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The BBGKY Equation in the Interaction Site Model for Polyatomic Molecular Fluids

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We extend the atom-atom interaction site model to a fluid of polyatomic molecules in an external field by deriving the first Born-Bogoliubov-Green-Kirkwood-Yvon(BBGKY) hierarchy for a nonuniform system. It is shown that the intramolecular structure contributes to the density gradient as well as the intermolecular correlations. By invoking the mechanical equilibrium conditions for microscopic forces we also obtain new expression for the gradient of the pressure tensor in inhomogeneous fluids. The BBGKY equation provides a consistency check on any theories of the interaction site variety. An examination of the so-called RISM theory[1)] of uniform fluids shows that the latter is inconsistent with respect to the BBGKY condition.

The interaction site model (ISM) for structured molecules in a uniform medium has been widely studied in literature.[1–17)] It has been applied to the hard polyatomics, soft polyatomics[2–17)] and to simulate real molecules (*e.g.* CO_2,[6)] benzene[15,18)] and water[7,11)]). One of the popular theories is the so-called reference interaction site model[1)] (RISM), based on certain approximation to the site-site direct correlation function (ss-dcf). Recently some inconsistencies inherent in RISM have been discovered[19–24)] and modifications to it have been proposed.[23,24)] It is desirable to have an alternative theoretical framework to RISM where exact relations are used. Here we present the formal results, the BBGKY hierarchy, for a nonuniform system using the ISM potential model. Applications will be postponed to a future study.

In section 2 we shall define the singlet (one-body) and pair (two-body) correlation functions in a grand canonical ensemble for polyatomic molecules (PM) in an external field. This picture may, say, correspond to the adsorption of structured molecules near a potential surface (the adsorbent phase). The first memeber of the Born-Bogoliubov-Green-Kirkwood-Yvon hierarchy is then derived. This equation is exact. We can interpret the results as specifying the linear momentum balance at the microscopic level.[25)] From the equivalence of the mechanical equilibrium conditions with the BBGKY equation[26)] we are able to express the pressure tensor in a nonuniform fluid in terms of the site–site correlation functions. This new expression can be contrasted with other known expressions of the pressure tensor.[27–30)] Since the BBGKY equation is exact, any ISM theories concerning the correlation functions must satisfy this equation. Thus we have a consistency condition based on the BBGKY. We analyze the conventional RISM[1)] theory in light of our new theoretical framework and discover that the Ornstein–Zernike-like equation given for the ss-dcf in the RISM is not exact. Its corrected form is one involving the incorporation of a Q factor (Section 5), whose form is explicitly given here.

The Grand Canonical Ensemble

In this section we give an explicit definition of the distribution function in a grand canonical ensemble. These explicit definitions will be found to be useful in the derivation of the BBGKY hierarchy.

For the simplicity in notation, we consider first a fluid of heteronuclear diatomics under the influence of an external potential, $U(.)$. There are N_a atoms of type a, and N_b, $(N_b=N_a)$, atoms of type b. We distinguish the pair interaction, u $(\alpha_i\gamma_j)$, between atom α_i in molecule i and atom γ_j in a different molecule j (*i.e.* intermolecular potential) and the pair interaction, $\bar{u}$ (a_ib_j), between atom a and atom b of the same molecule i(*i.e.* intramolecular potential). We shall be brief in our descriptions.[31,32)] Let V_N, $(N=N_a+N_b)$, be the sum of the atom-atom potential energies,

$$V_N = \sum_{i<j}\sum_{\alpha,\gamma} u(\alpha_i\gamma_i) + \sum_k u(a_kb_k) \tag{2.1}$$

and W_N be the sum of the one-body energies,

$$W_N = \sum_k\sum_\alpha U(\alpha_k) \tag{2.2}$$

The grand canonical partition function, $\Xi[U]$, is given by

$$\Xi[U] \equiv \sum_{\underset{\sim}{N}\geq\underset{\sim}{0}} \frac{z_a^{N_a}z_b^{N_b}}{N_a!N_b!}\int_\Gamma d\{N_a\}d\{N_b\}\exp(-\beta V_N-\beta W_N), \tag{2.3}$$

where z_α is the activity of species α $(\alpha=a,b)$, β is the reciprocal temperature, $(kT)^{-1}$, k=the Boltzmann constant, $\{N_a\}$ is the set of position vectors, $\{a_1,a_2,..,a_{N_a}\}$, where a_i represents the distance vector, $\mathbf{r}_i^a$; and $d\{N_a\}$, the product of the differentials $da_1da_2\cdots$ Γ is the phase space appropriate for the diatomics (we exclude the regions of phase space where chemical decomposition of the diatomics takes place). The singlet density, $\rho_a^{(1)}$ $(a_1;U)$, and the pair densities, $\rho_{ab}^{(2)}$ $(a_1b_2;U)$, and $\bar{\rho}_{ab}$ $(a_1b_1;U)$ are defined as,

$$\rho_a^{(1)}(a_1;U) \equiv \frac{1}{\Xi[U]}\sum_{\underset{\sim}{N}>\underset{\sim}{1}} \frac{z_a^{N_a}z_b^{N_b}}{(N_a-1)!N_b!} \times\int_\Gamma d\{N_a-1\}d\{N_b-1\}\exp(-\beta V_N-\beta W_N), \tag{2.4}$$

$$\rho_{ab}^{(2)}(a_1b_2;U) \equiv \frac{1}{\Xi[U]}\sum_{\underset{\sim}{N}\geq\underset{\sim}{2}} \frac{z_a^{N_a}z_b^{N_b}}{(N_a-1)!N_b(N_b-2)!} \times\int_\Gamma d\{N_a-1\}d\{N_b-1\}\exp(-\beta V_N-\beta W_N) \tag{2.5}$$

and

$$\bar{\rho}^{(2)}_{ab}(a_1b_1;U) \equiv \frac{1}{\Xi[U]} \sum_{\underset{\sim}{N} \geq \underset{\sim}{2}} \frac{z_a^{N_a} z_b^{N_b}}{(N_a-1)!\,N_b!} \times \int_{\Gamma} d\{N_a-1\} d\{N_b-1\} \exp(-\beta V_N - \beta W_N), \quad (2.6)$$

where the argument, ;U, inside the functions denotes the nonuniformity (when $U=0$, we have the homogeneous case). The overbar, –, denotes the intramolecular quantities. We have not specified the nature of the inhomogeneity, U. It should assume the form appropriate for the problem at hand. For example, in planar adsorption U has the form of Lennard-Jones 10–4 or 9–3 interaction,[33] or of the Boltzmann averaged form.[34] For electrified walls, the Coulombic forces should be added. However, our equations are general. With these definitions at our disposal, we can proceed to the derivation of the BBGKY equation.

The BBGKY Equation

With the definition of the singlet density in (2.4), it is possible to derive the first equation in the BBGKY hierarchy for the ISM. The procedure follows the same line as in the monatomic (MA) case.[35–37] In order to avoid tedious notation we propose the following abbreviations:

$$e^{\alpha}(\alpha_1) = \exp[-\beta U(\alpha_1)] \quad (3.1)$$

$$e^{+\alpha}(\alpha_1) = \exp[+\beta U(\alpha_1)] \quad (3.2)$$

$$E^{\alpha\gamma}(\alpha_i\gamma_j) = \exp[-\beta v(\alpha_i\gamma_j)] \quad (3.3)$$

also,

$$\hat{S}_{(a_1)}(\cdots) \int db_1 da_2 db_2 \cdots da_{N_a} db_{N_b}(\cdots) \quad (3.4)$$

and

$$f^{N_a-1}_{N_bN_b-2} = \frac{z_a^{N_a} z_b^{N_b}}{(N_a-1)!\,N_b(N_b-2)!} \quad (3.5)$$

where v is the pair potential, which becomes $\bar{u}$ for intramolecular interaction or u for intermolecular interaction. Thus Eq. (2.4) can be written as

$$\rho^{(1)}_a(a_1;U) = \frac{1}{\Xi[U]} \sum f^{N_a-1}_{N_b} \hat{S}_{(a_1)} E^{ab}(a_1b_1) E^{a\epsilon}(a_1\epsilon_2) \cdots e^{a}(a_1) \cdots \quad (3.6)$$

where we have exhibited three typical Boltzmann factors. Denoting the gradient operator with respect to $\mathbf{r}_a^1$ as ∇_1, we differentiate both sides of (3.6)

$$\nabla_1 \rho^{(1)}_a(a_1;U) = \Xi[U]^{-1} \sum f^{N_a-1}_{N_b} \hat{S}_{(a_1)} \times \left\{ \begin{array}{l} -\nabla_1 \beta \bar{u}(a_1b_1) E^{ab}(a_1b_1) \cdots \\ -\sum\limits_{\epsilon} (N_\epsilon - 1) \nabla_1 \beta u(a_1\epsilon_2) E^{a\epsilon}(a_1\epsilon_2) \cdots \\ -\nabla_1 \beta U(a_1) e^{a}(a_1) \cdots \end{array} \right\} \quad (3.7)$$

Applying the definitions of the singlet and pair densities, we obtain

$$\begin{aligned} \nabla_1 \rho^{(1)}_a(a_1;U) = &-\int db_1 \nabla_1 \beta \bar{u}(a_1b_1) \cdot \bar{\rho}^{(2)}_{ab}(a_1b_1;U) \\ &- \sum_{\epsilon} \int d\epsilon_2 \nabla_1 \beta u(a_1\epsilon_2) \cdot \rho^{(2)}_{a\epsilon}(a_1\epsilon_2;U) \\ &- \nabla_1 \beta U(a_1) \cdot \rho^{(1)}_a(a_1;U) \quad (3.8) \end{aligned}$$

(BBGKY: Diatomics)

This is the first member of the BBGKY equation for heteronuclear diatomic molecules immersed in an external field. We observe the appearance of the intramolecular pair density, $\bar{\rho}^{(2)}$, as well as the usual intermolecular one, $\rho^{(2)}$. Higher members of the hierarchy can be similarly derived. Equation (3.8) similar to the monatomic case is not closed. In order to solve for the densities, a closure relation is needed. However, the relation given is exact. Any theory concerning the correlation functions must satisfy (3.8) in order to be consistent. In fact, the first member of the BBGKY hierarchy is known to express the force equilibrium among the molecules. The consistency check is then a check on the mechanical equilibrium.

The Pressure Tensor

From a microscopic linear momentum balance, one can show[25–27,38] that the mechanical equilibrium condition in a nonuniform fluid is given by

$$\sum_{\nu} \nabla_{\nu} P^{\mu\nu}(q) = -\sum \rho^{(1)}_{\alpha}(q) \nabla_{\mu} U(q) \quad (4.1)$$

$$\mu, \nu = x, y, z$$

where $P^{\mu\nu}$ is the pressure tensor and U is the external potential. For structured molecules with non-central forces, $P^{\mu\nu}$ may be asymmetrical.[28–30] The well-known equivalence of the first BBGKY hierarchy and the mechanical equilibrium condition requires[26]

$$\begin{aligned} \sum_{\nu} \nabla_{\nu} \cdot \beta P^{\mu\nu}(q) = &\sum_{\alpha} \nabla_{\mu} \rho^{(1)}_{\alpha}(q;U) \\ &+ \sum_{\alpha} \sum_{\epsilon} \int d\epsilon_1 \nabla_{\mu} \beta \bar{u}(q\epsilon_1) \cdot \bar{\rho}^{(2)}_{\alpha\epsilon}(q\epsilon_1;U)(1-\delta_{\alpha\epsilon}) \\ &+ \sum_{\alpha} \sum_{\epsilon} \int d\epsilon_2 \nabla_{\mu} \beta u(q\epsilon_2) \cdot \rho^{(2)}_{\alpha\epsilon}(q\epsilon_2;U) \quad (4.2) \end{aligned}$$

We obtain a microscopic description of the pressure tensor (*via* its gradient) in terms of the site-site correlation functions and the inter- and intramolecular potentials. (N.B. the factor $(1-\delta_{\alpha\epsilon})$, is to remove the one-atom autocorrelation, $\bar{\rho}^{(2)}_{\alpha\alpha}$.) It is obvious to see that the first term on the righthand side (RHS) is the kinetic contribution (ideal gas term), while the second term is the interaction contribution due to the internal forces, $\nabla\bar{u}(\alpha_i\gamma_j)$; and the third term due to the usual intermolecular forces, $\nabla u(\alpha_i\gamma_j)$. The pressure tensor $P^{\mu\nu}$ is known[25–27] to be not uniquely defined. Its gradient, ∇P, however, is well behaved,[26] *i.e.* the microscopic $P^{\mu\nu}$ is defined modulo a divergenceless quantity.[28] Since our system is nonuniform ($U \neq 0$), the pressure tensor is asymmetric (the singlet density is anisotropic in the orientation space and the angular velocity in general lacks local orientational rigidity.[28–30]) Even though we are in an atomic picture,[39] the intramolecular contribution (the second term) shall contribute to the asymmetry and to the so-called body torque.[26,29] In the limit $\bar{\rho}^{(2)}=0$, we recover the familiar pressure tensor expression as given by Irving and Kirkwood,[25] Bearman and Kirkwood,[40] and Davis and Scriven.[41]

Analyses of the RISM

We have mentioned in Sect. 3 that any theory on the site-site functions should satisfy the consistency conditions posed by (3.8). We now check the RISM. The original theory[1] on the site-site direct correlation function (ss-dcf), $c^{(2)}_{\alpha\gamma}(\alpha_i\gamma_j)$, $(i\neq j)$, can be written *via* a matrix form,

$$[\omega^{-1}\delta/\rho^{(1)}-c^{(2)}]_{\alpha\xi}[\delta\rho^{(1)}\omega+F^{(2)}]_{\xi\gamma}=\delta_{\alpha\gamma}\delta_D \qquad (5.1)$$

(as we shall see shortly, this is not the exact Ornstein-Zernike (OZ) relation. Actually, it is an approximate form of the OZ relation). In (5.1), δ is the unit matrix (or the Kronecker delta, $\delta_{\alpha\gamma}$), $\delta_D(qr)$, is the Dirac delta function; ω is the intramolecular structure used in RISM[1] and is related to our intramolecular pair density, $\bar{\rho}^{(2)}$, *via*

$$\sum_{\xi}\rho^{(1)}_{\alpha}(\alpha)\delta_{\alpha\xi}\omega(\xi\gamma)=\rho^{(1)}_{\alpha}(\alpha)\delta_D(\alpha\gamma)\delta_{\alpha\gamma}+\bar{\rho}^{(2)}_{\alpha\gamma}(\alpha\gamma)(1-\delta_{\alpha\gamma}) \qquad (5.2)$$

and $F^{(2)}$ is the truncated (Ursell) pair correlation function,

$$F^{(2)}(\alpha_i\gamma_j)=-\rho^{(1)}_{\alpha}(\alpha_j)\rho^{(1)}_{\gamma}(\gamma_j)+\rho^{(2)}_{\alpha\gamma}(\alpha_i\gamma_j), \qquad (5.3)$$

In Eq. (5.1) the matrix multiplication conventions have been used (*i.e.* summation over repeated indices and integration over repeated arguments).

As was shown by Lebowitz and Percus[42-44] the basis of OZ is the matrix inverse properties of the two functional derivatives,

$$\frac{\delta(-\beta U)}{\delta\rho^{(1)}}\,\frac{\delta\rho^{(1)}}{\delta(-\beta U)}=\delta\delta_D \qquad (5.4)$$

With the definition (2.4) for the singlet density, it is easy to show[45] that the derivative $\delta\rho^{(1)}/\delta(-\beta U)$ is

$$\frac{\delta\rho^{(1)}_{\alpha}(\alpha)}{\delta(-\beta U(\gamma))}=\sum_{\xi}\rho^{(1)}_{\alpha}(\alpha)\delta_{\alpha\xi}\omega(\xi\gamma)+F^{(2)}_{\alpha\gamma}(\alpha\gamma) \qquad (5.5)$$

(Here we have suppressed the inhomogeneity, $;U$). Thus (5.5) accounts for the second factor on the LHS of (5.1). The first factor of (5.1) must correspond to the functional derivative $\delta(-\beta U)/\delta\rho^{(1)}$ in order to satisfy the exact mathematical condition (5.4). To estimate this so-called "compressibility" derivative,[46,47] we notice that Eq. (3.8) can be rearranged to give,

$$\begin{aligned}\nabla_1[-\beta U(a_1)]&=\nabla_1\ln\rho^{(1)}_{a}(a_1)\\&+\int db_1\nabla_1\beta u(a_1b_1)\bar{\rho}^{(2)}_{ab}(a_1b_1)/\rho^{(1)}_{a}(a_1)\\&+\sum\int d\varepsilon_2\nabla_1\beta u(a_1\varepsilon_2)\rho^{(2)}_{a\varepsilon}(a_1\varepsilon_2)/\rho^{(1)}_{a}(a_1)\end{aligned} \qquad (5.6)$$

Assuming the interchangeability of the two differential operators, ∇_1 and $\delta(.)/\delta\rho^{(1)}$ (see *e.g.* Percus[48]), we can functionally differentiate (5.6) to get,

$$\begin{aligned}\nabla_1\frac{\delta(-\beta U)}{\delta\rho^{(1)}}&=\nabla_1\frac{\delta\ln\rho^{(1)}}{\delta\rho^{(1)}}+\int db_1\nabla_1\beta\bar{u}\frac{\delta}{\delta\rho^{(1)}}\left(\frac{\bar{\rho}^{(2)}}{\rho^{(1)}}\right)\\&+\sum_{\xi}\int d\xi_2\nabla_1\beta u\frac{\delta}{\delta\rho^{(1)}}\left(\frac{\rho^{(2)}}{\rho^{(1)}}\right)\end{aligned} \qquad (5.7)$$

In comparison with the MA case, it is natural[49] to identify the ss-dcf which is the correlation function between atoms in different molecules as the last term on the RHS $\nabla_1 c^{(2)}_{\alpha\eta}$ of (5.7):

$$\nabla_1 c^{(2)}_{\alpha\eta}=-\sum_{\xi}\int d\xi_2\nabla_1\beta u\frac{\delta}{\delta\rho^{(1)}_{\eta}}\left(\frac{\rho^{(2)}_{\alpha\xi}}{\rho^{(1)}_{\alpha}}\right) \qquad (5.8)$$

The first term on the RHS (Eq. (5.7)) is due to the ideal gas (kinetic) contribution (see Eq. (4.2)); while the second term is due to contribution from intramolecular forces. We shall call this term Q, *i.e.*

$$\nabla_1 Q\equiv\nabla_1\frac{\delta\ln\rho^{(1)}}{\delta\rho^{(1)}}+\int db_1\nabla_1\beta u\frac{\delta}{\delta\rho^{(1)}}\left(\frac{\bar{\rho}^{(2)}}{\rho^{(1)}}\right) \qquad (5.9)$$

Comparing (5.7) with (5.4) and (5.1) shows that if the RISM assumption (5.1) were correct, the quantity Q in (5.9) should be given by

$$Q\overset{?}{=}\omega^{-1}\left(\frac{\delta}{\rho^{(1)}}\right) \qquad (5.10)$$

modulo a divergenceless quantity. The question mark on the "?" sign is to question the equality of the two sides. A check of the cluster expansions[23,24] for ω shows that this equality does not hold beyond the first density term; *i.e.* the quantity in (5.9) is not the same as was assumed in RISM to be $\omega^{-1}(\delta/\rho^{(1)})$:

$$\begin{aligned}\omega^{-1}\left(\frac{\delta}{\rho^{(1)}}\right)&=\Delta^{-1}\begin{pmatrix}\dfrac{\delta_D}{\rho^{(1)}_a} & -\dfrac{\bar{\rho}^{(2)}_{ab}}{\rho^{(1)}_a\rho^{(1)}_b}\\[2ex] -\dfrac{\bar{\rho}^{(2)}_{ba}}{\rho^{(1)}_b\rho^{(1)}_a} & \dfrac{\delta_D}{\rho^{(1)}_b}\end{pmatrix}\\&=\begin{pmatrix}\dfrac{\delta_D}{\rho^{(1)}_a}+\dfrac{\bar{\rho}^{(2)}_{ab}*\bar{\rho}^{(2)}_{ba}}{\rho^{(1)}_a\rho^{(1)}_a\rho^{(1)}_b}+\cdots & -\dfrac{\bar{\rho}^{(2)}_{ab}}{\rho^{(1)}_a\rho^{(1)}_b}-\cdots\\[2ex] -\dfrac{\bar{\rho}^{(2)}_{ba}}{\rho^{(1)}_b\rho^{(1)}_a}-\cdots & \dfrac{\delta_D}{\rho^{(1)}_b}+\dfrac{\rho^{(2)}_{ba}*\rho^{(2)}_{ab}}{\rho^{(1)}_b\rho^{(1)}_b\rho^{(1)}_a}+\cdots\end{pmatrix}\end{aligned} \qquad (5.11)$$

where Δ is the normalization factor. Therefore the RISM assumption (5.1) does not satisfy the BBGKY condition. (There was an additional assumption on the ss-dcf in RISM,[50] which we shall not comment here.) We conclude that the relation (5.1) is not a true Ornstein-Zernike relation (we base our definition of OZ on Eq. (5.4)). And the conventional RISM theory is not an exact theory in more ways[19-24] than one.

Discussions

From explicit definitions of the correlation functions in the interaction site model we have derived for the first time the BBGKY equation in a nonuniform system. We specialize to the case of the heteronuclear diatomics. Higher polyatomics can be easily treated along analogous lines. Since the BBGKY equation is equivalent to the mechanical equilibrium condition, we are able to express the pressure tensor in terms of both intra- and inter-molecular correlation functions. These connections confirm that the gradients of the density and the external potential are related to microscopic force balances. Therefore any equations relating the many-body distribution functions using the ISM approach much satisfy this microscopic force balance condition. We examined the reference interaction site model and found that its proposed Ornstein-Zernike-like equation is not consistent with the general form of the BBGKY equation.

In the monatomic case, other types of hierarchy were given for the gradient of the singlet density, *e.g.*

$$\nabla_1\rho^{(1)} = \rho^{(1)}\nabla_1(-\beta U) + \rho^{(1)}\int \mathrm{d}2\, \mathrm{c}^{(2)}\nabla_2\rho^{(1)} \tag{6.1}$$

as given by Lovett *et al.*[51] (See also[44,52,53]). Their implications in the polyatomic case shall also be investigated in the future.

In the MA Henderson[38] has derived the following pressure gradient relation based on the potential distribution theorem of Widom,[54]

$$\sum_{\nu} \nabla\beta P^{\mu\nu} = \rho^{(1)}\nabla \ln \rho^{(1)} - \rho^{(1)}\nabla \mathrm{c}^{(1)}, \qquad \text{(MA)} \tag{6.2}$$

where $\mathrm{c}^{(1)}$ is the one-body direct correlation function. Since the two-body dcf, $\mathrm{c}^{(2)}$, can be obtained from $\mathrm{c}^{(1)}$ *via* the functional differentiation[55]

$$\mathrm{c}^{(2)}(\mathrm{r}, \mathrm{r}') = \frac{\delta \mathrm{c}^{(1)}(\mathrm{r})}{\delta\rho^{(1)}(\mathrm{r}')}, \qquad \text{(MA)} \tag{6.3}$$

we could differentiate (6.2) with respect to $(\delta/\delta\rho^{(1)})$ (after interchanging the order with the gradient ∇)[48] to obtain

$$\nabla \mathrm{c}^{(2)} = -\sum_{\nu} \nabla \frac{\delta}{\delta\rho^{(1)}}\left(\frac{\beta P_{\mathrm{c}}^{\mu\nu}}{\rho^{(1)}}\right), \qquad \text{(MA)} \tag{6.4}$$

where $P_{\mathrm{c}}^{\mu\nu}$ is the configurational part of the pressure tensor. Equation (6.4) bears striking resemblance to our Eq. (5.8) after the substitution of (4.2). In this respect the monatomics exhibit similar behavior as our diatomic case. (In fact our diatomic equations should reduce to the MA case when the intramolecular potential is set equal to the intermolecular one; or when $\bar{\rho}^{(2)}=0$). In fact Eq. (6.4) lends support to our identification (5.8). The potential distribution theorem has played an important role in the computer simulations of the chemical potential in MA.[56–62] Its extension to polyatomics is under investigation.

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