

STATISTICAL-MECHANICAL THEORY OF MIXTURES IN THE ONE-CHAIN APPROXIMATION. II. MULTICOMPONENT SYSTEMS

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The free energy and radial distribution functions are calculated for a macroscopic system composed of an arbitrary number of different species in the OC approximation, consisting in retaining the simplest infinite subset of terms of the virial expansion.

1. Introduction

The generalization of the Ursell-Mayer virial expansion method [1, 2] to many-component systems has been given long ago (*cf.* [1, 3, 4] and references quoted there). Among others, the method of generation of subsequent terms of the density expansion made it possible to generalize the Percus-Yevick (PY) and hypernetted chain (HNC) approximate integral equations for the radial distribution function to the many-component systems [5]. However, as far as the authors know, no practical calculations of any property of a mixture have so far been performed by means of the PY or HNC methods, probably because of their fairly complicated form.

We have recently proposed so-called one-chain (OC) approximation [6], which providing qualitatively satisfactory results for one-component systems, has a much simpler form than the PY or HNC approximations (OC approximation may be considered as the approximate solution of the PY and HNC integral equations).

In the first part of this work [7] (hereafter called to as I) binary mixture have been considered in the OC approximation. This part contains a further generalization of the method presented there to the case of a system containing an arbitrary number of different species.

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2. Free energy

We begin with the calculation of the free energy F of the system. The notation used here is a simple generalization of the notation used in I.

Consider the system composed of N_i particles of the species i ($i = 1, \dots, n, \sum_i N_i = N$) contained in the volume Ω , and maintained at temperature T . The particles interact with each other through the $n(n+1)/2$ pair potentials $V_{ij}(r)$ ($i, j = 1, \dots, n$ denote the species and $V_{ij} = V_{ji}$), which are assumed to be dependent only on the relative distance r between a given pair of particles. It is also assumed that quantum effects are negligible, and the thermodynamical limit

$$N = \sum_i N_i \rightarrow \infty, \quad \Omega \rightarrow \infty, \quad \rho = \frac{1}{v} = \frac{N}{\Omega} = \text{finite} \quad (1)$$

is considered. We introduce also the notion of mole (or number) fractions and specific volume for particle i

$$x_i = N_i/N, \quad v_i = \frac{\Omega}{N_i} = \frac{v}{x_i}, \quad (2)$$

$$\sum_i x_i = 1, \quad \sum_i \frac{1}{v_i} = \frac{1}{v} = \rho \quad (3)$$

N , ρ , and v denote the overall number of particles, overall number density and overall specific volume of the system, respectively.

The virial expansion for F is easily obtained from the usually used expansion for the pressure (cf. [1, 2, 7])

$$F = F_{id} - kT \sum_m C_m \rho^{m-1} \quad (4)$$

where F_{id} is the ideal gas free energy per particle. The virial coefficients C_m may be expressed through the biconnected graphs. The rules of the construction of these graphs are given in I (the only difference being that now the labels denoting the species run from 1 to n , i.e., the graphs are constructed from multicoloured points).

The OC approximation consists in retaining for every C_m only one type of graphs, such that all the points of the OC graphs are connected into one polygon, i.e., every internal point is connected with two other internal points only. Of course, all possible labellings of such a graph must be taken into account.

Introduce the Fourier transforms γ_{ij} of the Mayer functions $f_{ij}(r)$:

$$f_{ij}(r) = \exp \left[-\frac{1}{kT} V_{ij}(r) \right] - 1, \quad \gamma_{ij}(q) = (2\pi^3)^{-1} \int dq e^{-iq \cdot r} f_{ij}(r). \quad (5)$$

Consider first the system containing only particles 1. We separate the class of OC graphs into two parts (cf. Fig. 1). The two first graphs in A_1 are added and subtracted to get the closed formulae in the summations.

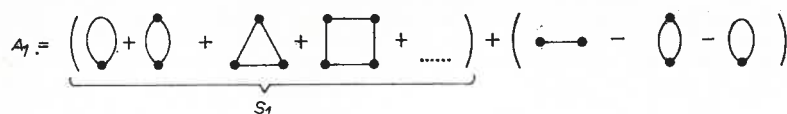


Fig. 1. OC graphs for free energy of one-component system

Now we shall concern ourselves only with the first part of the sum from Fig. 1. From the simple properties of the Fourier transforms one easily obtains the following expression for the sum of this class of graphs:

$$\begin{aligned}
 A_1 &= \frac{1}{4\pi} \int_0^\infty dq q^2 \sum_{n=1}^\infty \left(\frac{\gamma_{11}}{v_1} \right)^2 \frac{1}{2n} = \frac{1}{4\pi} \int_0^\infty dq q^2 S_1 = \\
 &= \frac{1}{4\pi} \int_0^\infty dq q^2 \frac{1}{2} \ln \left| \frac{v_1 - \gamma_{11}}{v_1} \right|. \quad (6)
 \end{aligned}$$

In order to simplify the notation we shall omit the integral before the sum and concentrate on the algebra of the γ_{ij} functions.



Fig. 2. Construction of the "double line" from particles of species n in the case of generalization from $n-1$ to n -component systems

The next step is to construct the class of two-component graphs A_2 from the class presented above. We replace each line of the one-component graph from A_1 by the "double line" (cf. Fig. 2).

$$\gamma_{11} \rightarrow \gamma_{11} + \frac{\gamma_{12}^2}{v_2 - \gamma_{22}} \quad (7)$$

The summation of graphs constructed from such lines leads to the formula similar to (6) in which we perform the replacement (7).

$$\begin{aligned}
 S_1 &\rightarrow \frac{1}{2} \ln \left| \frac{1}{v_1(v_2 - \gamma_{22})} [(v_1 - \gamma_{11})(v_2 - \gamma_{22}) - \gamma_{12}^2] \right| = \\
 &= \frac{1}{2} \ln \left| \frac{M^{(2)}}{(v_2 - \gamma_{22})v_1} \right|, \quad (8)
 \end{aligned}$$

$$M^{(2)} = \det \begin{pmatrix} v_1 - \gamma_{11} & -\gamma_{12} \\ -\gamma_{12} & v_2 - \gamma_{22} \end{pmatrix}. \quad (9)$$

To get the whole class of the two-component graphs corresponding to A_2 we must add to the class obtained above the class of the graphs constructed only from particles 2 (such graphs are not contained in the class of the "double line" graphs).

The sum of such graphs is (cf. (6))

$$\frac{1}{2} \ln \left| \frac{v_2 - \gamma_{22}}{v_2} \right|.$$

Therefore the sum of the whole class of graphs is

$$S_2 = \frac{1}{2} \ln \left| \frac{M^{(2)}}{v_1 v_2} \right|. \quad (10)$$

Further generalization is straightforward. To get the class A_3 of the three-component graphs we replace every line γ_{11} , γ_{12} , and γ_{22} in the two-component graphs by its "double line"

$$\gamma_{ij} \rightarrow \gamma_{ij} + \frac{\gamma_{i3}\gamma_{j3}}{v_3 - \gamma_{33}}, \quad (i, j = 1, 2).$$

The sum of such graphs is obtained by introducing these quantities instead of γ_{ij} in the formula (10).

Simple algebra leads to the following expression:

$$S_2 \rightarrow \frac{1}{2} \ln \left| \frac{M^{(3)}}{v_1 v_2 (v_3 - \gamma_{33})} \right|, \quad (11)$$

where

$$M^{(3)} = \det \begin{pmatrix} v_1 - \gamma_{11} & -\gamma_{12} & -\gamma_{13} \\ -\gamma_{12} & v_2 - \gamma_{22} & -\gamma_{23} \\ -\gamma_{13} & -\gamma_{23} & v_3 - \gamma_{33} \end{pmatrix}.$$

The whole class A_3 of the three-component graphs must contain the one-component graphs constructed of particles 3:

$$\frac{1}{2} \ln \left| \frac{v_3 - \gamma_{33}}{v_3} \right|,$$

which gives

$$S_3 = \frac{1}{2} \ln \left| \frac{M^{(3)}}{v_1 v_2 v_3} \right|$$

for the sum of the whole class of the three-component graphs. An analogous discussion can be continued for the n -component system, leading eventually to the substitution

$$S_1 \rightarrow S_n = \frac{1}{2} \ln \left| \frac{M^{(n)}}{v_1 v_2 \dots v_n} \right|. \quad (12)$$

Introduce the matrix notation

$$\begin{aligned}(\Gamma)_{ij} &= \gamma_{ij}, \\ (\mathcal{V})_{ij} &= v_i \delta_{ij},\end{aligned}\tag{13}$$

which enables us to rewrite formula (4) in the more symmetric way:

$$S_n = \frac{1}{2} \ln \det [(\mathcal{V} - \Gamma)\mathcal{V}^{-1}].\tag{14}$$

To get the expression for the free energy of the n -component system we must return to the prescriptions for the free energy graphs. In the construction presented above we added two graphs (*cf.* Fig. 1) which do not occur in the original expansion. We must therefore subtract these graphs from the results obtained above. We also have not taken into account the graphs from the second virial coefficient (two-point, one line graphs).

The complete expression for the free energy of the n -component system is therefore

$$\frac{F - F_{id}}{kT} = vB_2 + \frac{v}{4\pi^2} \int_0^\infty dq q^2 \{ \ln | \det \{ (\mathcal{V} - \Gamma)\mathcal{V}^{-1} \} | - H(q) - G(q) \},\tag{15}$$

where:

$$\begin{aligned}B_2 &= \frac{1}{2} \sum_{i,j=1}^n \gamma_{ij}(0)/v_i v_j, \\ H(q) &= -\frac{1}{2} \sum_{i,j=1}^n \gamma_{ij}^2(q)/v_i v_j, \\ G(q) &= - \sum_{i=1}^n \gamma_{ii}(q)/v_i.\end{aligned}$$

3. Final remarks

The formula for the free energy of the n -component system can be used to calculate all other thermodynamical functions of the considered system.

Another interesting information about the n -component system can be obtained from the radial distribution function. The generalization of the methods used in I for calculation of the rdfs of the two-component system for the case of the system composed of arbitrary number of species is also simple. We shall not present here the discussion, but only give the final formulae;

$$\begin{aligned}g_{ij}(r) &= \exp [-V_{ij}(r)/kT + \Psi_{ij}(r)] \\ \Psi_{ij}(r) &= \frac{1}{2\pi^3} \int dr e^{-iq \cdot r} \bar{\Psi}_{ij}(q).\end{aligned}$$

The elements $\overline{\Psi}_{ij}$ form the symmetrical matrix Ψ , which in the OC approximation can be expressed in the notation used in preceding Section as;

$$\Psi = V(V - \Gamma)^{-1}V - (V + \Gamma). \quad (16)$$

In the above $(V - \Gamma)^{-1}$ is the matrix inverse to $(V - \Gamma)$. The formulae (16) as well as all other formulae of this paper require the knowledge of $n(n+1)/2$ potentials V_{ij} of the intermolecular interactions. The formulae for rdf are rather simple. Similar formulae for $n(n+1)/2$ rdfs in the PY or HNC approximations can be obtained only by solving $n(n+1)/2$ integral equations.

Some numerical results will be presented separately.

REFERENCES

- [1] J. O. Hirschfelder, Ch. F. Curtiss, R. B. Bird, *Molecular Theory of Gases and Liquids*, J. Wiley and Sons, Inc., New York 1954.
- [2] G. E. Uhlenbeck, C. W. Ford, in: *Studies in Statistical Mechanics*, edited by J. de Boer and G. E. Uhlenbeck, Vol. I, North-Holland Publ. Co., Amsterdam 1962, Part B.
- [3] E. Meeron, *J. Chem. Phys.*, **28**, 630 (1958).
- [4] H. B. Levine, *Phys. Fluids*, **3**, 225 (1960).
- [5] K. Hiroike, *Progr. Theor. Phys.*, **24**, 317 (1960); T. Morita, K. Hiroike, *Progr. Theor. Phys.*, **25**, 537 (1961); K. Hiroike, Y. Fukui, *Progr. Theor. Phys.*, **43**, 660 (1970); K. Hiroike, T. Morita, *J. Chem. Phys.*, **52**, 5489 (1970).
- [6] A. Fuliński, *Acta Phys. Polon.*, **A37**, 177, 185 (1970); *Phys. Letters*, **31A**, 176 (1970); A. Fuliński, M. Jurkiewicz, *Phys. Letters*, **32A**, 126 (1970); *Acta Phys. Polon.*, **A39**, 167 (1971); A. Fuliński, *Acta Phys. Polon.*, **A39**, 181 (1971).
- [7] A. Fuliński, M. Jurkiewicz, *Acta Phys. Polon.*, **A40**, 487 (1971).