ON THE SUMMATION OF THE URSELL-MAYER CLUSTER EXPANSION. I. SIMPLE CHAIN APPROXIMATION

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The simplest infinite subset of graphs (consisting of polygons only) describing the Ursell-Mayer cluster expansion of the pressure and actual density in powers of the active density (fugacity) is resummed to a closed formula (SC approximation). It is shown that this approximation is sufficient for the illustration of the existence of phase transitions in macroscopic systems.

1. Introduction

One of the important, and still not completely solved, problems of statistical mechanics is the theory of condensed phases and first-order phase transitions (*cf.* [1–10]). It is now known that in order to describe a phase transition it is necessary to take into account the intermolecular interactions of infinite range in some way [3, 11–16]. Among other things, we have shown that summation of the simplest (topologically) infinite subset of diagrams representing the Ursell-Mayer virial expansion (the expansion of pressure in powers of the systems density [1, 17]) leads to a relatively simple closed approximate equation of state[1] which enables the explicit prediction of two first-order phase transitions [18, 19]. In this approximation the phase transition is obtained for the short-range two-particle interaction potential, whereas the long-rangeness of the interactions is incorporated into the resulting equation of state by retaining the terms which describe, although indirectly, the successive interactions of chains of particles of any length (up to infinity). The important point here is, perhaps, that consideration of the simplest class of such terms (in the formalism of the virial expansion) was sufficient to get these results.

The virial expansion, *i.e.* the expansion in powers of a system's density ϱ is certainly — from the physical point of view — one of the most natural expansions of the macroscopic

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[1] This form of the equation of state, henceforth called the OC (one chain) approximation, may be also considered as the approximate solution of the hypernetted chain [20, 21] and Percus-Yevick [21–23] approximations.

properties of the system, because density is one of the most natural (and most fundamental) parameters of state. However, it is by no means the most natural expansion from the formal point of view. Indeed, when calculating thermodynamic quantities on the basis of statistical mechanics it is found that the first natural expansion encountered is in powers of fugacity z (the cluster expansion), which must be further rearranged in order to get the virial expansion in powers of ϱ [17]. In the Yang-Lee formal theory of phase transitions [2, 5, 24–27], also, one looks for the analytic properties of the grand-canonical partition function considered as a function of the (complex) fugacity z.

It thus seems that it could be interesting, at least from the point of view of formal theory, to examine the partial summations of the cluster expansion, similar to those [18, 19] of the virial expansion. In this paper the simplest (topologically) subset of graphs of the cluster expansion of the pressure will be discussed; it is to be noted that the simplest subset of biconnected graphs of the virial expansion, giving rise to the OC approximation [18, 19], corresponds to a fairly complex (and by no means simplest) subset of connected graphs of the cluster expansion. Thus the approximation (called hereafter the SC — simple chain — approximation) which will be discussed in this paper is — in a sense — poorer than the OC approximation of the virial expansion. The second part of this work will be devoted to the summations of further, more complex, subsets of graphs, leading eventually to the formulas for the pressure and density of the system as functions of the fugacity z, equivalent to those in the OC approximation.

2. *Summation of simple chains*

Consider a system of N identical particles contained in volume Ω, kept at temperature T, and interacting with each other through the pair potential $V(r)$, which is assumed to have spherical symmetry. It is also assumed that quantum effects are negligible, and the thermodynamic limit,

$$N \to \infty, \quad \Omega \to \infty, \quad \frac{N}{\Omega} = \frac{1}{v} = \text{finite}, \tag{1}$$

is considered. In this case, the thermodynamics of the system may be obtained from the function $\chi(T, z)$, related to the grand-canonical Z_g and canonical Z_c partition functions and to the Helmholtz free energy per particle, A, through the relations[2]:

$$\chi(T, z) = \lim_{\Omega \to \infty} \frac{1}{\Omega} \ln Z_g(\Omega, T, z) = \lim_{N \to \infty} \frac{1}{Nv} \ln Z_c(Nv, T, N) + \ln (z\lambda)^3, \tag{2}$$

$$A(v, T) = -kT \lim_{N \to \infty} \frac{1}{N} \ln Z_c (Nv, T, N) = -kT[v\chi(T,z) - \ln(z\lambda^3)]. \tag{3}$$

The fugacity z (treated here as an independent variable) is defined by

$$z = \lambda^{-3} \exp (G/kT), \tag{4}$$

[2] We follow here the formalism of Ref. [17].

where G is the Gibbs free energy (free enthalpy) per particle, k the Boltzmann constant, and

$$\lambda = (\hbar^2/2\pi mkT)^{1/2},$$

m denoting the mass of the particle.

The equation of state in this formalism is obtained by expressing the pressure P and the number density ϱ of the system as functions of T and z:

$$P = -\left(\frac{\partial A}{\partial v}\right)_T = kT\chi(T, z), \tag{5}$$

$$\varrho = \frac{1}{v} = z\left(\frac{\partial \chi}{\partial z}\right)_T \tag{6}$$

the latter relation resulting from the derivation of Eq. (2) (it defines the proper value of the independent variable z in Eq. (2) [17]).

Now, the Ursell-Mayer cluster expansion leads to the following general result for the function $\chi(T, z)$:

$$\chi(T,z) = \sum_{l=1}^{\infty} b_l(T) z^l, \tag{7}$$

$$b_l(T) = \lim_{\Omega\to\infty} \frac{1}{\Omega}\frac{1}{1!}\int_{\Omega}\dots\int d\boldsymbol{r}_1 \dots d\boldsymbol{r}_l U_l(\boldsymbol{r}_1, \dots, \boldsymbol{r}_l), \tag{8}$$

where U_l is the Ursell cluster function. The latter may be expressed in terms of finite sets of connected graphs: U_l is equal to the sum of contributions from all possible l-point labeled connected linear graphs, each contribution being written in such a way that every line joining two points labeled i and j imparts a factor equal to the Mayer function f_{ij}:

$$f_{ij} = f(r_{ij}) = \exp\{-V(r_{ij})/kT\} - 1, \qquad r_{ij} = |\boldsymbol{r}_i - \boldsymbol{r}_j| \tag{9}$$

(*cf* Ref. [17] for more details). The expansion (7) is thus represented by an infinite set of labeled linear connected graphs.

The simplest interesting infinite subset of graphs representing the cluster expansion (7) is perhaps that composed of simple polygons[3] (including the first two-point one-line graph of b_2) topologically identical with, but physically not equivalent to[4], the simplest subset of graphs of the virial expansion, which forms the OC approximation. In this simple chain (SC) approximation, the Ursell cluster functions are:

$$U_1 = 1, \qquad U_2 = f_{12},$$

$$U_k = \frac{k!}{2k} f_{12} f_{23} \dots f_{k1}, \qquad k = 3, 4, \dots\dots \tag{10}$$

[3] The still simpler subset, that composed of pure Cayley Trees only [17], is equivalent to the second virial coefficient alone, and thus the contribution from it is uninteresting from the point of view of phase transitions. This subset will be considered in a subsequent part of this work.

[4] because of non-linear relations between the expansion variables, z and ϱ, of these two formalisms.

and thus (the technique used here is identical with that from Refs [18] and [19]),

$$b_1 = 1, \quad b_2 = \frac{1}{2}\int d\boldsymbol{r} f(r) = \frac{1}{2(2\pi)^3}\gamma(0), \tag{11}$$

$$b_k = \frac{1}{2k}\frac{1}{(2\pi)^3}\int d\boldsymbol{q}[\gamma(q)]^k, \quad k \geqslant 3,$$

where

$$\gamma(q) = \int d\boldsymbol{r} e^{i\boldsymbol{q}\cdot\boldsymbol{r}} f(r) = \frac{4\pi}{q}\int_0^\infty dr\, r \sin(qr) f(r) \tag{12}$$

for the spherically symmetrical potential $V(r)$. Inserting (11) into (7), we get

$$\chi(T,z) = z - Bz^2 + R_0(T,z), \tag{13}$$

with $B = -b_2(T)$ being the second virial coefficient of the gas under consideration, and

$$R_0(T,z) = -\frac{1}{2(2\pi)^3}\int d\boldsymbol{q}\left\{\ln|1-z\gamma(q)| + z\gamma(q) + \frac{1}{2}[z\gamma(q)]^2\right\}. \tag{14}$$

Equations (13) and (14) determine the pressure of the system as the function of the fugacity z. The density is calculated from the relation (6):

$$\varrho(T,z) = z - 2Bz^2 + zR_1(T,z), \tag{15}$$

with

$$R_1(T,z) = \left[\frac{\partial}{\partial z} R_0(T,z)\right]_T \tag{16}$$

$$= \frac{z^2}{2(2\pi)^3}\int d\boldsymbol{q}\,\frac{\gamma^3(q)}{1-z\gamma(q)}. \tag{16a}$$

For comparison, the pressure in the OC approximation (with $\varrho = 1/v$ as the independent variable) reads [18]:

$$\frac{P}{kT} = \varrho + B\varrho^2 - \frac{1}{2(2\pi)^3}\int d\boldsymbol{q}\left\{\ln|1-\varrho\gamma(q)| + \frac{\varrho\gamma(q)}{1-\varrho\gamma(q)} - \frac{1}{2}[\varrho\gamma(q)]^2\right\}. \tag{17}$$

3. Numerical results and conclusions

The computation of the integrals $R_0(T,z)$ and $R_1(T,z)$ (as well as of the integral involved in Eq. (17)) calls for some additional remarks. These integrals represent the sums of some parts (SC approximations) of the cluster series (7). The radius of convergence of the latter in this approximation is determined by the condition (the geometrical series):

$$|z| < z_{\max} = 1/\mathrm{Max}|\gamma(q)|. \tag{18}$$

Thus, for $|z| > z_{max}$, R_0 and R_1 may be treated as analytical continuations of the SC approximation to the cluster series. However, in this region of z the integrands in (14) and (16a) are singular at some values of the integration variable q (this reflects the divergence of the original series). We interpret these singular integrals as their Cauchy principal values; this interpretation seems to be the simplest one.[5] Besides, the same interpretation was ascribed to the integral in Eq. (17) in our earlier work [18, 19]. At the point $|z| = z_{max}$ the function R_1 is divergent and thus the density of the system is indefinite at this point. The value of z_{max}, being connected with the maximum of the function $\gamma(q) = \gamma(T; q)$, Eq. (12), depends on the temperature of the system and on the form of the intermolecular potential $V(r)$.

The numerical calculations were performed on the ODRA 1204 computer, for the Lennard-Jones 12–6 potential function:

$$V(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6]. \tag{19}$$

All computed quantities presented below are written in terms of the reduced parameters:

$$1/\varrho^+ = V^+ = \Omega/b_0 N, \quad T^+ = kT/\varepsilon, \quad P^+ = Pb_0/\varepsilon, \quad z^+ = zb_0, \quad b_0 = 2\pi\sigma^3/3. \tag{20}$$

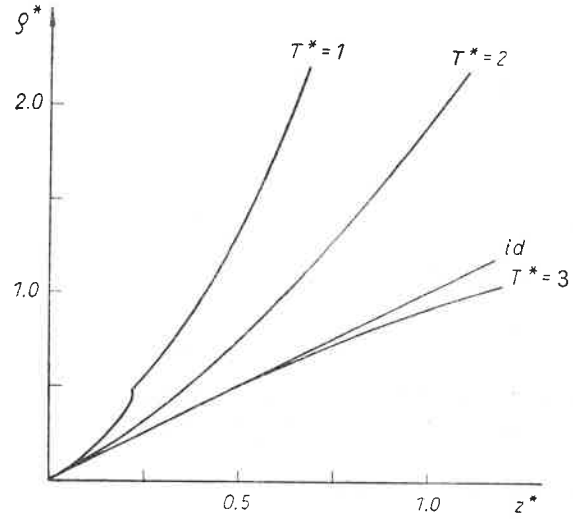

Fig. 1. Density ϱ^+ as a function of activity z^+ in the SC approximation for three values of temperature T^+. The straight line denoted *id.* shows the ideal gas relation $\varrho^+ = z^+$

Values of $\varrho^+(z^+)$ and $P^+(z^+)$, as given by the SC approximation, Eqs (13)–(16a), were computed for three values of the reduced temperature, $T^+ = 1, 2, 3$, and are presented in Figs 1 and 2. For $T^+ = 3$, ϱ^+ and P^+ are very near to the ideal gas values, $\varrho^+_{id} = z^+$, $P^+_{id} = T^+z^+$. For $T^+ = 1$, both ϱ^+ and P^+ are indefinite at $z^+ = 0.202$. The derivative

[5] A better interpretation of the function $R_1(T, z)$ is given by Eq. (16) — the integral $R_0(T, z)$ is convergent; however, the integral form (16a) is more convenient for numerical computations.

$(1/T^+)(\partial P^+/\partial z^+)_{T^+}$ is plotted against z^+ in Fig. 3, for $T^+ = 1$ and 2 (for $T^+ = 3$, this derivative is very near 1). For higher temperatures, $T^+ \geqslant 2$, no singularity is found in $\varrho^+(z^+)$ and $P^+(z^+)$.

It seemed that a comparison between the SC (cluster) and OC (virial) approximations would be interesting. For this purpose, P^+ was calculated as a function of $V^+(z^+)$ by combining the results presented in Figs 1 and 2 (SC approximation), whereas $P^+(V^+)$, as given

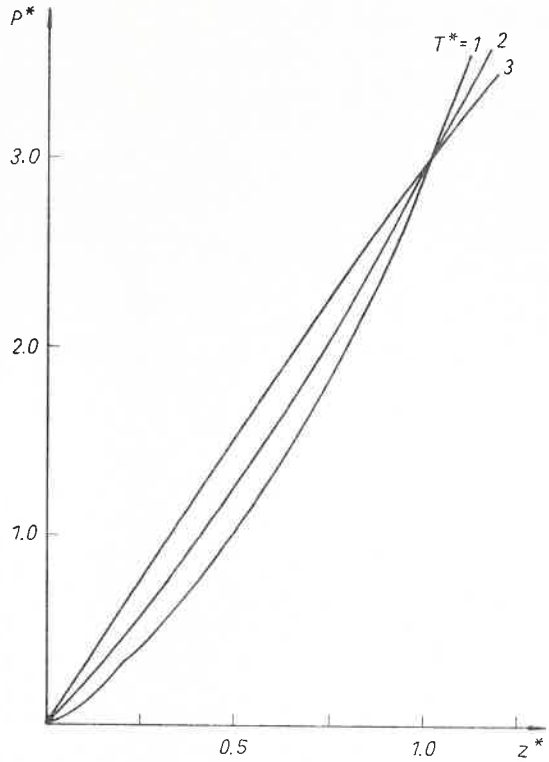

Fig. 2. Pressure P^+ as a function of activity z^+ in the SC approximation for three values of temperature T^+. Note that for $z^+ > 1$ the SC approximation predicts an inversion of the temperature dependence of the pressure

by Eq. (17) (OC approximation), was computed directly. The results for $T^+ = 1$ are shown in Fig. 4. It is seen that the OC approximation predicts, in general, lower values of P^+ than those obtained from SC formulas. Moreover, the isotherm calculated from the OC approximation possesses two discontinuities, whereas that from SC formulas only one, and the SC singularity appears at much lower values of V^+ (greater density) than the first OC discontinuity (proved to correspond to a gas-liquid transition [18, 19]). Note that the singularities in both OC and SC formulas are connected with the same value of the maximum of the function $\gamma(T; q)$. However, in the OC approximation it is the value of $v = \gamma_{\max}$ which determines the location of the singular point at the isotherm $P = P(v)$, whereas in the SC approximation this location is given by the value $z = 1/\gamma_{\max}$, which in turn determines the corresponding value of $v = v(z)$.

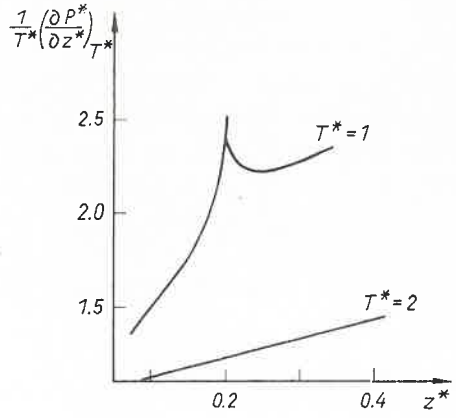

Fig. 3. Derivative of the pressure, $\left(\frac{\partial P^+}{\partial z^+}\right)_{T^+}$ *vs.* activity z^+

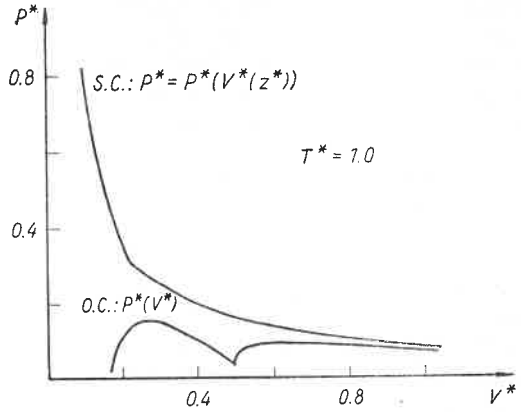

Fig. 4. Comparison of isotherms $P^+ = P^+(V^+)$ calculated from OC and SC approximations. The high-density portion of the OC isotherm is omitted

The results presented above seem to lead to the conclusion that SC approximation, which takes into account the simplest infinite subset of terms of the cluster expansion, is able to predict the singular character of macroscopic properties (of a many-body system) considered as functions of temperature and activity (fugacity, active density), or of temperature and actual density of the system. It should be stressed that the SC approximation takes into account a much smaller number of terms (graphs) of the cluster expansion than does the virial OC approximation. From the point of view of formal theory, the cluster SC approximation may thus be considered as being simpler than the virial OC approximation. Nevertheless, it is sufficient for illustrating the existence of phase transitions.

Let us note, however, that the results predicted by the SC approximation seem to look rather similar to the characteristics of the second-order phase transition[6] (λ-point; *cf.* especially

[6] This remark is due to Dr hab. K. Zalewski, to whom I am very indebted for the critical reading of the manuscript.

Figs 3 and 4), whereas those of the OC approximation adhere closer to the description of the first-order phase transition. A better understanding of the "mechanism" of the phase transitions described by these approximations may perhaps be gotten from comprehensive computations of other thermodynamic quantities (especially of heat capacity), or on the basis of the Yang-Lee theory [24–27].

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