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TRUNCATION PROCEDURE FOR HIGH ORDER REDUCED DISTRIBUTION FUNCTIONS

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The concept of the average force potentials is used to develop the truncation procedure for an arbitrary equation of the chain. The closed system of integral equations for the average force potentials is formulated. In the case when the truncation approximation involves the four-particle distribution function the expression for the configurational integral is derived. The internal energy and the pressure calculated in terms of the binary distribution function are thermodynamically compatible.

1. Introduction

In a recent series of papers¹) (see ref. 2 for a review) the method of conditional distributions due to Rott³) was used for the description of condensed states of matter. In the main first approximation of the method all kinds of first order phase transitions (solid–liquid, solid–gas and liquid–gas) in molecular systems were obtained and the existence of the triple point followed from the calculations in a natural way. The second approximation did not make a marked difference to the properties of the solid phase but considerably improved the values of the parameters of the liquid state⁴). This led in turn to a reduction of the distance between melting and crystallization lines on the $(T-V)$ phase diagram, increasing pressure of the solid–liquid phase transition, and decreasing of the triple point temperature. That is to say it led to an even better coincidence of the theoretical calculations with experimental data.

In the method of conditional distributions the whole volume V of an N-particle system is divided into N equal molecular cells. The probability

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density of distribution of a selected group of particles is considered under some restrictions on the distribution of the other particles[2,3]). In the first approximation all the states of the system where each molecular cell is occupied by a particle are taken into account. In the following approximations of the method, as in the multi-occupied cell theory proposed by Janssens and Prigogine[5]), two-particle, three-particle, etc. occupation of a cell are considered.

In each approximation reduced distribution functions can be introduced. They obey infinite chains of integro-differential equations. The problem of truncation of these chains was specifically solved within the framework of the method[1,2]). The initial chains of integro-differential equations were initially transformed to the form of integral equations with respect to the so-called average force potentials. Then truncation at the lowest order equations preserved binary correlations. It has been shown[1c]) that, when calculated in terms of the binary distribution function, the calorimetric and thermal equations of state are thermodynamically compatible. Some attempts have been made to generalize the truncation procedure to take into account correlations of an arbitrary order[2,6]). In the present paper we refine the truncation procedure and apply it to close the chain of integral equations at an arbitrary level.

The necessary definitions and the chains of integro-differential and integral equations are introduced in the next section. Then the closed system of an iterative type for the average force potentials is obtained. The particular case when truncated equations take account of three-particle correlations is considered in section 4. The expression for the configurational integral of the system is also obtained in section 4. In the last section we discuss the problem of long range correlations.

2. The concept of average force potentials

We shall consider the first approximation of the method where a simplified system of notations for distribution functions can be used and adopt here the usual notations of the BBGKY method.

The n-particle conditional distribution function $F_n(\boldsymbol{q}^{i_1}, \boldsymbol{q}^{i_2}, \ldots, \boldsymbol{q}^{i_n})$ defines the probability density of distribution of n particles in n cells which are a part of an N-particle system of the volume V. It is equal to an integral of the configurational part of the gibbsian distribution over the other cells under the condition that each cell is occupied by one, and only one, particle[2,3]):

$$F_n(\boldsymbol{q}^{i_1}, \boldsymbol{q}^{i_2}, \ldots, \boldsymbol{q}^{i_n}) = N! \int_{v_{i_{n+1}}} \mathrm{d}\boldsymbol{q}^{i_{n+1}} \ldots \int_{v_{i_N}} \exp(-\beta U_N)\, \mathrm{d}\boldsymbol{q}^{i_N},$$

$$U_N = \sum_{i_k < i_j}^{N} \Phi_{i_k i_j}; \qquad \beta = (kT)^{-1}; \qquad v = \frac{V}{N}; \qquad q^{i_k} \in v_{i_k}, \tag{1}$$

where Φ is a pairwise intermolecular potential, T is the absolute temperature and k is the Boltzmann constant. The factor $N!$ appears because of permutations of particles.

According to definition (1) the configurational integral of the system is defined by the one-particle distribution function:

$$Q_N = \int_{v_{i_1}} F_1(\boldsymbol{q}^{i_1})\,\mathrm{d}\boldsymbol{q}^{i_1}, \tag{2}$$

and the recurrence relation between two consecutive functions has the form

$$F_n(\boldsymbol{q}^{i_1}, \ldots, \boldsymbol{q}^{i_n}) = \int_{v_{i_{n+1}}} F_{n+1}(\boldsymbol{q}^{i_1}, \ldots, \boldsymbol{q}^{i_{n+1}})\,\mathrm{d}\boldsymbol{q}^{i_{n+1}}. \tag{3}$$

Now we introduce $3n$-dimensional space

$$\{n\} \equiv \boldsymbol{q}^{\{n\}} \equiv \{R\boldsymbol{q}^{i_1}, \boldsymbol{q}^{i_2}, \ldots, \boldsymbol{q}^{i_n}\}, \tag{4}$$

where the operator R puts the elements of row $(i_1, i_2, \ldots, i_n)$ in order of increasing numbers. The first derivative in such a space will be defined by

$$\frac{\partial}{\partial \boldsymbol{q}^{\{n\}}} = \sum_{k=1}^{n} \frac{\partial}{\partial \boldsymbol{q}^{i_k}}. \tag{5}$$

The operator (5) applied to the definition (1) gives rise to the nth equation of the initial chain

$$\frac{\partial F_n(\{n\})}{\partial \boldsymbol{q}^{\{n\}}} + \beta \frac{\partial U_n}{\partial \boldsymbol{q}^{\{n\}}} F_n(\{n\}) + \beta \sum_{l=n+1}^{N} \int_{v_{i_l}} \frac{\partial}{\partial \boldsymbol{q}^{\{n\}}} \left(\sum_{k=1}^{n} \Phi_{i_k i_l} \right) F_{n+1}(\{n\}, \boldsymbol{q}^{i_l})\,\mathrm{d}\boldsymbol{q}^{i_l} = 0,$$

$$U_n = \sum_{i_k < i_j}^{n} \Phi_{i_k i_j}. \tag{6}$$

The next important step is a transformation of the initial chain of integro-differential equations with respect to distribution functions to a new one containing potentials of average forces. To do this we first divide eq. (6) by the distribution function $F_n(\{n\})$. The result can be written as

$$\frac{\partial}{\partial \boldsymbol{q}^{\{n\}}} \left[\ln F_n(\{n\}) + \beta U_n + \beta \sum_{l=n+1}^{N} \varphi_{i_l}(\{n\}) \right] = 0, \tag{7}$$

where the potential of average forces exerted by a particle distributed within the cell v_{i_l} on the system of particles fixed in the cells $v_{i_1}, v_{i_2}, \ldots, v_{i_n}$ is introduced by

$$\frac{\partial}{\partial \boldsymbol{q}^{\{n\}}} \varphi_{i_l}(\{n\}) = \int_{v_{i_l}} \frac{\partial}{\partial \boldsymbol{q}^{\{n\}}} \left(\sum_{k=1}^{n} \Phi_{i_k i_l} \right) F_{n+1}(\boldsymbol{q}^{i_l}/\{n\})\,\mathrm{d}\boldsymbol{q}^{i_l}. \tag{8}$$

The twice conditional distribution function $F_{n+1}(\boldsymbol{q}^{i_l}/\{n\})$ is defined by the probability multiplication theorem

$$F_{n+1}(\{n\}, \boldsymbol{q}^{i_l}) = F_{n+1}(\boldsymbol{q}^{i_l}/\{n\}) F_n(\{n\}). \tag{9}$$

Then, eq. (7) can be formally integrated

$$F_n(\{n\}) = C_{\{n\}}(\beta, v)\exp\left\{-\beta\left[U_n + \sum_{l=n+1}^{N} \varphi_{i_l}(\{n\})\right]\right\}, \tag{10}$$

and after use of the recurrence relation (3) we obtain the new chain of integral equations with respect to the average force potentials:

$$\exp\left[-\beta \sum_{l=n+1}^{N} \varphi_{i_l}(\{n\})\right] = \frac{C_{\{n+1\}}}{C_{\{n\}}} \int_{v_{i_{n+1}}} \exp\left\{-\beta\left[\sum_{k=1}^{n} \Phi_{i_k i_{n+1}} + \sum_{l=n+2}^{N} \varphi_{i_l}(\{n+1\})\right]\right\} \mathrm{d}\boldsymbol{q}^{i_{n+1}}. \tag{11}$$

Normalization constants $C_{\{k\}}$ are functions of the thermodynamical variables and also depend on configuration of the cells $i_1, i_2, \ldots, i_k$.

The advantage of the new chain is that a system of equations in which sharply changing derivatives of the interparticle interaction potential are multiplied by sharply changing distribution functions, is replaced by a system involving rather smoothed average force potentials, so the new hierarchy is more suitable for approximations.

3. Truncation procedure

Owing to statistical effects the average force potentials are not additive even in the case of pairwise interatomic interaction*. We can decompose them into the sum of additive one-particle potentials and multiparticle perturbations. For example in the case of $n = 2$

$$\varphi_{i_3}(\{2\}) = \bar{\varphi}_{i_3}(\boldsymbol{q}^{i_1}) + \bar{\varphi}_{i_3}(\boldsymbol{q}^{i_2}) + \bar{\varphi}_{i_3}(\{2\}), \tag{12}$$

and we put $\varphi_{i_3}(\boldsymbol{q}^{i_1}) = \bar{\varphi}_{i_3}(\boldsymbol{q}^{i_1})$ to unify the notations.

In the general case the decomposition may be written as

$$\varphi_{i_l}(\{n\}) = \sum_{m=1}^{n} \sum_{C_m(\{n\})} \bar{\varphi}_{i_l}(\{m\}), \tag{13}$$

where $\Sigma_{C_m(\{n\})}$ means that the summation is over all possible ordered sets of m particles from the group of n particles. Of course eq. (13) holds for any particular number n of particles but it is convenient to represent the $(n+1)$ particle potential in the form in which the highest order term is separated from the others:

$$\varphi_{i_l}(\{n+1\}) = \bar{\varphi}_{i_l}(\{n+1\}) + \sum_{m=0}^{n-1} \sum_{C_m(\{n\})} \bar{\varphi}_{i_l}(\{m\}, \boldsymbol{q}^{i_{n+1}}) + \varphi_{i_l}(\{n\}). \tag{14}$$

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* Non-additive interactions can easily be included in this scheme.

To close the chain of equations (11) we may neglect the highest order term in (14)

$$\bar{\varphi}_{i_l}(\{n+1\}) = 0. \tag{15}$$

It is worth while to stress that this approximation involves the $(n+2)$ particle distribution function so that the $(n+1)$ particle correlations are preserved.

After substitution of expression (14) with the approximation (15) into eq. (11) we obtain the last equation of the closed chain

$$\exp[-\beta\varphi_{i_{n+1}}(\{n\})] = \frac{C_{\{n+1\}}}{C_{\{n\}}} \int\limits_{v_{i_{n+1}}} \exp\Big\{-\beta\Big[\sum_{k=1}^{n} \Phi_{i_k i_{n+1}} + \sum_{l=n+2}^{N} \sum_{m=0}^{n-1} \sum_{C_m(\{n\})} \bar{\varphi}_{i_l}(\{m\}, \boldsymbol{q}^{i_{n+1}})\Big]\Big\} \mathrm{d}\boldsymbol{q}^{i_{n+1}}, \tag{16}$$

which should be supplemented by the exact equations for smaller number of particles

$$\exp[-\beta\varphi_{i_{p+1}}(\{p\})] = \frac{C_{\{p+1\}}}{C_{\{p\}}} \int\limits_{v_{i_{p+1}}} \exp\Big\{-\beta\Big[\sum_{k=1}^{p} \Phi_{i_k i_{p+1}} + \sum_{l=p+2}^{N} \sum_{m=0}^{p} \sum_{C_m(\{p\})} \bar{\varphi}_{i_l}(\{m\}, \boldsymbol{q}^{i_{p+1}})\Big]\Big\} \mathrm{d}\boldsymbol{q}^{i_{p+1}},$$

$$1 \leqslant p \leqslant n-1. \tag{17}$$

To be really closed the system of equations (16) and (17) has to include equations for all possible configurations of up to $(n+1)$ cells which cannot be transformed in each other by translations, rigid body rotations or reflections.

According to eq. (8) each average force potential is not uniquely defined as one can always add to it a function of thermodynamical variables only. But it is convenient to define the average force potentials uniquely. To do this we adopt the following:

$$\frac{C_{\{p\}}}{C_{\{p+1\}}} = \frac{1}{v^p} \int\limits_{v_{i_1}} \mathrm{d}\boldsymbol{q}^{i_1} \ldots \int\limits_{v_{i_{p+1}}} \exp\Big\{-\beta \sum_{l=p+2}^{N} \sum_{m=0}^{p} \sum_{C_m(\{p\})} \bar{\varphi}_{i_l}(\{m\}, \boldsymbol{q}^{i_{p+1}})\Big\} \mathrm{d}\boldsymbol{q}^{i_{p+1}},$$

$$1 \leqslant p \leqslant n-1; \tag{18}$$

$$\frac{C_{\{n\}}}{C_{\{n+1\}}} = \frac{1}{v^n} \int\limits_{v_{i_1}} \mathrm{d}\boldsymbol{q}^{i_1} \ldots \int\limits_{v_{i_{n+1}}} \exp\Big\{-\beta \sum_{l=n+2}^{N} \sum_{m=0}^{n-1} \sum_{C_m(\{n\})} \bar{\varphi}_{i_l}(\{m\}, \boldsymbol{q}^{i_{n+1}})\Big\} \mathrm{d}\boldsymbol{q}^{i_{n+1}}. \tag{19}$$

With such a choice of relations between the normalization constants, the system of equations (16) and (17) becomes suitable for an iterational procedure and the uncertainty of the potentials is transferred onto the normalization constant C_1 of the unary distribution function. This function may be normalized to unity, but our purpose is the calculation of the configurational integral. The system of equations (16) and (17) results from the initial chain of integro-differential equations and therefore it does not contain enough information for this purpose. To obtain additional information the Gibbs–Helmholz equation has been used[1,2]) in the case of $n = 1$. Furthermore, such an approach is applied in the case of $n = 2$.

4. Configurational integral in the case of $n = 2$

We shall close the system of equations (11) at the second equation. So we adopt the following expressions for the first three distribution functions (in slightly simplified notations)

$$F_1(\boldsymbol{q}^1) = C_1(\beta, v)\exp\left\{-\beta \sum_{l\neq 1}^{N} \bar{\varphi}_l(\boldsymbol{q}^1)\right\}, \tag{20}$$

$$F_2(\boldsymbol{q}^1\boldsymbol{q}^i) = C_{1i}(\beta, v)\exp\left\{-\beta\left[\Phi_{1i} + \sum_{l\neq 1,i}^{N}[\bar{\varphi}_l(\boldsymbol{q}^1) + \bar{\varphi}_l(\boldsymbol{q}^i) + \bar{\varphi}_l(\boldsymbol{q}^1\boldsymbol{q}^i)]\right]\right\}, \tag{21}$$

$$\begin{aligned} F_3(\boldsymbol{q}^1\boldsymbol{q}^i\boldsymbol{q}^j) = C_{1ij}(\beta, v)\exp\Bigg\{-\beta\Bigg[\Phi_{1i} + \Phi_{1j} + \Phi_{ij} \\ + \sum_{l\neq 1ij}^{N}[\bar{\varphi}_l(\boldsymbol{q}^1) + \bar{\varphi}_l(\boldsymbol{q}^i) + \bar{\varphi}_l(\boldsymbol{q}^j) + \bar{\varphi}_l(\boldsymbol{q}^1\boldsymbol{q}^i) + \bar{\varphi}_l(\boldsymbol{q}^1\boldsymbol{q}^j) + \bar{\varphi}_l(\boldsymbol{q}^i\boldsymbol{q}^j)]\Bigg]\Bigg\}. \end{aligned} \tag{22}$$

The average force potentials obey the system of iterative equations

$$\exp[-\beta\bar{\varphi}_i(\boldsymbol{q}^1)] = \bar{Q}_{1i}^{-1}\int\limits_{v_i}\exp\left\{-\beta\left[\Phi_{1i} + \sum_{l\neq 1i}^{N}[\bar{\varphi}_l(\boldsymbol{q}^i) + \bar{\varphi}_l(\boldsymbol{q}^1\boldsymbol{q}^i)]\right]\right\}\mathrm{d}\boldsymbol{q}^i; \tag{23}$$

$$\begin{aligned} &\exp\{-\beta[\bar{\varphi}_j(\boldsymbol{q}^1) + \bar{\varphi}_j(\boldsymbol{q}^i) + \bar{\varphi}_j(\boldsymbol{q}^1\boldsymbol{q}^i)]\} \\ &\quad = \bar{Q}_{1ij}^{-1}\int\limits_{v_j}\exp\left\{-\beta\left[\Phi_{1j} + \Phi_{ij} + \sum_{l\neq 1ij}^{N}[\bar{\varphi}_l(\boldsymbol{q}^j) + \bar{\varphi}_l(\boldsymbol{q}^1\boldsymbol{q}^j) + \bar{\varphi}_l(\boldsymbol{q}^i\boldsymbol{q}^j)]\right]\right\}\mathrm{d}\boldsymbol{q}^j, \end{aligned} \tag{24}$$

where

$$\bar{Q}_1 = \int\limits_{v_1}\exp\left\{-\beta\sum_{l\neq 1}^{N}\bar{\varphi}_l(\boldsymbol{q}^1)\right\}\mathrm{d}\boldsymbol{q}^1, \tag{25}$$

$$\bar{Q}_{1i} = \frac{1}{v}\int\limits_{v_1}\int\limits_{v_i}\exp\left\{-\beta\sum_{l\neq 1i}^{N}[\bar{\varphi}_l(\boldsymbol{q}^i) + \bar{\varphi}_l(\boldsymbol{q}^1\boldsymbol{q}^i)]\right\}\mathrm{d}\boldsymbol{q}^1\,\mathrm{d}\boldsymbol{q}^i, \tag{26}$$

$$\bar{Q}_{1ij} = \frac{1}{v^2}\int\limits_{v_1}\mathrm{d}\boldsymbol{q}^1\int\limits_{v_i}\mathrm{d}\boldsymbol{q}^i\int\limits_{v_j}\exp\left\{-\beta\sum_{l\neq 1ij}^{N}[\bar{\varphi}_l(\boldsymbol{q}^j) + \bar{\varphi}_l(\boldsymbol{q}^1\boldsymbol{q}^j) + \bar{\varphi}_l(\boldsymbol{q}^i\boldsymbol{q}^j)]\right\}\mathrm{d}\boldsymbol{q}^j. \tag{27}$$

Expression (25) is needed for further calculations.

One can use two different expressions for the potential part of the internal energy of the system per particle. On the one hand the Gibbs–Helmholz relation gives it in terms of the configurational integral

$$U = -\frac{\partial}{\partial\beta}\ln Q; \qquad Q_N = Q^N. \tag{28}$$

On the other hand, according to the definition, the internal energy is determined by the normalized to unity binary distribution function

$$U = \tfrac{1}{2}\sum_{i\neq 1}^{N}\int\limits_{v_1}\int\limits_{v_i}\Phi_{1i}\hat{F}_2(\boldsymbol{q}^1\boldsymbol{q}^i)\,\mathrm{d}\boldsymbol{q}^1\,\mathrm{d}\boldsymbol{q}^i = \tfrac{1}{2}\sum_{i\neq 1}^{N}\langle\Phi_{1i}\rangle. \tag{29}$$

Normalized to unity distribution functions and their normalization constants are marked by sign $\wedge$, so according to (20)–(22) we have

$$\hat{C}_1 = \tilde{Q}_1^{-1}; \qquad \hat{C}_{1i} = (\tilde{Q}_1\tilde{Q}_{1i})^{-1}; \qquad \hat{C}_{1ij} = (\tilde{Q}_1\tilde{Q}_{1i}\tilde{Q}_{1ij})^{-1}. \tag{30}$$

Now we shall try to reduce eq. (29) to the form of eq. (28). To do this we differentiate the iterative equation (23) previously multiplied by $\tilde{Q}_{1i}$ with respect to the inverse of the temperature, then multiply the result by

$$\hat{C}_{1i}\exp\Big[-\beta\sum_{l\neq 1i}^{N}\bar{\varphi}_l(\boldsymbol{q}^1)\Big]$$

and integrate over $\boldsymbol{q}^1$. After some simple algebra we find

$$\begin{aligned}
&-\frac{\partial}{\partial\beta}\left(\ln\frac{\tilde{Q}_{1i}}{\tilde{Q}_1}\right) + 2\int\limits_{v_1}\frac{\partial}{\partial\beta}[\beta\varphi_i(\boldsymbol{q}^1)]\hat{F}_1(\boldsymbol{q}^1)\,\mathrm{d}\boldsymbol{q}^1\\
&\quad = \langle\Phi_{1i}\rangle + \int\limits_{v_1}\int\limits_{v_i}\frac{\partial}{\partial\beta}\Big[\sum_{j\neq 1i}^{N}\beta\bar{\varphi}_j(\boldsymbol{q}^1\boldsymbol{q}^i)\Big]\hat{F}_2(\boldsymbol{q}^1\boldsymbol{q}^i)\,\mathrm{d}\boldsymbol{q}^1\,\mathrm{d}\boldsymbol{q}^i.
\end{aligned} \tag{31}$$

The sum over i gives

$$\begin{aligned}
2U &= -\frac{\partial}{\partial\beta}\ln\left(\prod_{i\neq 1}^{N}\frac{\tilde{Q}_{1i}}{\tilde{Q}_1}\right) - 2\frac{\partial}{\partial\beta}(\ln\tilde{Q}_1)\\
&\quad - \sum_{\substack{j\neq 1i\\ i\neq 1}}^{N}\int\limits_{v_1}\int\limits_{v_i}\frac{\partial}{\partial\beta}[\beta\bar{\varphi}_j(\boldsymbol{q}^1\boldsymbol{q}^i)]\hat{F}_2(\boldsymbol{q}^1\boldsymbol{q}^i)\,\mathrm{d}\boldsymbol{q}^1\,\mathrm{d}\boldsymbol{q}^i.
\end{aligned} \tag{32}$$

To exclude the last term in eq. (32) we differentiate eq. (24) multiplied by $\tilde{Q}_{1ij}$ with respect to β, multiply the result by

$$\hat{C}_{1ij}\exp\Big\{-\beta\Big[\Phi_{1i} + \sum_{l\neq 1ij}^{N}[\bar{\varphi}_l(\boldsymbol{q}^1) + \bar{\varphi}_l(\boldsymbol{q}^i) + \bar{\varphi}_l(\boldsymbol{q}^1\boldsymbol{q}^i)]\Big]\Big\},$$

and integrate over $\boldsymbol{q}^1$ and $\boldsymbol{q}^i$. After excluding the mean values $\langle\Phi_{1j}\rangle$ and $\langle\Phi_{ij}\rangle$ with the help of expressions like (31) the final result becomes

$$\frac{\partial}{\partial\beta}\left(\ln\frac{\tilde{Q}_{1ij}\tilde{Q}_1}{\tilde{Q}_{1j}\tilde{Q}_{ij}}\right)=\int_{v_1}\int_{v_i}\frac{\partial}{\partial\beta}[\beta\tilde{\varphi}_j(\boldsymbol{q}^1\boldsymbol{q}^i)]\hat{F}_2(\boldsymbol{q}^1\boldsymbol{q}^i)\,\mathrm{d}\boldsymbol{q}^1\,\mathrm{d}\boldsymbol{q}^i$$

$$+\int_{v_1}\int_{v_j}\frac{\partial}{\partial\beta}[\beta\tilde{\varphi}_i(\boldsymbol{q}^1\boldsymbol{q}^j)]\hat{F}_2(\boldsymbol{q}^1\boldsymbol{q}^j)\,\mathrm{d}\boldsymbol{q}^1\,\mathrm{d}\boldsymbol{q}^j$$

$$+\int_{v_i}\int_{v_j}\frac{\partial}{\partial\beta}[\beta\tilde{\varphi}_1(\boldsymbol{q}^i\boldsymbol{q}^j)]\hat{F}_2(\boldsymbol{q}^i\boldsymbol{q}^j)\,\mathrm{d}\boldsymbol{q}^i\,\mathrm{d}\boldsymbol{q}^j. \qquad (33)$$

Summing over i and j ($i\neq j$; $i, j\neq 1$), i.e. over all possible configurations of cells v_i and v_j with respect to v_1 makes all the terms on the right-hand side of eq. (33) equal to each other, so that

$$\sum_{\substack{i\neq i\\ ij\neq 1}}^{N}\int_{v_i}\int_{v_j}\frac{\partial}{\partial\beta}[\beta\tilde{\varphi}_j(\boldsymbol{q}^1\boldsymbol{q}^i)]\hat{F}_2(\boldsymbol{q}^1\boldsymbol{q}^i)\,\mathrm{d}\boldsymbol{q}^1\,\mathrm{d}\boldsymbol{q}^i=\tfrac{1}{3}\frac{\partial}{\partial\beta}\left(\ln\prod_{\substack{i\neq j\\ ij\neq 1}}^{N}\frac{\tilde{Q}_{1ij}\tilde{Q}_1}{\tilde{Q}_{1j}\tilde{Q}_{ij}}\right). \qquad (34)$$

With these results eq. (29) is easily reduced to the form of eq. (28) with

$$Q=\tilde{Q}_1\left(\prod_{i\neq 1}^{N}\frac{\tilde{Q}_{1i}}{\tilde{Q}_1}\right)^{1/2}\left(\prod_{\substack{i\neq j\\ ij\neq 1}}^{N}\frac{\tilde{Q}_{1ij}\tilde{Q}_1}{\tilde{Q}_{1j}\tilde{Q}_{ij}}\right)^{1/6}. \qquad (35)$$

It should be stressed that because of the derivative with respect to the inverse of the temperature in eq. (28) the result (35) could include a factor which is a function of the volume only. But consideration of the boundary condition $\beta\to 0$ shows that this factor does not depend on volume and therefore eq. (35) uniquely defines the configurational integral in the approximation when triple correlations are taken into account.

Another possibility to derive an expression for the configurational integral is connected with the virial theorem for pressure. The theorem can be reduced to the form

$$p=(\beta v)^{-1}+\beta^{-1}\frac{\partial}{\partial v}\ln Q$$

by taking derivatives of eqs. (23) and (24) with respect to volume. These calculations are rather more tedious because they involve the Bogolubov's scale transformation of volume[7]) (see also ref. 1c). The result of the calculations is exactly the expression (35) and it proves thermodynamical compatibility of the calorimetric and thermal equations of state in our approach.

The transition from eq. (35) to the expression of the configurational integral in the case when the chain of integral equations was interrupted at the first equation is not evident. We cannot simply put $\tilde{\varphi}_l(\boldsymbol{q}^1\boldsymbol{q}^i)=0$ because it violates eq. (24). However, if we imagine that the situation $\tilde{\varphi}_l(\boldsymbol{q}^1\boldsymbol{q}^i)=0$ exists then from eq. (24) it follows that $\bar{Q}_{1ij}\bar{Q}_1 = \bar{Q}_{1j}\bar{Q}_{ij}$ and expression (35) becomes

$$Q = \bar{Q}_1\left(\prod_{i\neq 1}^{N}\frac{\tilde{Q}_{1i}}{\tilde{Q}_1}\right)^{1/2}. \tag{36}$$

This is a result of the previous papers[1,2]). Therefore the quantity

$$\Delta = \left(\prod_{\substack{i\neq j\\ ij\neq 1}}^{N}\frac{\tilde{Q}_{1ij}\tilde{Q}_1}{\tilde{Q}_{1j}\tilde{Q}_{ij}}\right)^{1/6}, \tag{37}$$

calculated under the condition $\bar{\varphi}_l(\boldsymbol{q}^1\boldsymbol{q}^j) = \bar{\varphi}_l(\boldsymbol{q}^i\boldsymbol{q}^j) = 0$, provides a measure of accuracy of the truncation procedure within the framework of the first equation of the chain.

5. Discussion

Eqs. (23), (24) and (35) present the thermodynamics of a molecular system when the chain of integral equations is truncated at the second equation. However, for $n > 2$ the formulae become very complicated and the system of iterative equations can hardly be solved even with the help of powerful computers.

On the other hand it is worth while to note that the system of equations (23) and (24) as well as eq. (23) with $\bar{\varphi}_l(\boldsymbol{q}^1\boldsymbol{q}^i) = 0$ involves correlation ranges which are compatible with the range of interparticle interaction, so the problem appears to take account of long range correlations which can play an important role in some situations. It seems that the general result [eqs. (16)–(19)] can provide a basis to handle this problem.

Another possibility of taking into account long range correlations is concerned with the method of construction of self-consistent equations for the average force potentials proposed by Barker[8]). The expansion of the configurational integral in the series of Mayer-like functions

$$f_{ij} = \exp\{-\beta[\Phi_{ij} - \bar{\varphi}_j(\boldsymbol{q}^i) - \bar{\varphi}_i(\boldsymbol{q}^j)]\} - 1$$

averaged with the distribution function

$$\mathcal{D}_N^{(0)} \sim \exp\left\{-\beta\sum_{i\neq j}^{N}\bar{\varphi}_j(\boldsymbol{q}^i)\right\},$$

is the basis of the method. The self-consistent equation results if one puts the second term $\langle f_{ij}\rangle$ in the expansion equal to zero. Of course the systematic approach implies the use of the cumulant expansion instead of the simple one used by Barker. But his result [eq. (23) with $\bar{\varphi}_l(\boldsymbol{q}^1\boldsymbol{q}^i) = 0$ and $\bar{Q}_1$ instead of $\bar{Q}_{1i}$ and $Q_N = Q_1^N$ for the configurational integral] remains unchanged. It is possible to go on and obtain the expansions* for the unary and binary distribution

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* Owing to the self-consistency condition all the connected graphs which have at least one field point joined to the others by only one line do not contribute to these expansions.

functions too. In the same approximation these expansions will be equivalent to eqs. (20) and (21) with $\bar{\varphi}_l(\boldsymbol{q}^1\boldsymbol{q}^l) = 0$ [the result of papers[1,2]]. Although generalization of Barker's method to take account of stronger fluctuations of density of the system (two-particle occupation of a cell, for example) is a rather difficult problem, still in the Mayer-like expansions of the configurational integral and distribution functions some classes of the diagrams can probably be summed and thus the long range correlations will partially be taken into account.

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