Generalisation of the density-functional theory and three-body interactions in classical fluids

LETTER TO THE EDITOR

Generalisation of the density-functional theory and three-body interactions in classical fluids

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Abstract. An external field coupled with the two-body density distribution function leads to a generalisation of the density-functional theory in which the free energy is regarded as a functional not only of the density but also of the two-body distribution function. The generalised formalism is applied to the liquid structure theory in the presence of a weak three-body potential. The first-order calculation shows that the three-body effects are fully incorporated into the theory through modification of the pair potential by virtue of the variational property of the free-energy functional.

Three-body forces to represent the covalency play a significant role in determining the structure of elemental semiconductors (Pearson *et al* 1984, Stillinger and Weber 1985, 1987, Biswas and Hamann 1985, 1987, Ding and Andersen 1986) and dichalcogenides (Vashishta *et al* 1989) such as $GeSe_2$ and $SiSe_2$ in condensed phase. Without the inclusion of such forces, for example, the diamond structure in pure elemental semiconductors is unstable against close-packed structures (Stillinger and Weber 1985, Biswas and Hamann 1985). Hence, for studying a general class of covalent materials where the effects both of covalency and of charge transfer are important, it is essential to treat three-body potentials in addition to short- and long-ranged two-body potentials. Recent detailed thermodynamic and structural analyses also indicate the existence of many-body interactions even in the rare gases (see Barker 1986 and references therein) and molten salts (Malescio *et al* 1985). The effective potential energy for ions in liquid metals may have many-body terms through the non-linear response functions of the electron gas (Ashcroft and Stroud 1978).

The possibility of incorporating a weak triplet potential into the integral-equation theory for the correlation function of classical liquids has thus far been considered on the basis of the diagrammatic method. Rushbrooke and Silbert (1967) found that the three-body effects are taken into account through replacing the pair potential by an effective potential in the hypernetted-chain (HNC) theory (Van Leeuwen *et al* 1959, Morita 1960); subsequently, Rowlinson (1967) obtained an effective potential consistent with the Percus–Yevick (Percus and Yevick 1958) equation. The effective potential is defined here by the condition that, if it is substituted for the actual pair potential in the statistical mechanical formula which is based on the assumption of pair-wise additivity, the extra terms resulting from the substitution will provide the appropriate correction due to the three-body potential (for a discussion of the effective potential see Stillinger

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(1972)). Casanova *et al* (1970) finally advanced those diagrammatic analyses to obtain a series-expansion formula for the correction which leads to the exact distribution function; Sinha *et al* (1977) later carried out a partial summation of the series expansion using the topological reduction technique to eliminate the pair potential with the correlation functions.

The purpose of the present paper is to reconsider this problem in terms of the density-functional theory (DFT) developed by Hohenberg and Kohn (1964), Kohn and Sham (1965), and Mermin (1965). The formualtion based on the DFT not only simplifies the treatment but also clarifies the physical nature of the approximations adopted. As compared with the cluster-expansion theory, a renormalisation of the inter-particle potential arising from strong multi-particle correlations (the topological reduction) is achieved in a natural way. To accommodate three-body interactions in the formulation, however, we have to generalise the DFT so that the free energy functional depends on the two-body distribution function as well as on the density.

Let us begin by assuming that a uniform system with density ρ_0 has an interaction energy consisting of two-body and three-body terms

$$U(r_1, \ldots, r_N) = \sum_{1 \leq i \leq j \leq N} v(r_i, r_j) + \sum_{1 \leq i \leq j \leq k \leq N} w(r_i, r_j, r_k)$$

where $v(r_i, r_j)$ depends only on the separation of atoms i and j, and $w(r_i, r_j, r_k)$, only on the shape and size of the i, j, k triangle. If a test particle identical to the system particles is introduced at the origin, the relative density $\rho(r)/\rho_0$ amounts to the radial distribution function $g(r)$ of the uniform system (Percus 1964). This observation provides a basis for the link between the integral-equation theory and the density-function theory.

In the absence of the three-body potential w, the conventional DFT (Hohenberg and Kohn 1964, Kohn and Sham 1965, Mermin 1965) in which the intrinsic Helmholtz free-energy $F[\rho(r)]$ of the non-uniform system with an external field $\varphi_{\text{ext}}(r)$ is regarded as a functional of the density $\rho(r)$, combined with the identity, $\varphi_{\text{ext}}(r) = v(r)$, gives (Ichimaru *et al* 1987) the exact equation for $g(r)$:

$$g(r) = \exp(-v(r)/k_B T + h(r) - c(r) + B(r)). \tag{1}$$

Here the two-body direct correlation function $c(r)$ is related to the pair correlation function $h(r) = g(r) - 1$ through the Ornstein–Zernike relation

$$h(r) = c(r) + \rho_0 \int dr_1 \, c(|r - r_1|)h(r_1). \tag{2}$$

The function $B(r)$, corresponding to the sum of all the bridge diagrams in the cluster-expansion theory, is expressed in terms of the direct correlation functions c_ν ($\nu \geq 3$) as

$$B(r) = \sum_{\nu \geq 3} \frac{1}{(\nu - 1)!} \rho_0^{\nu - 1} \int dr_1 \ldots dr_{\nu-1} \, c_\nu(r, r_1, \ldots, r_{\nu-1})h(r_1) \ldots h(r_{\nu-1}). \tag{3}$$

The functions c_ν are generated from the correlation part in the Helmholtz free energy by successive functional differentiation with respect to the density (Evans 1979, Ichimaru *et al* 1987).

Incorporation of the three-body potential into the formulation, however, requires us to generalise the DFT itself. To utilise the trick due to Percus, it is necessary to introduce an additional external field $\varphi_{\text{ext}}(r_1, r_2)$ coupled with the two-body density distribution

function $\rho_2(r_1, r_2)$. We can readily carry out such a generalisation following Mermin's prescription (Mermin 1965, Kohn and Vashishta 1983).

We now generalise the DFT to incorporate three-body potentials. Let us consider a uniform system with the Hamiltonian H_0 at a given temperature T and chemical potential μ. For the system under the influence of the external fields, $\phi_{ext}(r)$ and $\varphi_{ext}(r_1, r_2)$, the grand canonical density matrix operator is given by

$$\rho = \exp[-(H - \mu N)/k_B T]/\text{Tr} \exp[-(H - \mu N)/k_B T]$$

where

$$H = H_0 + \int dr\, \rho(r)\phi_{ext}(r) + \tfrac{1}{2}\int dr_1\, dr_2\, \rho_2(r_1, r_2)\varphi_{ext}(r_1, r_2).$$

The thermodynamic potential Ω is then calculated according to

$$\Omega = \text{Tr}\, \rho(H - \mu N + k_B T \ln \rho)$$

which may be regarded as a functional of ρ. The proof proceeds by *reductio ad absurdum* using the minimum property of $\Omega[\rho]$. We have thus obtained the following two theorems.

Theorem 1. In a grand canonical ensemble at a given temperature T, the density distribution functions, $\rho(r)$ and $\rho_2(r_1, r_2)$, uniquely determine the external fields, $\phi_{ext}(r) - \mu$ and $\varphi_{ext}(r_1, r_2)$, including the chemical potential μ.

Theorem 2. For given $\phi_{ext}(r) - \mu$ and $\varphi_{ext}(r_1, r_2)$, there exists a functional of $\rho(r)$ and $\rho_2(r_1, r_2)$,

$$\Omega = F[\rho(r), \rho_2(r_1, r_2)] + \int dr\, \rho(r)(\phi_{ext}(r) - \mu)$$

$$+ \tfrac{1}{2}\int dr_1\, dr_2\, \rho_2(r_1, r_2)\varphi_{ext}(r_1, r_2) \tag{4}$$

which takes an absolute minimum when $\rho(r)$ and $\rho_2(r_1, r_2)$ are the correct distribution functions associated with $\phi_{ext}(r)$ and $\varphi_{ext}(r_1, r_2)$; the minimum value is equal to the thermodynamic potential in the equilibrium. The intrinsic Helmholtz free energy F is a universal, temperature-dependent function of $\rho(r)$ and $\rho_2(r_1, r_2)$ alone.

We now turn to the derivation of the integral equations with three-body potential. If we assume the three-body potential w to be weak, it is possible to adopt a perturbational treatment in the calculation of (4). If $\rho_2(r_1, r_2)$ is expanded with respect to $\varphi_{ext}(r_1, r_2)$,

$$\rho_2(r_1, r_2) = \rho_2^{(0)}(r_1, r_2) + \rho_2^{(1)}(r_1, r_2) + \ldots \tag{5}$$

the zeroth-order term $\rho_2^{(0)}$ is a functional only of $\rho(r)$ and satisfies

$$\delta F[\rho(r), \rho_2^{(0)}(r_1, r_2)]/\delta\rho_2^{(0)}(r_1, r_2) = 0. \tag{6}$$

Substituting (5) for ρ_2 in (4) and retaining terms up to the first order in $\varphi_{ext}(r_1, r_2)$, we obtain

$$\Omega = F[\rho(r), \rho_2^{(0)}(r_1, r_2)] + \int dr\, \rho(r)(\phi_{ext}(r) - \mu)$$

$$+ \tfrac{1}{2}\int dr_1\, dr_2\, \rho_2^{(0)}(r_1, r_2)\varphi_{ext}(r_1, r_2) \tag{7}$$

where the variational condition (6) eliminates the contribution stemming from the derivative of F.

The generalised formalism should reduce to the original one in the limit of $\varphi_{\text{ext}}(r_1, r_2) = 0$, i.e.

$$F[\rho(r), \rho_2^{(0)}(r_1, r_2)] = F[\rho(r)].$$

Following the same procedure as is used in deriving (1), we thereby find that the variational equation for Ω, coupled with the trick, $\varphi_{\text{ext}}(r) = v(r)$ and $\varphi_{\text{ext}}(r_1, r_2) = w(0, r_1, r_2)$, yields the exact equation for $g(r)$ which is obtained by replacing $v(r)$ in (1) with

$$v'(r) = v(r) + \rho_0 \int dr_1 \, w(0, r, r_1)g(r_1)g[r, r_1]$$

$$+ \frac{\rho_0^2}{2} \int dr_1 \, dr_2 \, w(0, r_1, r_2)g(r_1)g(r_2) \frac{\delta g[r_1, r_2]}{\delta \rho(r)}. \tag{8}$$

Here $\rho(r) = \rho_0 g(r)$ is assumed and we have introduced the pair distribution function, $g[r_1, r_2; \rho(r)]$, of the inhomogeneous system with the density distribution $\rho(r)$ through

$$\rho_2^{(0)}(r_1, r_2) = \rho(r_1)\rho(r_2)g[r_1, r_2; \rho(r)].$$

To derive an explicit formula for the effective potential in the present scheme, we first note that when the triplet potential w is included, the direct correlation functions c_ν are given as a functional not only of $h(r)$ but also of $w(r_1, r_2, r_3)$. We thus decompose c_ν with $\nu \geq 3$ into two parts,

$$c_\nu = c_\nu^{(0)} + \Delta c_\nu \tag{9}$$

where $c_\nu^{(0)}$ stands for a collection of diagrams comprising the h-functions alone, that is, for the genuine two-body structure, and Δc_ν is a sum of the remaining diagrams involving w; the first few terms for $c_3^{(0)}$ have been obtained by Hernando (1986). Substituting (9) in (3) and rearranging the exponent in (1), we obtain the following effective potential:

$$v_{\text{eff}}(r) = v'(r) - \sum_{\nu \geq 3} \frac{k_B T}{(\nu - 1)!} \rho_0^{\nu - 1}$$

$$\times \int dr_1 \ldots dr_{\nu-1} \Delta c_\nu(r, r_1, \ldots, r_{\nu-1})h(r_1) \ldots h(r_{\nu-1}). \tag{10}$$

This is the density-functional counterpart of the exact diagrammatic result by Casanova *et al* (1970); the distinction between w and $[\exp(-w/k_B T)] - 1$ has no meaning in the first-order calculation with respect to w. The modification of the pair potential due to the three-body potential has been classified into two contributions: one results from the interaction term with the external field, the other from the correlation term in the intrinsic Helmholtz free-energy functional.

The integral equation for $g(r)$ now has the form

$$g(r) = \exp(-v_{\text{eff}}(r)/k_B T + h(r) - c(r) + B^{(0)}(r)) \tag{11}$$

where $v_{\text{eff}}(r)$ is given by (10) and $B^{(0)}(r)$ is the pair-potential bridge function. It has thus turned out that the three-body effects are fully taken into account through the renormalisation of the two-body potential and the structure of the integral-equation

scheme, (2) and (11), is essentially the same as that of the pair-potential theory by virtue of the variational property.

The HNC approximation (Van Leeuwen *et al* 1959, Morita 1960), one of the most widely applied integral-equation schemes, is defined by neglecting the three-body and higher-order direct correlation functions, that is setting $B(r) = 0$ in (1). To be consistent with this scheme, we may discard the multi-particle correlations involved in $g[r_1, r_2; \rho(r)]$ through the inhomogeneity by approximating $g[r_1, r_2; \rho(r)]$ in (8) with the radial distribution function $g(r)$ of the corresponding uniform system. Such a treatment yields

$$g(r) = \exp[-(v(r) + \Delta v(r))/k_B T + h(r) - c(r)] \tag{12}$$

where

$$\Delta v(r) = \rho_0 \int dr_1 \, w(0, r, r_1) g(r_1) g(|r - r_1|). \tag{13}$$

The correction (13) is equivalent to the leading term in the renormalised series expansion (Sinha *et al* 1977). Replacement of $g(r)$ by its weak coupling form, $\exp(-v(r)/k_B T)$, in (13) recovers the effective potential obtained by Rushbrooke and Silbert (1967) for the HNC equation. Since $w(0, r_1, r_2)$ and $g(|r - r_1|)$ depend only on the magnitude of r and r_1 and the direction cosine, $\cos \theta$, between r and r_1, the complexity involved in calculating (13) reduces to the double integral with respect to $|r_1|$ and $\cos \theta$. According to Schneider *et al* (1970), we can refine (13) using

$$g[r_1, r_2; \rho(r)] = g(|r_1 - r_2|) + \tfrac{1}{2}(\delta\rho(r_1) + \delta\rho(r_2)) \, \partial g(|r_1 - r_2|)/\partial\rho_0$$

with $\delta\rho(r) = \rho(r) - \rho_0$.

In conclusion we have extended the density-functional theory to take into account three-body forces. The perturbational calculation was then carried out for the correction due to the three-body potential and the correspondence with the previous diagrammatic results was established. The resulting equations (12) and (13) in conjunction with (2) give a closed set of equations for the correlation functions of classical liquids. We plan to apply the scheme described here to the calculation for the structure of chalcogenides in molten and glassy states using an effective two-body and three-body interaction potential.

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