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SOME PROPERTIES OF THE OPTIMALIZATION CONDITION IN THE PERTURBATION THEORY OF LIQUIDS*, **

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The optimalization procedure introduced into the perturbation theory of liquids by Andersen, Chandler and Weeks (ACW) is discussed. It is found that the original ACW variational condition (C-1) is consistent only for potentials possessing infinitely hard repulsive core. For realistic potentials, variation of the perturbation $W(r)$ at small distances must be accompanied by the appropriate variation in the reference potential, such that the whole interaction (defining the considered physical system) remains invariant. Corrected variational condition (C-2) is found, and the calculations for the Lennard-Jones fluid are performed. The correction influences the global properties of the system only slightly, but changes significantly the shape of optimalized $W(r)$ at small distances: $W(r)$ calculated from C-2 is always attractive, whereas $W(r)$ calculated from C-1 can be either attractive or repulsive.

1. Introduction

One of the best recent theories of simple liquids is the Andersen, Chandler, and Weeks (ACW) version [1–7] of the perturbation theory, especially in its optimized form [6, 7]. The main advantage of the optimized ACW theory lies in the possibility of arbitrary adjustment of the shape of perturbation interaction $W(r)$ inside the repulsive region, the latter playing the role of the reference (unperturbed) system. This property of the theory is connected with the lack of some graphs [8] in the expansion, which results in turn in appearance of the integrals containing only the functions of the perturbation interaction $W(r)$. It is thus possible to choose arbitrarily the values of $W(r)$ for small r, which

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fact is used in the optimalization of the theory. It has been argued [8, 9] that in unoptimized perturbation theories of this kind the balance between repulsive and attractive forces is violated and that the ACW optimalization is equivalent to the indirect restoring of this balance. The aim of this paper is to examine the ACW optimalization procedure from such point of view.

The ACW perturbation theory is constructed as follows: the true intermolecular pair potential $V(r)$ is divided into the repulsive reference potential $V_0(r)$ and the perturbation $W(r)$

$$V(r) = V_0(r) + W(r), \tag{1.1}$$

with

$$V_0(r) = \begin{cases} V(r)+\varepsilon & r < r_0, \\ 0 & r > r_0, \end{cases} \tag{1.2}$$

$$W(r) = \begin{cases} -\varepsilon & r < r_0, \\ V(r) & r > r_0; \end{cases} \tag{1.3}$$

where r_0 is the smallest distance at which $V(r)$ attains minimum, and, in the unoptimized theory, $\varepsilon = -V(r = r_0)$ is the depth of the potential well.

The perturbation theory requires the knowledge of the equation of state $p_0 = p_0(\varrho, T)$ and of the radial distribution function $g_0(r)$ of the reference system. These quantities are known with sufficient accuracy only for the hard-sphere fluid. Hence the choice (1.1)–(1.3) of the reference system can be practically realized exactly only for potentials $V(r)$ possessing the infinitely hard core, i. e., when $V(r) = \infty$ for $r < r_0$. For realistic potentials with strongly repulsive but finite interactions at small distances, further approximations are necessary, and ACW propose to approximate the reference pressure p_0 by the pressure p_{HS} of the equivalent system of hard spheres of diameter d, and the radial distribution function by

$$g_0(r) = e^{-V_0(r)/kT} y_0(r) \cong e^{-V_0(r)/kT} y_{\mathrm{HS}}(r; d) \tag{1.4}$$

with $y_{\mathrm{HS}}(r; d)$ — appropriate part of the radial distribution function of the hard-sphere fluid. The diameter d of equivalent hard spheres is to be calculated from $V_0(r)$ by the use of one of the proposed for this purpose relations (cf. Ref. [10]).

When the choice of the reference system is made, it is applied to the graph representation of the virial expansion. The fragments of graphs containing only the reference interactions are summed to lines representing pair distribution functions of the reference system. The thermodynamic functions and the radial distribution function of the whole system are approximated by sums of all appropriate ring or chain graphs, in which to every vertex at most two lines are attached. In the ACW version there are two kinds of lines: one representing $g_0(r) - 1 = h_0(r)$, and the second containing only the perturbation $W(r)$. The ACW approximation may be now optimized by the change of the shape of $W(r)$ for $r < r_0$. For this purpose, a variational criterion is needed, and ACW assume that the best choice of $W(r)$ is obtained from the condition of the minimalization of the ring contribution a_R to the free energy. According to ACW, this condition is written in the form

$$\frac{\delta a_R}{\delta \Phi(r)} = \tfrac{1}{2}\, kT\varrho C(r) = 0 \quad \text{for } r < d, \tag{1.5}$$

where $\Phi(r) = -W(r)/kT$, ϱ is the number density, T — temperature, k — Boltzmann's constant, and $C(r)$ denotes the chain contribution to the radial distribution function

$$g(r) = g_0(r)\exp\{C(r)\}. \tag{1.6}$$

a_R and $C(r)$ are

$$a_R = \varrho kT \sum_{n=2}^{\infty} \frac{1}{2n} \int dr C_{n-1}(r)\Phi(r) = -\frac{kT}{2(2\pi)^3\varrho} \int dq\{\ln[1-P(q)]+P(q)\}, \tag{1.7}$$

$$C(r) = \sum_{n=1}^{\infty} C_n(r) = \sum_{n=1}^{\infty} \frac{1}{(2\pi)^3\varrho^2} \int dq e^{-iq\cdot r} P^n(q) G_0(q)$$

$$= \frac{1}{(2\pi)^3\varrho^2} \int dq e^{-iq\cdot r} \frac{P(q)}{1-P(q)}\, G_0(q), \tag{1.8}$$

where $C_n(r)$ denotes the contribution from all chains containing n lines, and

$$P(q) = E(q)G_0(q), \quad E(q) = \int dr e^{+iq\cdot r}\Phi(r),$$

$$G_0(q) = \varrho + \varrho^2 \int dr e^{+iq\cdot r}[g_0(r) - 1]. \tag{1.9}$$

In the ACW optimalization procedure only the perturbation $W(r)$ is changed. The reference system $V_0(r)$ is kept constant, so that $g_0(r)$, p_0, and the diameter d of the equivalent hard-sphere system are determined by $V_0(r)$ given by Eq. (1.2) with $\varepsilon = -V(r = r_0)$. Now, such procedure is fully consistent only for the potentials $V(r)$ containing infinitely hard core. We shall show below that, when $V(r) < \infty$ for $0 < r < r_0$, the requirement (1.5) of minimalization of a_R is not equivalent to the requirement of vanishing of the chain function $C(r)$. Besides, the natural physical condition of invariance of the true potential $V(r)$ — i. e., the requirement that we shall consider still the same physical system — implies that the changes in $W(r)$ must result in appropriate changes in $V_0(r)$. Corrections of this type to the ACW procedure will be considered in subsequent sections.

2. *Variational condition*

We shall calculate in this section the correct form of the functional derivative from the variational condition (1.5). Let

$$\Phi \to \Phi + \delta\Phi \text{ so that } V = V_0 - kT\Phi = \text{const.} \tag{2.1}$$

Expand the logarithm in Eq. (1.7) into the power series, and substitute the relations (1.9) and (2.1). Neglecting terms of the order of δ^2, we get

$$(a+\delta a)_{\mathrm{R}} = A\int dq \sum_{n=2}^{\infty} \frac{1}{n}\left\{\int dr_1 e^{iq\cdot r_1}[\Phi(r_1)+\delta\Phi(r_1)]\int dr_2 e^{iq\cdot r_2}[F_0(r_2)+\delta F_0(r_2)]\right\}^n, \tag{2.2}$$

and hence

$$\delta a_{\mathrm{R}} = A\int dr \int dq e^{iq\cdot r}\frac{P(q)}{1-P(q)}\{G_0(q)\delta\Phi(r)+E(q)\delta F_0(r)\}, \tag{2.3}$$

where

$$A = \frac{kT}{2(2\pi)^3\varrho}, \qquad F_0(r) = \varrho\delta^{(3)}(r)+\varrho^2[g_0(r)-1]. \tag{2.4}$$

Comparing Eq. (2.3) with Eq. (1.8) we find that

$$\frac{\delta a_{\mathrm{R}}}{\delta\Phi(r)} = \tfrac{1}{2}\,kT\varrho[C(r)+K(r)] \tag{2.5}$$

with

$$K(r) = \left[2A\varrho\int dq e^{iq\cdot r}\frac{P(q)E(q)}{1-P(q)}\right]\frac{\delta g_0(r)}{\delta V_0(r)}, \tag{2.6}$$

where the relation $\delta F_0 = \varrho^2\delta g_0$, and the condition (2.1) $kT\delta\Phi = \delta V_0$, have been used.

The correction $K(r)$ to the relation (1.5) is thus proportional to the change in the radial distribution function of the reference system evoked by the change in the division of the whole potential into the perturbation and the reference parts. The functional derivative $\delta g_0/\delta V_0$ is given by a rather complicated expression and is connected with three- and four-particle distribution functions. If, however, the approximation (1.4) is assumed for $g_0(r)$, we shall have

$$kT\frac{\delta g_0(r)}{\delta V_0(r)} \cong -g_0(r)+kTg_0(r)\left(\frac{\partial g_{\mathrm{HS}}(r;d)}{\partial d}\right)\frac{\delta d}{\delta V_0(r)}. \tag{2.7}$$

The change in the diameter d of the equivalent reference system, caused by the variation of the reference potential, should be rather small, because only the height of $V_0(r)$, not its range, is influenced by the changes in $W(r)$, and, for $r < d$, $V_0(r)$ is already high. The second term of the right-hand side of Eq. (2.7) may thus be neglected, and the correction $K(r)$ to the ACW relation (1.5) may be approximated by the expression

$$K(r) \cong -g_0(r)D(r), \tag{2.8}$$

with $D(r)$ given by the factor in the parentheses in Eq. (2.6). It is seen that for the hard-sphere reference system $K(r) = 0$ for $r < d$.

3. *Numerical results*

The numerical calculations were performed for the Lennard-Jones potential

$$V(r) = 4\varepsilon[(\sigma/r)^{12}-(\sigma/r)^{6}], \quad r_0 = \sqrt[6]{2}\,\sigma. \tag{3.1}$$

The diameter of equivalent hard spheres was determined from the Barker-Henderson-type condition [10]

$$d = -\int_0^{r_0}\left\{\exp\left[-\frac{V(r)+\varepsilon}{kT}\right]-1\right\}dr, \tag{3.2}$$

and the zeroth-order approximation for the radial distribution function of the reference system:

$$g_0(r) \cong g_0^0(r) = \exp\{-V_0(r)/kT\} \tag{3.3}$$

was used. According to the ACW procedure, the perturbation $W(r)$, calculated according to Eq. (1.3), was kept fixed for $r \geqslant d$, and was varied for $r < d$. Four-parameter functions (third-order polynomial in r, and its inverse) were used as trial functions. The calculations were performed in two versions: in the first (C–1), only the perturbation $W(r)$ was varied, with $V_0(r)$ kept constant, given by Eq. (1.2) with ε taken from the Lennard-Jones potential (3.1), and in the second (C–2), both $W(r)$ and $V_0(r)$ were varied simultaneously with $V(r)$, Eq. (1.1), kept constant. C–1 corresponds to the original ACW procedure, C–2 takes into account the correction (2.8) due to the condition of the invariance of the original potential. It is found that the global thermodynamic properties of the system are influenced only slightly by the correction (2.8). This is understandable because the factor $g_0(r)$ in $K(r)$

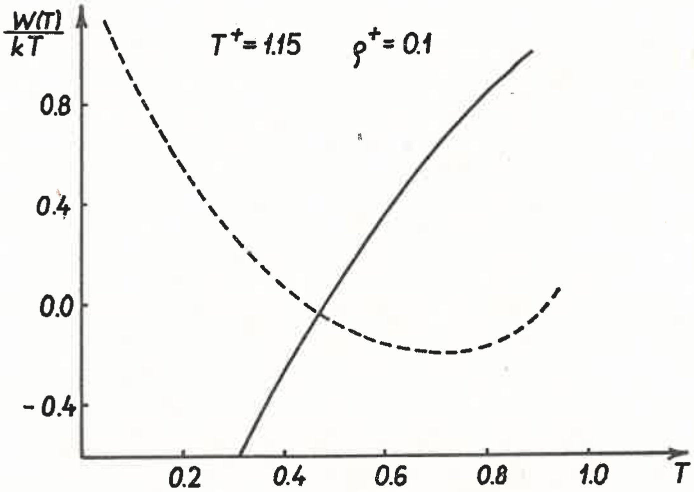

Fig. 1. Comparison of the shapes of the optimalized perturbation potential $W(r)$, in the range $0 < r < d = 1$ calculated from the original ACW condition (dashed line), and from the corrected condition (full line). $kT/\varepsilon = 1.15$, $\varrho\sigma^3 = 0.1$

cuts off the whole correction rather quickly for diminishing r, so that $K(r)$ gives noticeable contribution to the integrands only in the narrow region just below d.

On the other hand, the correction (2.8) influences significantly the shape of the optimalized perturbation interaction. We have found that, for all considered values of temperature and density, $W(r)$ for $r < d$ is always attractive, when is determined from the corrected variational condition C–2. In contrary, the original ACW condition C–1, in which V_0 is kept constant, leads to different shapes of the best variational function $W(r)$, corresponding to attractive as well as repulsive correction forces. Typical examples are shown in Figs 1 – 3, where the variational $W(r)$ determined from C–1 are shown by dashed

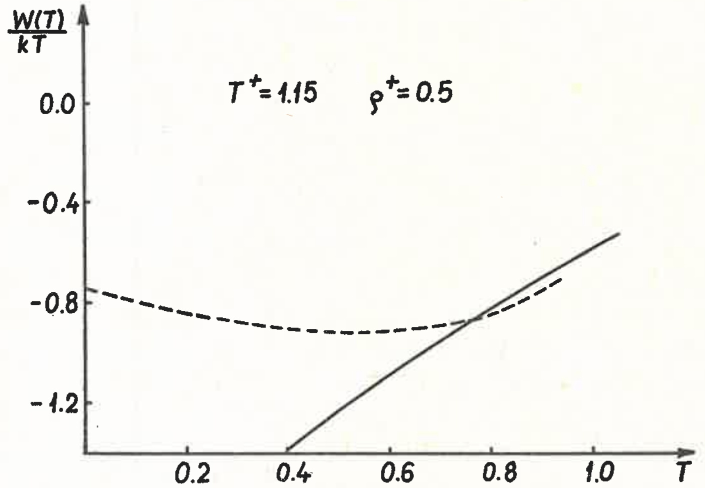

Fig. 2. The same as in Fig. 1, for $\varrho\sigma^3 = 0.5$

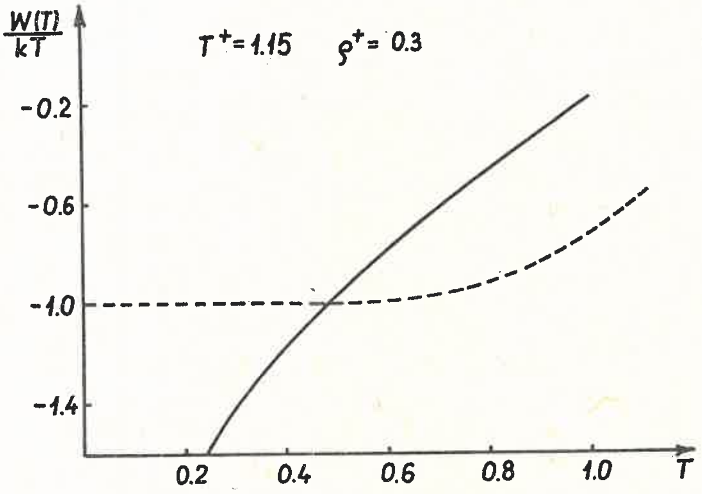

Fig. 3. The same as in Fig. 1, for $\varrho\sigma^3 = 0.3$

lines, and these determined from C–2 — by full lines. This result seems to support our earlier conjecture [8, 9] that the optimalization restores (partially at least) the natural balance between repulsive and attractive forces, violated in the perturbation theories in favour of the repulsion.

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