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Perturbation theory for correlation functions of non-ideal systems

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Abstract. The paper is concerned with the development of perturbation theory for non-ideal systems of particles. An approach similar to cluster expansions is used. The given perturbation theory can be used when the disturbance of the interaction potential $\Delta\phi$ is higher than kT but is of a short-range nature.

1. Introduction

The thermodynamic perturbation theory for the correlation functions of weakly non-ideal systems was developed by Mayer and Montroll (1941) and De Boer (1948). These studies were based on the method of cluster expansion, and an ideal gas was selected as a reference system.

With the development of analytical and numerical methods it became possible to build up a perturbation theory of non-ideal systems, in which the results obtained for non-ideal systems of particles with a model interaction potential were used as a reference system. The model interaction potential can be short-range, long-range or of a general nature. There are various modifications of the perturbation theory for non-ideal systems depending on the selection of zero approximation (see for example Bazarov 1957, Ebeling *et al* 1966, Gubbins *et al* 1971, Fulinski 1972, Lado 1974).

The correlation functions of a system of hard spheres are mainly used as zero approximation for neutral liquids (Gubbins *et al* 1971). The corrections due to the Lennard-Jones potential were found by expanding in the Taylor series. Two types of corrections were obtained; one associated with the difference between the repulsive part of the Lennard-Jones and the hard-sphere potential, the other connected with the attractive part of the Lennard-Jones potential. In this case the part of the potential describing the attraction of the particles is considered as a small disturbance with respect to kT .

Another method was proposed in the work by Lado (1974). The integral equation for the disturbing correction of the correlation function was obtained from integral equations of the Percus-Yevick type and convolution hypernetted chains (CHNC) were used for the reference and disturbing systems.

The perturbation theory for correlation functions has also been considered for both plasmas and electrolytes. In the work by Ebeling *et al* (1966) a chain of equations BBGKY for correlation functions is used to study the disturbance due to the short-range part of the potential. Bazarov (1957) uses the approach associated with expansion by

functional derivatives of the function $f(r) = \exp(-\beta\Delta\phi) - 1$ (where $\beta = 1/kT$ is the inverse temperature, $\Delta\phi$ is the potential disturbance and $f(r) \ll 1$).

Modern high-speed electronic computers make it possible to use the method of molecular dynamics and the Monte-Carlo method for accurate analysis of correlation functions of standard model non-ideal systems of particles whose interaction potentials include both the short-range and long-range parts. In this case the correlation functions calculated with the help of computers can be taken as the zero approximation of the perturbation theory. The corrections associated with the potential variation are defined by the perturbation theory. The potential variations are usually of a short-range nature, since the short-distance potential parts are not adequately known, whereas the behaviour of the large-distance potential parts is always known much more accurately.

In the present paper an approach associated with cluster expansion is used to build up a perturbation theory for correlation functions. The developed perturbation theory is applicable when the potential change is short-range but not small compared to kT . A similar formulation of the problem is to be found in a paper by Zelener *et al* (1976) dealing with the perturbation theory for thermodynamic values.

2. The perturbation theory for a single-component system

Let us consider two systems, each consisting of N identical particles with coordinates \mathbf{q}_i in thermodynamic equilibrium in a volume V at a temperature T . Let the potential of interaction between the particles in one system be ϕ and in the other system ϕ^0 . In this case we have

$$\Delta\phi(r) = \phi(r) - \phi^0(r)$$

where the potentials include both short-range and long-range parts. For the system with ϕ the correlation function has the following form:

$$g_N(q)_m = N!v^m[(N-m)!Q_N]^{-1} \int_V \dots \int_V \exp\left(-\beta \sum_{i<j} \phi_{ij}\right) d(q)_{N-m} \quad (1)$$

where $(q)_m = (q_1, \dots, q_m)$, $(q)_{N-m} = (q_{m+1}, \dots, q_N)$, $v = V/N$, $\beta = 1/kT$ is the inverse temperature, $\phi_{ij} = \phi(|\mathbf{q}_i - \mathbf{q}_j|)$, and $Q_N = \int_V \dots \int_V \exp(-\beta \sum_{i<j} \phi_{ij}) d(q)_N$. The index N of the correlation function means that we consider a prior-limit expression for the correlation function.

Introducing the functions f_{ij} similar to the Mayer functions

$$f_{ij} = f(r_{ij}) = \exp(-\beta\Delta\phi_{ij}) - 1$$

we can rewrite expression (1) in the following manner:

$$g_N(q)_m = N!v^m \prod_{i<j}^m (1+f_{ij}) [(N-m)!Q_N]^{-1} \int_V \dots \int_V \exp\left(-\beta \sum_{i<j} \phi_{ij}^0\right) \times \prod_{i<j}'^N (1+f_{ij}) d(q)_{N-m} \quad (2)$$

where the prime following the product symbol indicates that the product has no factors containing f_{ij} , in which i and j are at the same time less than or equal to m .

Let us develop the product $\prod_{i < j}^{N'} (1 + f_{ij})$; then we obtain

$$g_N(q)_m = (Q_N^0 / Q_N) \prod_{i < j}^m (1 + f_{ij}) \sum_{n=0}^{N-m} (v^n n!)^{-1} \int_V \dots \int_V g_N^0(q)_m, (q)_n \times \left(\sum_{x_{m+n}}' \prod_{x_{m+n}} f_{ij} \right) d(q)_n \tag{3}$$

where $Q_N^0 = \int_V \dots \int_V \exp(-\beta \sum_{i < j} \phi_{ij}^0) d(q)_N$, and $(q)_n = (q_{m+1}, \dots, q_{m+n})$. The primed sum includes all possible products of the factors f_{ij} . Each product must be dependent on all the coordinates $(q)_n$, but no product may have factors containing f_{ij} , where i and j are at the same time less than or equal to m ($1 \leq i < j \leq N$). The other coordinates $(q)_{N-(m+n)}$ can be used for the integration. So the result is expressed in terms of $g_N^0(q)_m, (q)_n$. As the integrals do not depend on the numbering of the coordinates, one must multiply by a factor $(N - m)! / [(N - m - n)! n!]^{-1}$.

Further transformations can be done by using an algebraic method due to Ruelle (1964). However for our purposes this method should be somewhat modified. Let us consider the finite-dimensional vector space A_{N-m+1} of sequences ψ :

$$\psi = \{ \psi[(q)_m, (q)_0], \psi[(q)_m, (q)_1], \dots, \psi[(q)_m, (q)_{N-m}] \}$$

such that for each m and n ($n = 0, \dots, N - m$) $\psi[(q)_m, (q)_n]^\dagger$ is a bounded Lebesgue measurable function on V^{m+n} . It will be convenient also to write

$$\psi[(q)_m, (q)_n] = \psi[(q)_m, Q] = \psi[\mathbf{q}_1, \dots, \mathbf{q}_m, \mathbf{q}_{m+1}, \dots, \mathbf{q}_{m+n}].$$

Now let us define a product of sequences η , and $\psi \in A_{N-m+1}$ (Ruelle 1964):

$$\eta * \psi[(q)_m, Q] = \sum_{R \subset Q} \eta[(q)_m, Q \setminus R] \psi[(q)_m, R] \tag{4}$$

where the summation extends over all subsequences R of Q and $Q \setminus R$ is the subsequence of Q obtained by striking out the elements of R in Q . The sum includes $\sum_{k=0}^n n! [k!(n-k)!]^{-1} = 2^n$ terms.

Let us consider the $N - m + 1$ projections (Halmos 1958):

$$P_k \psi = \{ 0, 0, \dots, \psi[(q)_m, (q)_k], 0, \dots, 0 \} \quad (k = 0, \dots, N - m).$$

It is easily seen that $P_k P_k = P_k$. So we get

$$\eta * P_k \psi[(q)_m, Q] = \theta(n - k) \sum_{R_k \subset Q} \eta[(q)_m, Q \setminus R_k] \psi[(q)_m, R_k]. \tag{5}$$

Here we use the θ function; it is defined by $\theta(i) \equiv 0$ for $i < 0$ and $\theta(i) \equiv 1$ for $i \geq 0$ and R_k is $(\mathbf{q}_{j_1}, \dots, \mathbf{q}_{j_k})$ ($j_1 < \dots < j_k$). For instance

$$\begin{aligned} \eta * P_0 \psi &= \{ \eta[(q)_m, (q)_0] \psi[(q)_m, (q)_0], \dots, \eta[(q)_m, (q)_{N-m}] \psi[(q)_m, (q)_0] \} \\ \eta * P_1 \psi &= \left\{ 0, \eta[(q)_m, (q)_0] \psi[(q)_m, (q)_1], \dots, \sum_{R_1 \subset (q)_{N-m}} \eta[(q)_m, Q \setminus R_1] \psi[(q)_m, R_1] \right\} \\ &\vdots \\ \eta * P_{N-m} \psi &= \{ 0, 0, \dots, 0, \eta[(q)_m, (q)_0] \psi[(q)_m, (q)_{N-m}] \}. \end{aligned}$$

$^\dagger \psi[(q)_m, (q)_n] = D_{(q)_m} \psi(q)_n$ (Ruelle 1969).

If ψ is the unit element $\psi = \{1, 0, 0, \dots, 0\}$ then $\eta * P_0 \psi = \eta$ and $\eta * P_k \psi = 0$ for $k > 0$.

Now let us consider the sequence $w = \{w[(q)_m, (q)_0], \dots, w[(q)_m, (q)_{N-m}]\}$ where $w[(q)_m, (q)_0] = g_N^0(q)_m$ and $w[(q)_m, (q)_n] = g_N^0[(q)_m, (q)_n] (\sum'_{X_{m+n}} \prod_{X_{m+n}} f_{ij})$ for $n = 1, \dots, N-m$. The prime following the sum means that the summation extends over all products $\prod_{X_{m+n}} f_{ij}$ depending on all the coordinates $(q)_n$, but the products have no factors containing f_{ij} , in which i and j are at the same time less than or equal to m .

Let us consider the set of $N-m+1$ sequences $\eta^l (l = 0, \dots, N-m)$ of the following form: $\eta^l = \{1, 0, \eta^l(q)_2, \dots, \eta^l(q)_{N-m}\}$. Thus none of the functions $\eta^l(q)_n$ depend on coordinates $(q)_m$ and $\eta^l(q)_n = \theta(N-m-l-n) \tilde{\eta}^l(q)_n$, where $\tilde{\eta}^l(q)_n = g_{N-m-l}^0(q)_n \times (\sum_{X_n} \prod_{X_n} f_{ij})$, g_{N-m-l}^0 is the correlation function of the system consisting of $N-m-l$ identical particles with interaction potentials ϕ^0 ; the sum indicates that the summation extends over all products $\prod_{X_n} f_{ij}$ depending on all the coordinates $(q)_n$. Notice that for $n > N-m-l$, $\eta^l(q)_n \equiv 0$. Now consider a sequence of unknown functions $u = \{u[(q)_m, (q)_0], \dots, u[(q)_m, (q)_{N-m}]\}$.

The equation $w = \sum_{k=0}^{N-m} (\eta^k * P_k u)$ defines a single sequence u which is easily seen from the coordinate form of this equation:

$$\begin{aligned}
 w[(q)_m, (q)_0] &= u(q)_m \\
 w[(q)_m, (q)_1] &= u[(q)_m, (q)_1] \\
 w[(q)_m, (q)_2] &= \tilde{\eta}^0(q)_2 u(q)_m + u[(q)_m, (q)_2] \\
 w[(q)_m, (q)_3] &= \tilde{\eta}^0(q)_3 u(q)_m + \sum_{R_1 \subset (q)_3} \tilde{\eta}^1[(q)_3 \setminus R_1] u[(q)_m, R_1] + u[(q)_m, (q)_3] \\
 &\vdots \\
 w[(q)_m, (q)_n] &= \sum_{k=0}^{N-m} \theta(n-k) \sum_{R_k \subset Q} \theta(N-m-n) \tilde{\eta}^k[Q \setminus R_k] u[(q)_m, R_k] \tag{6} \\
 &\vdots \\
 w[(q)_m, (q)_{N-m}] &= \tilde{\eta}^0(q)_{N-m} u(q)_m + \sum_{R_1 \subset (q)_{N-m}} \eta^1[(q)_{N-m} \setminus R_1] u[(q)_m, R_1] + \dots \\
 &\quad + u[(q)_m, (q)_{N-m}]
 \end{aligned}$$

Each new unknown function $u[(q)_m, (q)_n]$ appears in a new equation, therefore, we may easily invert (6).

Let us define the polynomial $w\{(q)_m, t\}$ in a variable t :

$$w\{(q)_m, t\} = g_N^0(q)_m + \sum_{n=1}^{N-m} t^n w_n^m / n!$$

where $w_n^m = \int_V \dots \int_V w[(q)_m, (q)_n] d(q)_n$. If $t = v^{-1}$ then we obtain

$$g_N(q)_m = (Q_N^0 / Q_N) \prod_{i < l} (1 + f_{ij}) w\{(q)_m, v^{-1}\}.$$

We can rewrite this expression in the following form:

$$g_N(q)_m = (Q_N^0/Q_N) \prod_{i<j}^m (1+f_{ij}) \sum_{n=0}^{N-m} (v^n n!)^{-1} \sum_{k=0}^{N-m} \theta(n-k) n! [k!(n-k)!]^{-1} \\ \times \theta(N-m-n) \tilde{\eta}_{n-k}^k u_k^m \\ = \prod_{i<j}^m (1+f_{ij}) \sum_{k=0}^{N-m} (v^k k!)^{-1} u_k^m [Q_{N-m-k} Q_N^0 / Q_N Q_{N-m-k}^0]$$

where

$$u_k^m = \int_V \dots \int_V u[(q)_m, (q)_k] d(q)_k, \quad \tilde{\eta}_{n-k}^k = \int_V \dots \int_V \tilde{\eta}^k(q)_{n-k} d(q)_{n-k}$$

and we use

$$\int_V \dots \int_V d(q)_{N-m-k} \exp\left(-\beta \sum_{i<j}^{N-m-k} \phi_{ij}^0\right) \\ \times \left[\sum_{l=0}^{N-m-k} (N-m-k)! [l!(N-m-k-l)!]^{-1} \left(\sum_{X_l} \prod f_{ij}\right) \right] = Q_{N-m-k}.$$

Using the cluster integrals \mathcal{C}_k^m :

$$\mathcal{C}_k^m = u_{k-1}^m / k!$$

we have for the correlation functions

$$g_N(q)_m = \prod_{i<j}^m (1+f_{ij}) \sum_{k=1}^{N-m+1} k \mathcal{C}_k^m [Q_{N-m-k+1} Q_N^0 / Q_N Q_{N-m-k+1}^0]$$

At $N \rightarrow \infty, V \rightarrow \infty, V/N = v$ the expression $Q_{N-1} N! / Q_N (N-1)!$ does not depend on N and is equal to activity (Isihara 1971), therefore when approaching the thermodynamic limit $g_N(q)_m$ assumes the forms:

$$g(q)_m = v^m \prod_{i<j}^m (1+f_{ij}) \sum_{k=1}^{\infty} k \bar{\mathcal{C}}_k^m s^{m+k-1} \tag{7}$$

where

$$s = z/z_0 v, \quad z_0 = Q_{N-1}^0 N! / Q_N^0 (N-1)!; \quad \bar{\mathcal{C}}_k^m = \lim_{\substack{V \rightarrow \infty \\ N \rightarrow \infty \\ v = V/N}} \mathcal{C}_k^m.$$

Using relation (7) at $m = 1$ we get

$$v^{-1} = \sum_{k=1}^{\infty} k \bar{\mathcal{C}}_k^1 s^k. \tag{8}$$

Since $\bar{\mathcal{C}}_1^1 = 1$ we may invert (8) at least for sufficiently large v

$$s = v^{-1} - 2 \bar{\mathcal{C}}_2^1 / v^2 + (8(\bar{\mathcal{C}}_2^1)^2 - 3 \bar{\mathcal{C}}_3^1) / v^3 + \dots \tag{9}$$

Then insert (9) into (7) to obtain the following expression for the correlation functions:

$$g(q)_m = \prod_{i<j}^m (1+f_{ij}) \sum_{k=0}^{\infty} D_k^m / v^k \tag{10}$$

where $D_0^m = \mathcal{C}_1^m = g^0(q)_m, D_1^m = -2(\bar{\mathcal{C}}_2^m - m \bar{\mathcal{C}}_2^1)$ and so on.

Notice that the D_k^m are the functions of v . For the perfect gas case the D_k^m does not depend on v ($g^0(q)_m \equiv 1$).

Expression $u = w - [\sum_{k=0}^{N-m} (\eta^k * P_k u) - u]$ gives us a set of recurrence relations between the cluster functions, which is easily seen from the coordinate form of this vector equation

$$u[(q)_m, (q)_n] = w[(q)_m, (q)_n] - \sum_{k=0}^{n-1} \sum_{R_k \subset Q} \tilde{\eta}^k(Q \setminus R_k) u[(q)_m, R_k].$$

The integral form of this expression is ($\eta_1^k \equiv 0$):

$$u_n^m = w_n^m - \sum_{k=0}^{n-2} n! [k!(n-k)!]^{-1} \tilde{\eta}_{n-k}^k u_k^m$$

where $u_0^m = w_0^m = g^0(q)_m$ and $u_1^m \equiv w_1^m$. This expression with any recurrence relations between w_k^m and $\tilde{\eta}_{n-k}^k$ may be also useful for convergence estimations of the expression (7).

Finally, we may notice that if $\phi^0 \equiv 0$ then the expression (7) reproduces the perfect gas case ($s = z$) (De Boer 1948).

3. Conclusion

The present paper generalizes the method of cluster expansions as applied to the correlation functions of non-ideal systems. The obtained series of the perturbation theory (7) associates the correlation functions of the disturbed system with the correlation functions of the reference system. The main parameter which determines the convergence of series (7) is the parameter a^3/v where $a^3 \sim \int_V \int_V |f_{ij}| g^0(q)_2 d(q)_2 / V$. The second parameter which appears in the terms of series (7) starting from D_2^m is the correlation radius r_0 of the reference system. It should be noted that expansion (7) may well converge in spite of the fact that these systems themselves may be strongly non-ideal. In this case the convergence of the series (7) is defined by the smallness of a^3/v , while the parameter r_0^3/v is no longer small. It is hoped that the method proposed can be used to build up a perturbation theory for non-thermodynamic quantities such as transport coefficients, fluctuations and microfield distributions.

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