THERMODYNAMIC PERTURBATION THEORY
OF SIMPLE LIQUIDS

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It was proven that after averaging over the canonical Gibbs ensemble, the mean perturbation energy was singled out of the classical partition function before the expansion in a series of perturbation theory. Therefore, the term that formally coincides with first order perturbation theory in a decomposition of the Helmholtz free energy bears no relationship to perturbation theory. Then the proper series of the thermodynamic perturbation theory always starts with a second order infinitesimal. Therefore, the well-known condition of applicability of the thermodynamic perturbation theory, “…the requirement that the perturbation energy per particle be small compared with T…” (L. D. Landau and E. M. Livshits, Statistical Physics, Vol. V, Pt. I), can be substantially weakened. The most important factor for applicability of thermodynamic perturbation theory is the value of many-particle correlations in an unperturbed system, but not the smallness of the perturbation potential.

Keywords: thermodynamic perturbation theory, simple liquids.

INTRODUCTION

A simple liquid is generally understood as a system of identical classical particles with a pair centrosymmetric interaction potential [1]. For the interparticle pair interaction potential

\[ W(r) = U(r) + V(r), \]

the potential \( V(r) \) is regarded as a small addition to the potential \( U(r) \). In a Hamiltonian of a system of \( N \) particles, we accordingly define the total potential energies \( W_Q(r) \), \( U_Q(r) \), and \( V_Q(r) \) for the whole system. Then we introduce the following small dimensionless values,

\[ \varepsilon(r) = V(r)/T = \beta V(r), \quad \tau(r) = \exp(-\varepsilon(r)) - 1, \]

where \( \beta \) is a conventional symbol for the reciprocal temperature \( T \). The equations of perturbation theory given below can be expressed in terms of \( \varepsilon(r) \) or \( \tau(r) \).

For a system of \( N \) particles found in a volume \( V \), we define their density \( \rho \) and occupancy \( \eta \),

\[ \rho = \frac{N}{V}, \quad \eta = \frac{\pi}{6} \rho d_{HS}^3. \]

The latter equation will be used for a liquid of hard spheres (HSs) with a diameter \( d_{HS} \) and an interaction potential \( U_{HS}(r) \).

Let us consider the configuration part of the partition function of the \( Q_W \) system for the pair interaction potential between particles (1) (below \( W(i,j) = W(r_{ij}); r_{ij} \) is the distance between the \( i \) and \( j \) particles),
\[ Q_W = V^{-N} \prod_{i \neq j=1}^{N} \Phi_W(i, j)d1 \ldots dN, \quad \Phi_W(i, j) = \exp[-\beta W(i, j)], \quad \beta F_W = -\ln(Q_W), \] (4)

where \( i, j = 1, \ldots, N \) are the vectors of particle coordinates in the arguments of the functions and variables or the numbers of the particles during enumerations; \( F_W \) is the configuration part of the Helmholtz thermodynamic potential (below simply the Helmholtz free energy). By definition, \( S \) is the partial distribution function \( g_S(W; 1, \ldots, S) \) defined as

\[ g^S g_S(W; 1, \ldots, S) = \frac{N!}{(N-S)!} \frac{1}{V^N Q_W} \prod_{i \neq j=1}^{N} \Phi_W(i, j)d(S+1) \ldots dN. \] (5)

For a homogeneous system, the distribution functions depend only on the relative distance between particles, and the radial distribution function (RDF) is

\[ g(W; r) = \frac{1}{V} \int g_2(W; 1, 2)d1. \] (6)

The standard perturbation theory is formulated as follows. Expanding the partition function (4) in terms of \( V_2(r) \), we obtain a perturbation theory series [2]

\[ \beta F_W = -\ln Q_{U+V} = \beta F_U + \beta V_2 \cdot 1/2[\beta V_2 - \beta^2 V_2] + \ldots. \] (7)

Here the averaging is performed “… with the aid of the “unperturbed” Gibbs distribution …” [2]; i.e., for example, \( \bar{F}_2 = \langle V_2 \rangle_U \). The second term of the decomposition in (7) is

\[ \beta \bar{V}_2 = N \cdot \bar{v}(r) = N \cdot 2\pi \int \bar{v}(r)g(U; r)r^2dr. \] (8)

The condition of applicability of the perturbation theory is “… the requirement that the perturbation energy per particle be small compared with \( T \) …” [2], i.e., that \( \bar{v}(r) \) in (8) be small.

The thermodynamic first order perturbation theory was the basis for WCA (Weeks, Chandler, Andersen) theory of simple liquids [3-5]. Further elaboration of this theory [6-9] showed that calculations of thermodynamic characteristics for model (Lennard-Jones, repulsion, exponentially decaying, etc.) potentials even in first order perturbation theory were comparable in accuracy to the conventional molecular dynamic (MD) methods. It appeared, however, that \( \bar{v}(r) \) in (8) was generally not small, reaching 5 and more. In this case, the first term of the decomposition in (7) was of the order (or higher than) the zeroth order term in magnitude. To substantiate the use of perturbation theory in this case, the estimates of the second term of the decomposition in (7), obtained by the MD method, are given. The authors of [5] gave an estimate of the Lennard-Jones potential that was 200 times smaller than the one obtained in the first order perturbation theory.

This unusual situation would seemingly be correlated with the peculiarities of WCA theory. Indeed, WCA theory was developed for the potentials which sharply increase after particles approach one another. Therefore, these potentials in the range of relatively small distances are replaced by the hard sphere potential. Then these unusual properties of perturbation theory can be correlated with the specifics of van der Waals potentials (i.e., the hard sphere plus the perturbation potential) with HS liquid taken as an unperturbed liquid. This is conventionally explained by the fact that “inclusion” of perturbation in HS liquids (at least, for dense systems) cannot significantly distort the structure of the HS liquid in view of its small compressibility [10, 11].

Note that the formulation of thermodynamic perturbation theory for simple liquids in terms of \( \lambda \) decompositions (i.e., gradual inclusion of perturbation) [11] is equivalent to (7). The advantage of this approach lies in the fact that using MD data, one can evaluate the second order infinitesimal term in (7) [5, 11], which is difficult to do directly for (7) (see below).

The simplest van der Waals potential is the HS potential plus a rectangular well, or the SW (Square-Well) potential. The perturbation theory for the SW potential is based on the discrete representation method suggested in [12]. First studies in this field [13-16] and related problems are discussed in review [10]. The authors of [16] specially analyzed the convergence of the perturbation theory series for this potential and noted that the third term in (7) was substantially smaller than the second.