \tilde{v}(k).$$

Passing to spherical coordinates in the $k$–space and integrating by parts, we obtain

$$\tilde{W} = \frac{1}{2\pi^2} \left\{ \ln[1 + \tilde{v}(k)] \int_0^\infty \frac{k^3}{3} - \frac{1}{3} \int_0^\infty \frac{k^3}{1 + \tilde{v}(k)} dk \right\}. \tag{38}$$

Similarly, we transform the integral on the right-hand side of the formula (33):

$$-\int_{k \in \Omega} \frac{dk}{(2\pi)^3} [c_1\tilde{v}_{11}(k) + c_2\tilde{v}_{22}(k)]$$

$$= -\frac{1}{2\pi^2} \left\{ c_1\tilde{v}_{11}(k) + c_2\tilde{v}_{22}(k) \int_0^\infty \frac{k^3}{3} - \frac{1}{3} \int_0^\infty \frac{k^3}{1 + \tilde{v}(k)} dk \right\}. \tag{39}$$

It should be noted, that the terms outside the integrals in expressions (38) and (39) become zero for non-singular potentials, and are mutually compensated for singular potentials because of the relation (32). Therefore, adding the right-hand sides of formulas (38) and (39) and substituting the result into formula (34), we obtain the final expression for the Helmholtz free energy

$$F = TN[c_1 \ln c_1 + c_2 \ln c_2] + TN \ln[n(\lambda_1)_{c_1}(\lambda_2)_{c_2}]$$

$$+ \frac{N^2}{2V} [c_1^2\tilde{v}_{11}(0) + 2c_1c_2\tilde{v}_{22}(0) + c_2^2\tilde{v}_{22}(0)] \tag{40}$$

$$- \frac{TV}{12\pi^2} \int_0^\infty \frac{k^3}{1 + \tilde{v}(k)} [\tilde{v}(k) - n\beta[c_1\tilde{v}_{11}(k) + c_2\tilde{v}_{22}(k)]] dk,$$

where $\tilde{w}(k)$ is defined by the formula (37).

8. Conclusion

According to the formula (34), the Helmholtz free energy is represented as the sum of three contributions. The first contribution is the free energy of an ideal gas. The second contribution is the configurational energy in the Gorsky-Bragg-Williams approximation [24, 25, 26, 27, 28]. The third contribution is the integral term, which we shall call the ergodic contribution.

Let us discuss the dependence of each of these contributions on the temperature $T$ and the composition of the solution $x$ ($x = c_1, c_2 = 1 - x$).

1. The free energy of an ideal gas (the first line in (34)) is proportional to temperature and is a concave function $x$ on the whole interval $0 \leq x \leq 1$. 

2. The configuration part of the free energy in the Gorsky-Bragg-Williams approximation does not depend on temperature. The conditions of noncatastrophicity of the potentials (5) and (4) imply that values \( \tilde{v}_{12}(k) \) at all values \( k \) (including \( k = 0 \)) are related by inequalities

\[
\left| \tilde{v}_{12}(k) \right| \leq \sqrt{\tilde{v}_{11}(k) \tilde{v}_{22}(k)} = \frac{\tilde{v}_{11}(k) + \tilde{v}_{22}(k)}{2}.
\]

Under these restrictions, this contribution is also a concave function of the composition \( x \).

3. The ergodic contribution to the free energy of the solution is defined by the integral term in the formula (34). The integrand of this term has the following form

\[
\phi(\beta, x, k) = \frac{\ln\left[1 + n\beta(x\tilde{v}_{11}(k) + (1-x)\tilde{v}_{22}(k)) + x(1-x)(n\beta)^2 \det \tilde{v}(k)\right]}{\beta}.
\]

The second derivative of this function with respect to the variable \( x \) is everywhere negative, therefore, in contrast to the two previous contributions, both the function itself and the ergodic contribution to Helmholtz free energy are a convex function of the composition \( x \). Thus, without taking into account the ergodic contribution to the free energy, the phase separation of the solution into phases is impossible. A phase transition in a binary solution occurs only if there is such an interval of compositions \([a; b]\) \((0 < a < b < 1)\), in which the Helmholtz free energy (40) is a convex function of the composition. The number of critical points in a binary solution is equal to the number of positive solutions of the equation \( \frac{\partial^2 F(x, T)}{\partial x^2} = 0 \) with respect to temperature \( T \).

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References

[1] Baxter R J 1984 Exactly Solved Models in Statistical Mechanics (London: Academic Press)
[2] Guggenheim E A 1952 Mixtures. The theory of the equilibrium properties of some simple classes of mixtures, solutions and alloys (Oxford: Clarendon Press)
[3] Boublk T, Nezbeda I and Hlavatý K 1980 Statistical Thermodynamics of Simple Liquids and Their Mixtures (Amsterdam: Elsevier)
[4] Prigogine I R 1957 The Molecular Theory of Solutions (Amsterdam: North-Holland)
[5] Smirnova N A, Victorov A V 2000 Quasiliattice Equations of State for Molecular Fluids Equations of State for Fluids and Fluid Mixtures, ed J V Sengers, R F Kayser, et al (Amsterdam: Elsevier) chapter 7 pp 255–288
[6] Zubarev D N 1954 Evaluation of configuration integrals for a system of particles with Coulomb interaction Doklady 95 757–60
[7] Zakharov A Yu 1990 Exact Calculation Method of Partition Function for One-Component Classical Systems with Two-Body Interactions Phys. Lett. A 147 442–4
[8] Zakharov A Yu and Loktionov I K 1999 Classical statistics of one-component systems with model potentials Theor. and Math. Phys. 119 532–9
[9] Zakharov A Yu 2000 Functional integration and method of factorization in classical statistical mechanics Russ. J. Phys. Chem. 74 40–5
[10] Loktionov I K 2000 Determination of the critical parameters of a classical one-component system with model interaction potential High Temperature 38 494–6
[11] Loktionov I K 2015 Prediction of equilibrium thermodynamic properties of simple liquids in the model with four-parametric oscillating interaction potential Technical Physics 85 317–26
[12] Ruelle D 1963 Classical Statistical Mechanics of a System of Particles Helv. Phys. Acta 36 183–97
[13] Fisher M E 1964 The Free Energy of a Macroscopic System Arch. Rat. Mech. Anal. 17 377–410
[14] Dobrushin R L 1964 Investigation of Conditions for the Asymptotic Existence of the Configuration Integral of Gibbs’ Distribution Theory Probab. Appl. 9 566—81
[15] Ruelle D 1969 Statistical Mechanics. Rigorous results (New York: Benjamin)
[16] Baus M and Tejero C F 2008 Equilibrium Statistical Mechanics. Phases of Matter and Phase Transitions (New York: Springer)
[17] Pines D and Bohm D 1952 A Collective Description of Electron Interactions: II. Collective vs Individual Particle Aspects of the Interactions Phys. Rev. 85 338–53
[18] Percus J K and Yevick G J 1958 Analysis of Classical Statistical Mechanics by Means of Collective Coordinates Phys. Rev. 110 1–13
[19] Edwards S F 1959 The statistical thermodynamics of a gas with long and short-range forces. Phil. Mag. 4 1171–82
[20] Edwards S F and Schwartz M 2003 Statistical Mechanics in Collective Coordinates J. Stat. Physics. 110 497–502
[21] Whittaker E T and Watson G N 1927 A course of modern analysis (Cambridge: Cambridge University Press) p 172
[22] Weyl H 1916 Über die Gleichverteilung von Zahlen mod. Eins Math. Annalen 77 313–52
[23] Zagrebnov V A and Pastur L A 1978 Singular interaction potentials in classical statistical mechanics Theor. Math. Phys. 36 784–97
[24] Gorsky W 1928 Röntgenographische Untersuchung von Umwandlungen in der Legierung Cu Au Z. Physik 50 64—81
[25] Bragg W L and Williams E J 1934 The Effect of Thermal Agitation on Atomic Arrangement in Alloys Proc. R. Soc. Lond. A 145 699–730
[26] Bragg W L and Williams E J 1935 The Effect of Thermal Agitation on Atomic Arrangement in Alloys—II. Proc. R. Soc. Lond. A. 151 540–66
[27] Williams E J 1935 The Effect of Thermal Agitation on Atomic Arrangement in Alloys—III. Proc. R. Soc. Lond. A. 152 231–52
[28] Püschl W, Numakura H and Pfeiler W (2007) Point Defects, Atom Jumps, and Diffusion Alloy Physics: A Comprehensive Reference, ed. W Pfeiler (Weinheim: Wiley-VCH) chapter 5 pp 173–280