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TRUNCATION PROCEDURE FOR HIGH ORDER REDUCED DISTRIBUTION FUNCTIONS

II. THE COMPATIBILITY PROBLEM

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The problem of the compatibility of the results obtained from approximate expressions for the junior distribution functions is viewed under a broad aspect. This paper concerns the compatibility of the calculated values of not only the energy and pressure but also of the higher-order derivatives of the free energy with respect to the thermodynamic variables (such as the heat capacity) as well as of the chain of integro-differential equations, the normalization relations, and the satisfaction of the correlation weakening conditions. The degree of agreement with the requirements mentioned is suggested to be useful as a possible a priori measure of applicability of a certain approximation adopted for calculating the correlation functions over a wide range of thermodynamic variables. The consideration is made within the framework of the conditional distribution method.

1. Introduction

A large variety of the presently existing methods which are used for the calculation of the approximate values of the junior particle distribution functions gives fairly accurate values of certain thermodynamic properties of molecular systems in a certain range of thermodynamic variables[1,2]. However, all attempts to use any of the methods separately in a wide range of thermodynamic variables or for the calculation of different thermodynamic properties of a system have failed. One of the reasons of this is the thermodynamic incompatibility of the results arising from approximate expressions for the particle distribution functions. In some works (see, for example, refs. 3–7) the authors discuss different aspects of the thermodynamic compatibility problems and the possibilities to obtain the approximate distribution functions which would give consistent results for thermodynamic properties of the system under study.

The problem may be formulated generally as follows. On the basis of the Gibbsian distribution it is possible to get a large number of identities for the particle correlation functions (such as the BBGKY hierarchy and the thermodynamic relations between the free energy and its derivatives), which can be satisfied only with exact distribution functions. The distribution functions obtained on the basis of different approximate methods very often satisfy only one of the identities and as a rule that one which was used to calculate the correlation function. But the successive validity of the identities for the first, second etc. derivatives (both with respect to the space coordinates of the particles and to the thermodynamic variables) may provide a good a priori measure of accuracy of the approximations used.

The present program could be realized within the framework of the conditional distribution method^{2}) (see also ref. 8). A characteristic feature of the method is the introduction of approximations which consecutively take account of a more and more complete set of particle configurations involved in the system. So, the first main approximation of the method takes into account such configurations for which every molecular cell, into which the system volume is conventionally divided, contains one particle. In the subsequent approximations of the method two-particle, three-particle etc. occupations of a cell are taken into consideration.

In earlier papers, with the help of the average force potential approximation which is typical for the conditional distribution method, approximate expressions were obtained for one- and two-particle distribution functions and the free energy of a molecular system satisfying the requirement of thermodynamic compatibility^{9}). The use of the self-consistent procedure for the calculation of the average force potentials based on the thermodynamic compatibility condition has led to satisfactory results in a wide range of thermodynamic variables, including the solid, liquid and compressed gas phases. The generalization of the average force potential approximation has resulted in a general scheme of truncation of the chain of integro-differential equations for the distribution functions at an arbitrary level and has shown thermodynamic compatibility when the chain is truncated at the third equation^{10}) (hereafter to be referred to as I).

In the following we consider different aspects of the compatibility problem as concerns the results obtained with the particle distribution functions in the first approximation of the conditional distribution method. In view of the further use of both multiparticle interaction potentials and multiparticle average force potentials as well as the necessity of operating with sums of such potentials over all possible distributions of particles over the cells we introduce in the following section special $\hat{C}$-operators and define the rules for operating with them. The exact relations between the particle distribution functions which follow from the Gibbsian distribution will be presented. Multiparticle interactions are taken into account in these relations. The relations are expressed in a form which is convenient for subsequent use.

In section 4 a system of integral equations for a sequence of the average force potentials is introduced and is used to develop chains of the integro-differential equations for the distribution functions with the derivatives both with respect to the particle coordinates and to the temperature and volume. Expressions for the thermodynamic functions are obtained in the next section. The consistency of the expressions obtained and some numerical results are discussed in section 6.

2. Algebra of $\hat{C}$-operators

Consider a group of particles and introduce functions $\omega_{l_{m+1}l_{m+2}\cdots l_{m+s}}(q^{l_1}q^{l_2}\cdots q^{l_m})$ of the coordinates of m particles depending also on the positions of the cells over which the other s particles are distributed. Examples of ω are multiparticle potentials of the average forces (see eq. (4.2)) exerted by s particles distributed over their cells on m particles at q^{l_1}, $q^{l_2}, \ldots, q^{l_m}$ in other m cells ($l_1, l_2, \ldots$ being the cell numbers). In the following the shorthand notations

$$\begin{aligned}&\omega_{l_{m+1}\cdots l_{m+s}}(q^{l_1}\cdots q^{l_m}) = \omega_{\{s\}}(l_1 l_2 \cdots l_m) = \omega_{\{s\}}(\{m\}),\\ &l_1 \neq l_2 \neq \cdots \neq l_m \neq l_{m+1} \neq \cdots \neq l_{m+s}\end{aligned} \tag{2.1}$$

will be used.

Here$\{k\}$ is meant to be a k-element set

$$\{k\} = l_1, l_2, \ldots, l_k.$$

If it is necessary to emphasize that the set of m particles is divided into two groups, the following notations will be used

$$\omega(\{m\}) = \omega(\{(m-k)+k\}) = \omega(\{(m-k); k\}). \tag{2.2}$$

Specifically, if one of the particles is selected, say, with number $l_k \in \{m\}$, the notation

$$\omega(\{m\}) = \omega(\{m-1, l_k\}) \tag{2.3}$$

may be used.

Next,in order to perform the summation over all the possible combinations we introduce $\hat{C}$-operators which are defined by the following expressions

$$\hat{C}^p_m \omega_{\{s\}}(\{m\}) = \sum_{l_m > l_{m-1} > \cdots > l_1} \omega_{\{s\}}(\{m\}), \tag{2.4}$$

$$\hat{C}^p_m \omega_{\{m\}}(\{s\}) = \sum_{l_m > l_{m-1} > \cdots > l_1} \omega_{\{m\}}(\{s\}). \tag{2.5}$$

Here the set $\{m\}$ is a subset of $\{p\}$, $(\{m\} \subseteq \{p\})$, and the sets $\{s\}$ and $\{p\}$ do not intersect $(\{s\} \cap \{p\} = \emptyset)$. It is also worthwhile to introduce the operator $\hat{C}_0^0$ as a unit operator

$$\hat{C}_0^0 \omega(\{0 + s\}) = \omega(\{s\}). \tag{2.6}$$

For $m = 1$ relation (2.5) becomes

$$\hat{C}_1^p \omega_{\{1\}}(\{m\}) = \sum_{\substack{l_k \in \{p\} \\ l_k \notin \{m\}}} \omega_{l_k}(\{m\}). \tag{2.7}$$

Let $\{m\} \subseteq \{s\} \subseteq \{p\}$. Then it follows directly from eq. (2.7) that

$$\hat{C}_1^{p-s} + \hat{C}_1^{s-m} = \hat{C}_1^{p-m}. \tag{2.8}$$

More general expressions are also possible. Since the operators in eqs. (2.4) and (2.5) are equivalent, the relations will be considered further in this section only for the operator defined in eq. (2.4). Then the subscript s may be omitted.

Now, let us divide the set $\{p\}$ into two subsets $\{p - s\}$ and $\{s\}$. Selecting successively all the possible combinations of m elements from the two subsets, we can write

$$\hat{C}_m^p \omega(\{m\}) = \sum_{k=0}^{m} \hat{C}_{m-k}^{p-s} \hat{C}_k^s \omega(\{(m-k) + k\}). \tag{2.9}$$

The operators $\hat{C}_{m-k}^{p-s}$ and $\hat{C}_k^s$ in the right-hand side of eq. (2.9) commute since $\{p - s\} \cap \{s\} = \emptyset$.

In order to extend relation (2.9) to $m > s$, we assume that

$$\hat{C}_m^p \omega = 0, \tag{2.10}$$

if $p < 0$ or $m < 0$ or $p < m$. It should be noted that the notation for the operator $\hat{C}$ always involves both the set to choose from (the superscript), and the set to be chosen (the subscript). This makes it possible to determine the indices of the function ω under the action of this operator and the range of summation for the operator.

The sum over all the combinations in the initial set $\{p\}$ may be composed neglecting or taking into account the fact that it has been divided into two subsets as

$$\sum_{m=0}^{p} \hat{C}_m^p \omega(\{m\}) = \sum_{l=0}^{p-s} \sum_{k=0}^{s} \hat{C}_l^{p-s} \hat{C}_k^s \omega(\{l + k\}). \tag{2.11}$$

It should be noted that eq. (2.8) results from eq. (2.9) if $m = 1$ is assumed in the latter. Moreover, taking $s = 1$ and $p = n + 1$ in eq. (2.9) we find with the definition (2.10)

$$(\hat{C}_m^{n+1} - \hat{C}_m^n)\omega(\{m\}) = \hat{C}_{m-1}^n \omega(\{m-1, l_{n+1}\}). \tag{2.12}$$

There are also relations containing different orders of summation in the right-hand and the left-hand sides

$$\begin{aligned} \hat{C}_m^n \hat{C}_s^{n-m} \omega_{\{s\}}(\{m\}) &= \hat{C}_{m+s}^n \hat{C}_s^{m+s} \omega_{\{s\}}(\{m\}) \\ &= \hat{C}_{m+s}^n \hat{C}_m^{m+s} \omega_{\{s\}}(\{m\}). \end{aligned} \tag{2.13}$$

For $s = 1$ this relation becomes

$$\hat{C}_m^n \hat{C}_1^{n-m} \omega_{\{1\}}(\{m\}) = \hat{C}_{m+1}^n \hat{C}_1^{m+1} \omega_{\{1\}}(\{m\}). \tag{2.14}$$

In the left-hand side of eq. (2.13) m elements are selected from n, and the summation is carried out over all the combinations of s particles from the remaining $n - m$. Then a new set of m particles is selected and procedure is repeated again; this is the order of summation over all the combinations of m elements from n. In the right-hand side of eq. (2.13) the summation is more symmetrical: $m + s$ elements are selected from the group of n, and the summation is performed over all the combinations of s (or, equivalently, m) elements in the selected subset; then all the possible combinations of $m + s$ elements from n are taken into account.

If the quantities independent of the coordinates and the particle indices (some constants) are used as $\omega_{\{s\}}(\{m\})$, the expressions (2.8) through (2.14) reduce to the relations between the binomial coefficients.

3. Exact relations for the distribution functions

Consider a canonical ensemble of a system of N particles. With multiparticle interactions of an arbitrary order the potential energy of the system may be written as

$$\tilde{U}_N = \sum_{1 \le i < j \le N} \tilde{\phi}(ij) + \sum_{1 \le i < j < k \le N} \tilde{\phi}(ijk) + \cdots = \sum_{m=0}^{N} \hat{C}_m^N \tilde{\phi}(\{m\}), \tag{3.1}$$

$$\tilde{\phi}(\{0\}) = 0, \quad \tilde{\phi}(\{1\}) = 0.$$

If only multiparticle interactions of order t or less are considered, then in expression (3.1) it must be assumed that

$$\tilde{\phi}(\{t+s\}) = 0, \quad s \geqslant 1. \tag{3.2}$$

It is a peculiar feature of the multiparticle interaction potential $\phi(\{m\})$ that the potential becomes independent of the coordinates of the rest of the particles if at least one of the m particles removes to infinity. The resulting constant may for convenience be assumed to be zero. This choice will be implied in the following.

The potential energy (3.1) of the system enters into the configuration part of the Gibbsian distribution

$$\bar{\mathscr{D}}_N = \exp(-\beta \bar{U}_N), \tag{3.3}$$

and the configuration integral of the system in the F_{11}-approximation of the conditional distribution method is given by

$$\bar{Q}_N = N! \int_{\bar{v}_1} \mathrm{d}\bar{\boldsymbol{q}}^1 \cdots \int_{\bar{v}_N} \exp(-\beta \bar{U}_N)\, \mathrm{d}\bar{\boldsymbol{q}}^N, \tag{3.4}$$

where $\bar{v}_k = V/N$ is the molecular volume.

Now, using N.N. Bogoliubov's idea[11]) on scale transformations of the configuration space of the system, we introduce the molecular unit volume $v_k = 1$

$$\bar{v}_k = \lambda v_k, \quad \bar{\boldsymbol{q}}^k = \lambda^{1/3} \boldsymbol{q}^k, \quad \mathrm{d}\bar{\boldsymbol{q}}^k = \lambda\, \mathrm{d}\boldsymbol{q}^k, \quad \lambda = \bar{v}_k. \tag{3.5}$$

Upon applying the scale transformation (3.5) to expression (3.4) the configuration integral will depend on the volume and temperature only through the transformed expression for the interparticle potential

$$\phi(\{m\}) = -\beta \bar{\phi}(\{m\}, \lambda) = -\beta \bar{\phi}(\{m\}, \bar{v}), \quad U_N = -\beta \bar{U}_N \tag{3.6}$$

by

$$\bar{Q}_N = N! \lambda^N Q_N = N! \bar{v}^N Q_N, \tag{3.7}$$

$$Q_N = \int_{v_1} \mathrm{d}\boldsymbol{q}^1 \cdots \int_{v_N} \mathrm{d}\boldsymbol{q}^N \exp U_N. \tag{3.8}$$

The part Q_N of the configuration integral taken here for subsequent consideration determines the difference of the thermodynamic properties of the system from the ideal gas properties. The corresponding part of the free energy is

$$F = \ln Q_N. \tag{3.9}$$

Differentiation of eq. (3.9) with respect to temperature T and volume $\bar{v}$ gives equations for the energy and pressure

$$F_\alpha = L_\alpha F = \langle L_\alpha U_N \rangle, \tag{3.10}$$

$$\alpha = T, \bar{v}; \quad L_\alpha = \partial / \partial \alpha. \tag{3.11}$$

The brackets denote statistical averaging over the Gibbsian distribution or the corresponding reduced distribution function

$$\langle A(\{m\})\rangle = \int_{v_1} \mathrm{d}\boldsymbol{q}^1 \cdots \int_{v_m} A(\{m\})F(\{m\})\,\mathrm{d}\boldsymbol{q}^m, \tag{3.12}$$

where $F(\{m\})$ is the m-particle distribution function normalized to unity in the F_{II}-approximation.

Repeated differentiation of eq. (3.10) with respect to the thermodynamic variables gives properties such as the heat capacity

$$F_{\alpha\beta} = L_\alpha L_\beta F = \langle L_\alpha L_\beta U_N\rangle + \langle(\Delta L_\alpha U_N)(\Delta L_\beta U_N)\rangle, \tag{3.13}$$

where

$$\Delta L_\alpha A(\{m\}) = L_\alpha A(\{m\}) - \langle L_\alpha A(\{m\})\rangle. \tag{3.14}$$

The thermodynamic compatibility problem consists in satisfying all the differential relations between the left-hand sides (for example $L_\alpha F_\beta = L_\beta F_\alpha = F_{\alpha\beta}$), while calculating the right-hand sides of expressions (3.10) and (3.13) with approximate distribution functions. Naturally, the problem will be solved if the single integration of eq. (3.10) or the double integration of eq. (3.13) results in one and the same value of the free energy for all allowable sets of the thermodynamic variables α and β. If we proceed to higher derivatives of the free energy, the thermodynamic compatibility problem becomes more and more complicated, but the resultant information may appear to be useful for the choice of a more satisfactory approximation for the truncation of the chains of equations*.

Consider also the derivatives of the particle distribution functions over the particle coordinates and the thermodynamic variables. Only the first derivatives will be taken here. In the following, alongside with the operator L_α of differentiation with respect to the thermodynamic variables used above, we will use also the operator of differentiation with respect to the coordinates of the l_kth particle

$$L_k = (\partial/\partial \boldsymbol{q}^{l_k}). \tag{3.15}$$

The letter L will be used to denote the derivatives both with respect to $\boldsymbol{q}^k$ and to T or v.

Now we introduce the n-particle distribution function normalized to unity

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* Within the canonical ensemble we do not consider the isothermal compressibility $(1/v)(\partial v/\partial p)_T$ which is expressed in the well-known way in terms of two- and one-particle distribution functions on the basis of the functions of the number of particles. As is known[12]), the asymptotics and the normalization of the distribution functions are different in the canonical and the grand canonical ensemble, and this problem is beyond the discussion of the present work.

$$F(\{n\}) = Q_N^{-1} \int\limits_{v_{l_{n+1}}} \mathrm{d}\boldsymbol{q}^{l_{n+1}} \cdots \int\limits_{v_{l_N}} \exp(U_N)\, \mathrm{d}\boldsymbol{q}^{l_N}. \tag{3.16}$$

Integral relations of the form

$$\underbrace{\int\limits_{v_{l_k}} \mathrm{d}\boldsymbol{q}^{l_k} \cdots \int\limits_{v_{l_n}}}_{n+1-k} F(\{n\})\, \mathrm{d}\boldsymbol{q}^{l_n} = \underbrace{\int\limits_{v_{l_k}} \mathrm{d}\boldsymbol{q}^{l_k} \cdots \int\limits_{v_{l_{n+m}}}}_{n+m+1-k} F(\{n+m\})\, \mathrm{d}\boldsymbol{q}^{l_{n+m}} \tag{3.17}$$

are valid for the distribution functions of different orders.

The application of the operator L to eq. (3.16) gives

$$LF(\{n\}) = \langle LU_N \rangle_{\{n\}} - L(\ln Q_N) F(\{n\}). \tag{3.18}$$

The average with respect to the coordinates of $N-n$ particles is denoted by brackets with the subscript $\{n\}$

$$\langle A(\{n+m\}) \rangle_{\{n\}} = \int\limits_{v_{l_{n+1}}} \mathrm{d}\boldsymbol{q}^{l_{n+1}} \cdots \int\limits_{v_{l_{n+m}}} A(\{n+m\}) F(\{n+m\})\, \mathrm{d}\boldsymbol{q}^{l_{n+m}}. \tag{3.19}$$

Then, bearing in mind that

$$L \ln Q_N = \langle LU_N \rangle, \tag{3.20}$$

and using notation (3.14) we may write for the derivative of the distribution function

$$LF(\{n\}) = \langle \Delta(LU_N) \rangle_{\{n\}}. \tag{3.21}$$

In order to express eq. (3.21) in a form convenient for subsequent use, the terms in the potential energy of the system will be rearranged with the aid of eq. (2.11) as

$$\begin{aligned} U_N &= \sum_{m=0}^{N-n} \sum_{k=0}^{n} \hat{C}_m^{N-n} \hat{C}_k^n \phi(\{k+m\}) \\ &= \sum_{m=0}^{N-n} \hat{C}_m^{N-n} \psi(\{n;m\}). \end{aligned} \tag{3.22}$$

The above expression involves an interaction potential for a group of n particles with a complex of m particles belonging to the remaining part of the system

$$\begin{aligned} &\psi(\{n;m\}) = \sum_{k=0}^{n} \hat{C}_k^n \phi(\{k+m\}), \\ &\psi(\{0,m\}) = \phi(\{m\}), \quad \psi(\{n;0\}) = U_n. \end{aligned} \tag{3.23}$$

It should be emphasized that the expressions (3.22) and (3.23) are basic for the further considerations.

With the potentials ψ eq. (3.21) becomes

$$LF(\{n\}) = \sum_{s=0}^{N-n}{}' \hat{C}_s^{N-n}\langle \Delta L\psi(\{n;s\})\rangle. \tag{3.24}$$

If $L = L_k$, then $\langle L_k U_N\rangle = 0$ because of eq. (3.20), and eq. (3.24) is a chain of integro-differential equations for the distribution functions. The first term of the right-hand side ($s = 0$) is $[L_1 U_N]F(\{n\})$, and the others involve the major distribution functions up to the $n + (t - 1)$ order where t is the maximum order of the multiparticle interaction considered (see eq. (3.2)). The term with the $(n + t)$-particle distribution function drops out because of the differentiation with respect to the coordinate of one of the particles from the set $\{n\}$. When only pairwise interaction is taken into account ($t = 2$), the chain (3.24) becomes the well-known chain of equations defining the integro-differential relation between the two consecutive distribution functions $F(\{n\})$ and $F(\{n + 1\})$[2]).

If $L = L_\alpha$ is the operator of differentiation with respect to the thermodynamic variables the chain (3.24) contains alongisde with the major distribution functions up to the order $(n + t)$ also the junior functions entering into the expression for $\langle \mathrm{LU_N}\rangle$. The latter however can always be expressed in terms of the integrals of $F(\{n\})$ according to eq. (3.17).

The chain of equations composed of the derivatives with respect to the thermodynamic variables have been considered within the grand canonical ensemble in the unconditional distribution method (see ref. 13) with pairwise interparticle interaction, but they have not been widely used since.

Thus, the compatibility problem involves not only the thermodynamic relations (3.10) and (3.13) but also the integro-differential equations (3.24) and the normalization relations (3.17). The correlation weakening conditions (see ref. 11) should be satisfied too.

4. Integro-differential equation chain

In order to formulate a closed system of equations for the distribution functions and the average force potentials, we will proceed from the integral relation (3.17) with $m = 1$ and $k = n + 1$ as was done in refs. 2, 8, 10. Then the normalization conditions for the distribution functions are automatically satisfied and the compatibility of equations (3.10), (3.13) and (3.24), when the correlation weakening condition is observed, should be discussed.

Following I, we will look for a multiparticle distribution function of the form

$$F(\{n\}) = \exp\{[\sigma(\{n\}) + U_n + \hat{C}_1^{N-n}\varphi_{\{1\}}(\{n\})]\}, \tag{4.1}$$

where

$$U_n = \psi(\{n;0\}) = \sum_{m=0}^{n} \hat{C}_m^n \phi(\{m\})$$

is the potential energy of the system of n particles; $\sigma(\{n\})$ is the normalization constant which is a function of the thermodynamic variables and which depends only on the mutual location of the cells in which the n particles are distributed but is independent of their coordinates; $\varphi_{\{1\}}(\{n\}) = \varphi_{l_k}(\{n\})$ is the average force potential exerted by the particle distributed within the cell $l_k \not\in \{n\}$ on the system of n particles under consideration*. A detailed discussion of the terms in eq. (4.1) with a pairwise interparticle interaction is considered in I.

Similarly to eq. (3.1) potentials φ of the average forces are expressed in terms of the m-particle contributions ω as

$$\varphi_{\{1\}}(\{n\}) = \sum_{m=0}^{n} \hat{C}_m^n \omega_{\{1\}}(\{m\}), \quad \omega_{\{1\}}(\{0\}) = 0. \tag{4.2}$$

Such an expression is also convenient for the normalization constants

$$\sigma(\{n\}) = \sum_{m=0}^{n} \hat{C}_m^n \epsilon(\{m\}), \quad \epsilon(\{0\}) = 0. \tag{4.3}$$

The distribution function then becomes

$$F(\{n\}) = \exp\left\{\sum_{m=0}^{n} \hat{C}_m^n [\epsilon(\{m\}) + \phi(\{m\}) + \hat{C}_1^{N-n}\omega_{\{1\}}(\{m\})]\right\}. \tag{4.4}$$

As has been demonstrated in I, the potentials ω (denoted by $\bar{\varphi}$ in I) are determined up to arbitrary constants. The integral equations for the average force potentials remain valid when multiparticle interactions are taken into account if the substitution

$$\sum_{k=1}^{n} \phi_{i_k i_{n+1}} \to \sum_{m=0}^{n} \hat{C}_m^n \phi(\{m-1, l_{n+1}\})$$

is made.

If the normalization constants are chosen according to I, the potentials

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* In principle, the potentials $\varphi_{\{k\}}(\{n\})$ of the average forces exerted by the particles distributed within a group of k cells, which cannot be reduced to the sum of the one-cell potentials $\varphi_{\{1\}}(\{n\})$, should be also included into definition (4.1). Such a possibility is however not discussed here as well as a possibility to express the distribution functions by eq. (4.1) since the purpose of this work is the derivation of approximate expressions for the distribution functions.

$\omega_{\{1\}}(\{m\})$ become zero when any particle or a group of particles from the set $\{m+1\}$ moves to infinity. This defines the potentials uniquely and the correlation weakening conditions are automatically satisfied.

For the subsequent treatment it seems useful to rearrange relation (4.4) to a somewhat different form. For this purpose we introduce the notation

$$\Omega_{\{1\}}(\{k;r\}) = \sum_{s=0}^{k} \hat{C}_s^k \omega_{\{1\}}(\{s+r\}) \tag{4.5}$$

similarly to eq. (3.23).

Then with eq. (2.11) it will be found that

$$\sum_{m=0}^{n} \hat{C}_m^n \omega_{\{1\}}(\{m\}) = \sum_{r=0}^{n-k} \hat{C}_r^{n-k} \Omega_{\{1\}}(\{k;r\}). \tag{4.6}$$

In a similar way

$$\begin{gathered} \sum_{m=0}^{n} \hat{C}_m^n \epsilon(\{m\}) = \sum_{r=0}^{n-k} \hat{C}_r^{n-k} \pi(\{k;r\}), \\ \pi(\{k;r\}) = \sum_{s=0}^{k} \hat{C}_s^k \epsilon(\{s+r\}). \end{gathered} \tag{4.7}$$

Making use of the property (2.8) we write

$$\begin{aligned} &\hat{C}_1^{N-n} \hat{C}_r^{n-k} \Omega_{\{1\}}(\{k;r\}) \\ &\quad = \hat{C}_r^{n-k}[\Omega(\{k;r\}) - \hat{C}_1^{n-(k+r)} \Omega_{\{1\}}(\{k;r\})], \end{aligned} \tag{4.8}$$

where

$$\Omega(\{k;r\}) = \hat{C}_1^{N-(k+r)} \Omega_{\{1\}}(\{k;r\}). \tag{4.9}$$

With these notations eq. (4.4) becomes

$$\begin{aligned} F(\{n\}) = \exp\Bigg\{ \sum_{r=0}^{n-k} \hat{C}_r^{n-k} [\pi(\{k;r\}) + \psi(\{k;r\}) + \Omega(\{k;r\}) \\ - \hat{C}_1^{n-(k+r)} \Omega_{\{1\}}(\{k;r\})] \Bigg\}. \end{aligned} \tag{4.10}$$

The potentials $\psi(\{k;r\})$ are defined by eq. (3.23).

Before proceeding to the derivation of a chain of integro-differential equations for the distribution functions, it seems to be useful to find a recurrence relation between the derivatives of the potentials Ω. To this end, the operator L will be applied to eq. (3.17) for $m = 1$ with eq. (4.10) substituted into the left-hand side of the euqlaity and with the same relation substituted into the right-hand side, the only difference being that $(n+1)-k$ is used rather than $(n-k)$. With the aid of eq. (2.12) and after substituting r instead of $(r-1)$ it is found that

$$\sum_{r=0}^{n-k} \hat{C}_r^{n-k} \langle L[\hat{C}_1^{n-(k+r)} \Omega_{\{1\}}(\{k; r, l_{n+1}\}) + \Omega_{l_{n+1}}(\{k; r\}))\rangle_{\{k\}}$$

$$= \sum_{r=0}^{n-k} \hat{C}_r^{n-k} \langle L[\pi(\{k; r, l_{n+1}\}) + \psi(\{k; r, l_{n+1}\}) + \Omega(\{k; r, l_{n+1}\})]\rangle_{\{k\}}. \qquad (4.11)$$

Then use can be made of eq. (2.14) to get

$$\sum_{r=0}^{n-k} \hat{C}_r^{n-k} \hat{C}_1^{(n-k)-r} \Omega_{\{1\}}(\{k; r, l_{n+1}\})$$

$$= \sum_{r=0}^{n-k-1} \hat{C}_{r+1}^{n-k} \hat{C}_1^{r+1} \Omega_{\{1\}}(\{k; r, l_{n+1}\})$$

$$= \sum_{r=1}^{n-k} \hat{C}_r^{n-k} \hat{C}_1^{r} \Omega_{\{1\}}(\{k; r-1, l_{n+1}\}). \qquad (4.12)$$

With the last term in the left-hand side included, eq. (4.11) can be rewritten after an obvious transformation of indices

$$\sum_{r=0}^{n-k} \hat{C}_r^{n-k} \hat{C}_1^{r'} \langle L\Omega_{\{1\}}(\{k; r'-1\})\rangle_{\{k\}}$$

$$= \sum_{r=0}^{n-k} \hat{C}_r^{n-k} \langle L[\pi(\{k; r'\}) + \psi(\{k; r'\}) + \Omega(\{k; r'\})]\rangle_{\{k\}}, \quad \{r'\} = \{r, l_{n+1}\}. \qquad (4.13)$$

We now write down the first ($n = k$ and $n = k + 1$) equations from chain (4.13)

$$\langle L\Omega_{l_{k+1}}(\{k; 0\})\rangle_{\{k\}} = \langle L[\pi(\{k; l_{k+1}\}) + \psi(\{k; l_{k+1}\}) + \Omega(\{k; l_{k+1}\}))\rangle_{\{k\}}, \qquad (4.14)$$

$$\langle L\Omega_{l_{k+2}}(\{k; 0\})\rangle_{\{k\}} + \langle L[\Omega_{l_{k+1}}(\{k; l_{k+2}\}) + \Omega_{l_{k+2}}(\{k; l_{k+1}\})]\rangle_{\{k\}}$$

$$= \langle L[\pi(\{k; l_{k+2}\}) + \psi(\{k; l_{k+2}\}) + \Omega(\{k; l_{k+2}\})]\rangle_{\{k\}}$$

$$+ \langle L[\pi(\{k; l_{k+1} l_{k+2}\}) + \psi(\{k; l_{k+1} l_{k+2}\}) + \Omega(\{k; l_{k+1} l_{k+2}\})]\rangle_{\{k\}}. \qquad (4.15)$$

Any particle which does not belong to the set $\{k\}$ may be taken as the l_{k+1}th particle in eq. (4.14) ($l_{k+1} \notin \{k\}$). Therefore the expressions in the first brackets in the right- and left-hand sides of eq. (4.15) cancel against each other. Continuing this procedure, we find for arbitrary $n = k + s$

$$\hat{C}_1^{s} \langle L\Omega_{\{1\}}(\{k; s-1\})\rangle_{\{k\}} = \langle L[\pi(\{k; s\}) + \psi(\{k; s\}) + \Omega(\{k; s\})]\rangle_{\{k\}}. \qquad (4.16)$$

In order to eliminate π, eq. (4.16) is integrated with respect to the variables of a set of particles $\{k\}$ and the resultant relation is subtracted from eq. (4.16). This leads to the desired recurrence relation

$$\hat{C}_1^{s} \langle \Delta L\Omega_{\{1\}}(\{k; s-1\})\rangle_{\{k\}} = \langle \Delta L[\psi(\{k; s\}) + \Omega(\{k; s\})]\rangle_{\{k\}}. \qquad (4.17)$$

So, for $k = 1$ and $s = 1, 2$, eq. (4.17) becomes

$$[\Delta L\omega_{l_2}(l_1)]F(l_1) = \left\langle \Delta L\left\{\phi(l_1l_2) + \sum_{l_3\neq l_1l_2} [\omega_{l_3}(l_1l_2) + \omega_{l_3}(l_2)]\right\}\right\rangle_{l_1};$$

$$\langle \Delta L[\omega_{l_3}(l_1l_2) + \omega_{l_3}(l_2) + \omega_{l_2}(l_1l_3) + \omega_{l_2}(l_3)\rangle_{l_1}$$
$$= \langle \Delta L\{\phi(l_1l_2l_3) + \phi(l_2l_3) + \sum_{l_4\neq l_1l_2l_3} [\omega_{l_4}(l_1l_2l_3) + \omega_{l_4}(l_2l_3)]\}\rangle_{l_1}. \tag{4.18}$$

If potential energy U_N contains interactions of an order not higher than t (see eq. (3.2)), for $s \geqslant t$, relation (4.17) is simplified to

$$\hat{C}_1^s\langle \Delta L\Omega_{\{1\}}(\{k; s-1\})\rangle_{\{k\}} = \langle \Delta L\Omega(\{k; s\})\rangle_{\{k\}}. \tag{4.19}$$

With the new form (4.10) for the distribution functions and the recurrence relation (4.17) for the average force potentials we can proceed to the evaluation of the particle distribution functions $F(\{n\})$. Applying the operator C to eq. (4.17) and using the property (2.14) and the definition (4.9), we find in the left-hand side

$$\hat{C}_s^{N-k}\hat{C}_1^s\Omega_{\{1\}}(\{k; s-1\}) = \hat{C}_{s-1}^{N-k}\hat{C}_1^{N-k-(s-1)}\Omega_{\{1\}}(\{k; s-1\})$$
$$= \hat{C}_{s-1}^{N-k}\Omega(\{k; s-1\}). \tag{4.20}$$

After summing the resultant relation with respect to s from 1 to m and subtracting equal terms in the left- and right-hand sides of the equation, we find

$$[\Delta L\Omega(\{k; 0\})]F(\{k\})$$
$$= \sum_{s=1}^{m} \hat{C}_s^{N-k}\langle \Delta L\psi(\{k; s\})\rangle_{\{k\}} + \hat{C}_m^{N-k}\langle \Delta L\Omega(\{k; m\})\rangle_{\{k\}}. \tag{4.21}$$

Then $n = k$ is substituted into eq. (4.10) and after applying the operator L we find

$$LF(\{k\}) = \{L[\pi(\{k; 0\}) + \psi(\{k; 0\}) + \Omega(\{k; 0\})]\}F(\{k\}). \tag{4.22}$$

Now we integrate eq. (4.22) with respect to the coordinates of the set $\{k\}$. Then the left-hand side becomes zero (because of the normalization of the distribution functions to unity if $L = L_\alpha$ or because of the conditions of space symmetry if $L = L_k$), i.e.

$$\langle L[\pi(\{k; 0\}) + \psi(\{k; 0\}) + \Omega(\{k; 0\})]\rangle = 0. \tag{4.23}$$

Subtracting eq. (4.23) from eq. (4.22) gives

$$LF(\{k\}) = \{\Delta L[\psi(\{k; 0\}) + \Omega(\{k; 0\})]\}F(\{k\}). \tag{4.24}$$

Using eq. (4.21) and transforming the indices results in a chain of the integro-differential equations for the distribution functions

$$LF(\{n\}) = \sum_{s=0}^{m} \hat{C}_s^{N-n} \langle \Delta L \psi(\{n; s\}) \rangle_{\{n\}} + \hat{C}_m^{N-n} \langle \Delta L \Omega(\{n; m\}) \rangle_{\{n\}}. \tag{4.25}$$

For $m \geqslant t$ the potentials Ω should satisfy the relations

$$\langle \Delta L \Omega(\{n; m\}) \rangle_{\{n\}} = 0, \quad m \geqslant t, \tag{4.26}$$

as follows from the comparison of expression (4.25) with the exact equation (3.24).

When conditions (4.26) are observed in the formulation of a closed set of the equations for the distribution functions or the average force potentials, the compatibility of the integro-differential chain (4.25) with the normalization equation chain (3.17) is ensured.

5. Thermodynamic compatibility

Now let us use relation (4.16) taking $k = 0$ and $L = L_\alpha$. Then, with

$$\begin{aligned} &\Omega_{\{1\}}(\{0; s\}) = \omega_{\{1\}}(\{s\}), \\ &\Omega(\{0, s\}) = \omega(\{s\}) = \hat{C}_1^{N-s} \omega_{\{1\}}(\{s\}), \\ &\pi(\{0; s\}) = \epsilon(\{s\}), \quad \psi(\{0, s\}) = \phi(\{s\}) \end{aligned} \tag{5.1}$$

eq. (4.16) may be written as

$$\hat{C}_1^{s} \langle L_\alpha \omega_{\{1\}}(\{s-1\}) \rangle = \langle L_\alpha [\epsilon(\{s\}) + \phi(\{s\}) + \omega(\{s\})] \rangle. \tag{5.2}$$

Applying the operator C_s^N to this relation, and summing with respect to s from 1 to m and using eq. (2.14) one gets

$$0 = \sum_{s=0}^{m} \hat{C}_s^N \langle L_\alpha [\epsilon(\{s\}) + \phi(\{s\})] \rangle + \hat{C}_m^N \langle L_\alpha \omega(\{m\}) \rangle. \tag{5.3}$$

The quantities $\epsilon(\{s\})$ are independent of the particle coordinates. Therefore, when multiparticle interactions of order higher than m are neglected, eq. (5.3) leads to the following expression for the first thermodynamic derivatives of the free energy

$$F_\alpha^{(m)} = \sum_{s=0}^{m} \hat{C}_s^N \langle L_\alpha \phi(\{s\}) \rangle = -L_\alpha \sum_{s=0}^{m} \hat{C}_s^N \epsilon(\{s\}) - \hat{C}_m^N \langle L_\alpha \omega(\{m\}) \rangle. \tag{5.4}$$

If the maximum order of the multiparticle interactions included is t and $m \geqslant t$, relation (5.4) becomes

$$F_\alpha = -L_\alpha \sum_{s=0}^{m} \hat{C}_s^N \epsilon(\{s\}) - \hat{C}_m^N \langle L_\alpha \omega(\{m\}) \rangle, \quad m \geqslant t. \tag{5.5}$$

The above equation can be integrated, if the last term in the right-hand side $\hat{C}_m^N\langle L_\alpha\omega(\{m\})\rangle$ is expressed as a derivative with respect to α of some function of the thermodynamic variables. The simplest truncation approximation which provides thermodynamic compatibility of the free energy and its first derivatives is the relation

$$\omega_{l_{m+1}}(\{m\}) = 0, \quad m \geqslant 2. \tag{5.6}$$

This very approximation was considered in I. In this case the free energy is given by the expression

$$F = -\sum_{s=0}^{m} \hat{C}_s^N \epsilon(\{s\}), \tag{5.7}$$

which is in agreement both with the results for $m = 2$ (see refs. 2 and 8) and $m = 3$ (see ref. 10, upon the corresponding redefinition of Q in terms of ϵ).

Let us now take the second thermodynamic derivatives of the free energy, considering only pairwise interparticle interactions ($t = 2$). In this case eq. (3.13) may be rewritten as

$$\begin{aligned} F_{\alpha\beta} = \hat{C}_2^N\{&\langle L_\alpha L_\beta\phi(l_1l_2)\rangle + \langle\Delta L_\alpha\phi(l_1l_2)\Delta L_\beta[\phi(l_1l_2) \\ &+ \hat{C}_1^{N-2}(\phi(l_1l_3) + \phi(l_2l_3)) + \hat{C}_2^{N-2}\phi(l_3l_4)]\rangle\}. \end{aligned} \tag{5.8}$$

Here the operator C_2^N acts on the indices (l_1, l_2) and the operators C_1^{N-2} and C_2^{N-2} on the indices (l_3, l_4). Relation (5.8) expresses $F_{\alpha\beta}$ in terms of two-, three- and four-particle distribution functions.

Applying the operator L_β to eq. (5.4) and keeping in mind that $t = 2$, we obtain on the one hand

$$F_{\alpha\beta} = -L_\alpha L_\beta \sum_{s=0}^{m} \hat{C}_s^N \epsilon(\{s\}) - \hat{C}_m^N L_\beta\langle L_\alpha\omega(\{m\})\rangle, \tag{5.9}$$

and on the other hand

$$\begin{aligned} F_{\alpha\beta} = \hat{C}_2^N L_\beta\langle L_\alpha\phi(\{2\})\rangle &= \hat{C}_2^N\langle L_\alpha L_\beta\phi(l_1l_2)\rangle \\ &+ \hat{C}_2^N\langle L_\alpha\phi(l_1l_2)L_\beta \ln F_{11}^{(1)}(l_1l_2)\rangle. \end{aligned} \tag{5.10}$$

The use of eq. (4.25) for $n = 2$ brings relation (5.10) to the form

$$\begin{aligned} F_{\alpha\beta} = \hat{C}_2^N\{&\langle L_\alpha L_\beta\phi(l_1l_2)\rangle + \langle\Delta L_\alpha\phi(l_1l_2)\Delta L_\beta[\phi(l_1l_2) \\ &+ \hat{C}_1^{N-2}(\phi(l_1l_3) + \phi(l_2l_3)) + \hat{C}_2^{N-2}\phi(l_3l_4)]\rangle \\ &+ \hat{C}_m^{N-2}\langle\Delta L_\alpha\phi(l_1l_2)\Delta L_\beta\Omega(l_1l_2;\{m\})\rangle\}. \end{aligned} \tag{5.11}$$

When conditions (4.26) are valid, the last term in eq. (5.11) is zero and the other terms are the same as in the exact relation (5.8). But in a general case it can be found from the comparison of eq. (5.11), (5.9) and (5.8) that

$$F_{\alpha\beta} = -L_\alpha L_\beta \sum_{s=0}^{m} \hat{C}_s^N \epsilon(\{s\}) - \hat{C}_m^N L_\beta \langle L_\alpha \omega(\{m\})\rangle$$
$$- \hat{C}_2^N \hat{C}_m^{N-2} \langle \Delta L_\alpha \phi(\{2\}) \Delta L_\beta \Omega(\{2; m\})\rangle. \tag{5.12}$$

The above relation can be integrated if the last term in the right-hand side becomes zero and moreover the conditions of integrability of the first derivatives are observed. In this case the free energy and its first and second derivatives calculated with the approximate junior correlation functions will be mutually consistent.

6. Discussion

First, let us discuss a possibility of making relations (3.17), (4.25), (5.5) and (5.11) compatible. As has been emphasized, the normalization conditions were adopted as a starting point and the approximations under discussion should not violate these conditions. When this is not the case, not all the resultant relations would remain valid after introducing the approximations. The approach suggested in I to the derivation of a closed system of integral equations for the average force potentials, ensures the validity of the normalization relations and the correlation weakening conditions.

The condition

$$\hat{C}_m^N \langle L_\alpha \omega(\{m\})\rangle = L_\alpha B(T, \bar{v}) \tag{6.1}$$

is most important for thermodynamic compatibility of the results. Here B is some function of the thermodynamic variables. If eq. (6.1) is satisfied, the energy and pressure equations will be compatible.

In order to preserve the validity of the integro-differential chain up to the nth equation, conditions (4.26) must be observed and that provides also the compatibility of the thermodynamic derivatives of the free energy up to a certain order. For example, eq. (5.12) would be integrable, if, besides equations (6.1), conditions (4.26) for $n = 2$ and $m \geqslant 2$ are fulfilled. If multiparticle interactions are considered, i.e. $t > 2$, the relations for $F_{\alpha\beta}$ become more complicated and their compatibility requires the values $n = t$ and $m \geqslant t$. In other words, the chain should be truncated at a stage corresponding to the $(2t)$-particle distribution function or a higher one.

Let us consider the truncation procedure (5.6), which was discussed earlier in more detail. Condition (6.1) is observed and $B = 0$ so that truncation at an arbitrary level provides thermodynamic compatibility at the level of the first derivatives of the free energy. In order to satisfy the first equation of the chain (4.25) ($n = 1$) the following condition should be fulfilled

$$\langle \Delta L \hat{C}_1^{N-m}[\omega_{\{1\}}(\{l_1, m-1\}) + \omega_{\{1\}}(\{m-1\})]\rangle_{l_1} = 0, \qquad l_1 \notin \{m-1\}, \quad l_1 \in \{m\}. \tag{6.2}$$

For $L = L_1$ condition (6.2) is satisfied by approximation (5.6) (since $L_1\omega_{\{1\}}(\{m-1\}) = 0$) and the first equation of the integro-differential chain appears to be compatible with the results mentioned in this section.

If, however, $L = L_\alpha$, the second term remains in the square brackets of eq. (6.2) after adopting approximation (5.6), and condition (6.2) will be violated so that the first equation of the integro-differential chain composed with the derivatives with respect to the thermodynamic variables would not be compatible with the chain of the integral normalization relations and the thermodynamic results.

Next we consider the case $n = 2$. Relation (4.26) becomes

$$\begin{aligned}&\langle \Delta L \hat{C}_1^{N-m}[\omega_{\{1\}}(\{l_1 l_2, m-2\}) + \omega_{\{1\}}(\{l_1, m-2\}) \\ &\quad + \omega_{\{1\}}(\{l_2, m-2\}) + \omega_{\{1\}}(\{m-2\})]\rangle_{l_1 l_2} = 0.\end{aligned} \tag{6.3}$$

For $L = L_1$ eq. (6.3) contains the same combination of potentials as in eq. (6.2) with $L = L_\alpha$ (the two last terms are cancelled by the operator L_1).

Let us consider also a possibility of making the second derivatives (5.12) compatible with the other relations. The minimum value of m which allows for such compatibility is two. Relation (4.26) then becomes

$$\left\langle \Delta L \sum_{l_5 \neq l_1 l_2 l_3 l_4} [\omega_{l_5}(l_1 l_2 l_3 l_4) + \omega_{l_5}(l_1 l_3 l_4) + \omega_{l_5}(l_2 l_3 l_4) + \omega_{l_5}(l_3 l_4)] \right\rangle_{l_1 l_2} = 0 \tag{6.4}$$

and together with the two other relations

$$\begin{aligned}&\left\langle \Delta L \sum_{l_5 \neq l_1 l_2 l_3 l_4} [\omega_{l_5}(l_1 l_2 l_3 l_4) + \omega_{l_5}(l_2 l_3 l_4)] \right\rangle_{l_1} = 0, \\ &\left\langle L_\alpha \sum_{N \geqslant l_5 > l_4 > \cdots > l_1 \geqslant 1} \omega_{l_5}(l_1 l_2 l_3 l_4) \right\rangle = L_\alpha B(T, \bar{v}).\end{aligned} \tag{6.5}$$

we have a set of the integro-differential equations, which, being satisfied, provides compatibility of the two first equations of the integro-differential chain and the first and the second thermodynamic derivatives of the free energy. Indeed, eqs. (6.4) and (6.5) together with the integral iterative equations for ω is too complicated even for the present-time computers. However, the compatibility of the first derivatives and the first equations of the integro-differential chain which is achieved when the conditions

$$\begin{aligned}&\left\langle \Delta L \sum_{l_4 \neq l_1 l_2 l_3} [\omega_{l_4}(l_1 l_2 l_3) + \omega_{l_4}(l_2 l_3)] \right\rangle_{l_1} = 0, \\ &\left\langle L_\alpha \sum_{N \geqslant l_4 > l_3 > l_2 > l_1 \geqslant 1} \omega_{l_4}(l_1 l_2 l_3) \right\rangle = L_\alpha B(T, \bar{v})\end{aligned} \tag{6.6}$$

are fulfilled, is already a realistic problem. Moreover, with such a truncation the normalization relations between the three junior distribution functions and the second equation of the integro-differential chain at $L = L_1$ are satisfied. It should be noted that since the equation set involves a three-particle distribution function, also three-particle (alongside with the two-particle) interactions $\phi(\{3\})$ can be taken into account and this does not actually introduce additional complications to the computer solution of this problem.

Some idea of the accuracy of approximation (5.6) may be gained from the comparison of the computed values of $\epsilon(\{1\}) = \epsilon_1$, $\epsilon(\{2\}) = \epsilon_{1i}$ and $\epsilon(\{3\}) = \epsilon_{1ij}$. The integro-differential chain was truncated at the first equation ($\omega_{\{1\}}(\{2\}) = 0$). The average force potentials were assumed cylindrically symmetrical with respect to the axis connecting the centers of the cells v_1 and v_i. The potentials $\omega_{\{1\}}(\{1\}) = \omega_i(\boldsymbol{q}^1)$ were calculated with the iterative procedure described in refs. 2 and 8. There the molecular cell centers were placed at the sites of a face-centered lattice, and the values of the temperature ($\theta = k_B T/\epsilon = 1$) and the molecular volume* corresponded to the range of existence of the crystal. The pairwise interparticle interaction was described by the Lennard-Jones potential (6–12).

The average force potentials $\omega_i(\boldsymbol{q}^1)$ were determined only for the nearest neighbours; the second and the third neighbours were fixed at the centers of the corresponding cells, and the average force potentials were assumed to be equal to the point interaction potentials. The computed values ϵ_1, ϵ_{1i} and ϵ_{1ij} are presented in table I. Since the thermodynamic properties are invariant under the symmetry transformations of the crystal lattice, ϵ_1 is the same for all the cells; ϵ_{1i} are equal for all the nearest neighbours and for more remote neighbours they are approximately the same as the point interaction potential between the particles at the centers of the corresponding cells; ϵ_{1ij} are different from zero only when the cells v_1 and v_i are nearest neighbours of the cell v_j. There are four different configurations of the three cells for which the angles between the lines connecting the cell centers $v_j - v_1$ and $v_j - v_i$ are equal to $\gamma_1 = \pi$, $\gamma_2 = 2\pi/3$, $\gamma_3 = \pi/2$, $\gamma_4 = \pi/3$, consistent with the mentioned condition.

In the calculation of ϵ_{1ij} together with $\omega_{\{1\}}(\{2\})$ it was also assumed that $\omega_{\{1\}}(\{3\}) = 0$. This resulted however in the violation of the normalization of the three-particle distribution functions and the deviation of ϵ_{1ij} from zero is a quantitative measure of the violation. The data presented in the table demonstrate that the ϵ_{1ij} values amount to hundredths of unity except the configuration at $\gamma = \pi/3$ (all the three particles are nearest neighbours) and the case of not too small volumes v. A self-consistent procedure of calculation of the

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* The values of temperature and volume are reduced to the parameters ϵ and σ of the potential.

TABLE I

$\bar{v}$		0.90	0.94	0.98	1.00	1.02	1.06	1.10
ϵ_1		−1.25	−2.37	−3.11	−3.36	−3.56	−3.82	−3.60
ϵ_{1i}		0.284	0.383	0.440	0.457	0.468	0.475	0.464
ϵ_{1ij}	γ_1	0.1857	0.1240	0.0799	0.0628	0.0486	0.0265	0.0104
	γ_2	0.1444	0.1097	0.0828	0.0725	0.0628	0.0505	0.0411
	γ_3	0.0329	0.0303	0.0288	0.0284	0.0283	0.0284	0.0296
	γ_4	−0.5030	−0.3322	−0.2523	−0.2247	−0.2013	−0.1647	−0.1630

potentials $\omega_{\{1\}}(\{2\})$ at consistent truncation ($\omega_{\{1\}}(\{3\}) = 0$, $\omega_{\{1\}}(\{2\}) \neq 0$, $\omega_{\{1\}}(\{1\}) \neq 0$) would probably give somewhat reduced values of ϵ_{1ij} as compared with the data presented in the table.

As is known[14]), near the melting line there is quite a wide range for which the perturbation theory employing the crystal energy series expansion with respect to the particle displacements from the lattice sites and its various modifications are not valid. However, in that very range the approach under consideration gives the most satisfactory results.

In conclusion it seems worthwhile to consider the situation connected with a one-dimensional model system involving pairwise interactions of only the nearest neighbours. Truncation of the chain of equations by the assumption $\omega_{\{1\}}(\{2\}) = 0$ and subsequent application of the iteration procedure with $\omega_{\{1\}}(\{1\}) = 0$ as the zeroth approximation lead to exact expressions for the free energy of the system and the unary distribution function. Exact expressions for multiparticle distribution functions will also be obtained only if all the particles under consideration form a chain of the nearest neighbours. If, however, the two particles considered are not nearest neighbours, the binary function becomes equal to the product of two unary functions and is already inexact.

The number of iterations necessary to achieve the solution of the iterative equation gives an idea on the correlation length in the system. So, for $\bar{v} = 0.9\sigma^3$ and $\theta = 1$ the solution with an accuracy of $\approx 10^{-4}$ has required ≈ 100 iterations and the correlation length was of the order of 100σ. This example clearly shows that with the assumption $\omega_{\{1\}}(\{2\}) = 0$ the long-range correlations are included into the expressions for the thermodynamic quantities but do not manifest themselves adequately in the behaviour of the multiparticle distribution functions.

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