

Liquids and liquid mixtures : Deduction of the BGY equation considering the angular distribution function

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Abstract. The Born-Green-Yvon equation for molecular fluid has been deduced considering the orientational distribution functions. The isotropic and anisotropic parts of the distribution function have been separated. The expressions deduced can be used in the case of mixtures and for the non-central type of intermolecular potential energy.

Keywords. Integer differential equation; Born-Green-Yvon equation; orientational distribution function; spherical harmonics; Clebsch-Gordon coefficients; liquid mixtures.

1. Introduction

Most of the theoretical work based on statistical mechanics to study the liquid state considered the molecules to be spherical in shape and intermolecular forces acting between them to be centric one. But this deviates from the result of the experimental liquids where the liquids studied were polyatomic in nature and intermolecular forces are non-central one. Buckingham (1967), Stillinger (1972) and Deutch (1973) discussed in detail the problem. All these observations necessitate the study of the liquid state considering the noncentral type of intermolecular potential energy function.

Born-Green-Yvon (1946), Kirkwood (1935) and others studied the liquid state extensively starting from the integro-differential equation of molecular assembly. The calculations were made considering the central type of potential energy functions. Machine simulation studies made by Alder (1959) and others considered the same type of intermolecular potential energy functions. Studies on angle-dependent potentials like Stockmayer (1941) potential or Kihara type of potential are scanty. In this paper the integro-differential equation of Born-Green-Yvon has been deduced considering the non-central forces.

2. Integro-differential equation

In this derivation the molecules are considered to be in ground electronic and vibrational states. The intermolecular potential energy is assumed to depend only

on the intermolecular separation and on the molecular orientation. We consider a classical system of N particles in a volume V at temperature T . The distribution function expresses the probabilities of observing different configurations of sets of h -particle out of the total number N .

The h -particle orientational distributions function can be written as (Buckingham 1967)

$$\begin{aligned} g(\mathbf{r}^h w^h) &= g(\mathbf{r}_1 w_1, \mathbf{r}_2 w_2 \dots \mathbf{r}_h w_h) \\ &= \frac{\Omega^h}{\rho^h} f(\mathbf{r}^h w^h). \end{aligned} \quad (1)$$

where $f(\mathbf{r}^h, w^h)$ is the generic distribution function and defined as

$$f(\mathbf{r}^h w^h) d\mathbf{r}_1 \dots d\mathbf{r}_h dw_1 \dots dw_h$$

is the probability of finding a molecule in each of the h -volume element $d\mathbf{r}_1 \dots d\mathbf{r}_h$ and in the orientational volume $dw_1 \dots dw_h$. ρ = Average density and $\Omega = \int dw^h$. In order to deduce the integro-differential equation we consider the intermolecular potential energy to be additive in nature and can be written as

$$\Phi(\mathbf{r}^h w^h) = \sum_{i < j} \varphi(\mathbf{r}_i, w_i w_j). \quad (2)$$

The generic distribution function can be written as

$$f(\mathbf{r}^h w^h) = \frac{1}{(N-h)!} \frac{\int \dots \int \exp(-\beta\Phi) d\mathbf{r}_{h+1} \dots d\mathbf{r}_N dw_{h+1} \dots dw_N}{Z} \quad (3)$$

where Z = configurational partition function and

$$\beta = 1/kT = \frac{1}{N!} \int \exp(-\beta\Phi) d\mathbf{r}_1 \dots d\mathbf{r}_N dw_1 \dots dw_N. \quad (4)$$

The relation between the potential of the mean force and the orientation distribution function can be deduced by defining a quantity (Hill 1950), $W(\mathbf{r}^h, w^h)$ by

$$\exp\left[-\frac{W(\mathbf{r}^h w^h)}{kT}\right] = V^h \frac{(N-h)!}{h!} f(\mathbf{r}^h w^h), \quad (5)$$

where the multiplication of RHS by V^h makes it dimensionless. Now proceeding in the similar way as done by Kirkwood, i.e. differentiate (5) with respect to the co-ordinate of one of the h molecules 1 ... h say a we find

$$\begin{aligned} \nabla_a W(\mathbf{r}^h w^h) &= \nabla_a \Phi(\mathbf{r}^h w^h) \\ \text{where } \nabla_a \Phi(\mathbf{r}^h w^h) &= \frac{\int \dots \int \exp(-\beta\Phi) \nabla_a \Phi d\mathbf{r}_{h+1} \dots d\mathbf{r}_N dw_{h+1} \dots dw_N}{\int \dots \int \exp(-\beta\Phi) d\mathbf{r}_1 \dots d\mathbf{r}_N dw_1 \dots dw_N}. \end{aligned} \quad (6)$$

Equation (6) from the usual definition of the angular distribution can be written as

$$-\nabla_a \Phi(\mathbf{r}^h w^h) = -kT \nabla_a \ln g(\mathbf{r}^h w^h). \quad (7)$$

For $a = 1$ equation (6) can be written as

$$-kT \nabla_1 \ln g(\mathbf{r}^h w^h) = \overline{\nabla_1 \Phi(\mathbf{r}^h w^h)}. \quad (8)$$

But from (2)

$$\nabla_1 \Phi(\mathbf{r}^h w^h) = \sum_{i < j} \nabla_1 \varphi(r_{ij} w_i w_j), \quad (9)$$

so that (8) reduces to

$$\begin{aligned} -kT \nabla_1 \ln g(\mathbf{r}^h w^h) &= \frac{\sum_{i < j} \int \dots \int \exp(-\beta \Phi) \nabla_1 \varphi(r_{ij} w_i w_j) d\mathbf{r}_{h+1} \dots d\mathbf{r}_N dw_{h+1} \dots dw_N}{\int \dots \int \exp(-\beta \Phi) d\mathbf{r}_1 \dots d\mathbf{r}_N dw_1 \dots dw_N}. \end{aligned} \quad (10)$$

The sum in (10) can be broken up in two parts, i.e. $i = 2 \dots h$ and $i = h + 1 \dots N$

$$\begin{aligned} \text{i.e. } \int \int \nabla_1 \varphi(r_{ij} w_i w_j) \left[\int \dots \int \exp(-\beta \Phi) d\mathbf{r}_{h+1} \dots d\mathbf{r}_{i-1} d\mathbf{r}_{i+1} \dots \right. \\ \left. d\mathbf{r}_N dw_{j-1} dw_{j+1} \dots dw_N \right] d\mathbf{r}_i dw_j. \end{aligned}$$

Then considering the definition of $f(\mathbf{r}^h w^h)$ and $g(\mathbf{r}^h w^h)$ (10) can be written as

$$\begin{aligned} -kT \nabla_1 \ln g(\mathbf{r}^h w^h) &= \sum_{i=2}^h \nabla_1 \varphi(r_{ij} w_i w_j) + \iint \nabla_1 \varphi(r_{ij} w_i w_j) \\ &g^{[h+1]}(\mathbf{r}^{h+1} w^{h+1}) dr dw, \end{aligned} \quad (11)$$

where $g^{[h+1]} = g^{(h)}(\mathbf{r}_1 \mathbf{r}_{h+1} w_1 w_{h+1}) - g^{(h)}(\mathbf{r}_2 \mathbf{r}_{h+1} w_2 w_{h+1})$

for $h = 2$ (11) can be written as

$$\begin{aligned} -kT \nabla_1 \ln g^{(2)}(r_{12} w_1 w_2) &= \nabla_1 \varphi(r_{12}, w_1 w_2) + \rho \int \dots \int \nabla_1 \varphi(r_{13}, w_1 w_3) \\ &g^{[3]}(r_3 w_3) d\mathbf{r}_3 dw_3 \end{aligned} \quad (12)$$

which is the well-known integro-differential equation and applying the superposition approximation (12) can be reduced to the Born-Green-Yvon equation.

3. Separation of isotropy and anisotropy

Equation (11) can be separated into the isotropic and anisotropic part considering the intermolecular potential energy function, as (Buckingham 1967)

$$\varphi(r_{12}, w_1 w_2) = \varphi_0(r_{12}) + \varphi_a(r_{12}, w_1 w_2). \quad (13)$$

where $\varphi_0(r_{12})$ is the unweighted orientational average of the potential

$$\varphi_0(r_{12}) = \langle \varphi(r_{12}, w_1 w_2) \rangle = \frac{1}{4\pi} \int dw_1 dw_2 \varphi(r_{12} w_1 w_2). \quad (14)$$

For simple liquids $\varphi_0(r_{12})$ can be considered as Lennard-Jones type of pair potential. We can separate the isotropic and anisotropic part of the distribution function in the same way, i.e., by considering

$$g^{(2)}(r_{12}, w_1 w_2) = g^{(2)}(r_{12}) h^{(2)}(w_1 w_2). \quad (15)$$

So the integro-differential equation can be written as

$$\begin{aligned} -kT \frac{\partial \ln g^{(2)}(r_{12})}{\partial r_1} - kT \frac{\partial \ln h^{(2)}(w_1 w_2)}{\partial w_1} = - \frac{\partial \varphi_0(r_{12})}{\partial r_1} - \frac{\partial \varphi_a(r_{12}, w_1 w_2)}{\partial w_1} \\ + \rho \int \frac{\partial \varphi(r_{13})}{\partial r_1} \frac{g^{(3)}}{g^{(2)}} d\mathbf{r}_3 + \rho \int \frac{\partial \varphi_a(r_{13}, w_1 w_3)}{\partial w_1} \frac{h^{(3)}}{h^{(2)}} dw_3. \end{aligned}$$

The integro-differential equations corresponding to the isotropic and anisotropic part of the distribution function can be written as

$$\begin{aligned} kT \frac{\partial \ln g^{(2)}(r_{12})}{\partial r_1} = - \frac{\partial \varphi_0(r_{12})}{\partial r_1} - \rho \int \frac{\partial \varphi(r_{13})}{\partial r_1} \cdot \frac{g^{(3)}}{g^{(2)}} d\mathbf{r}_3. \\ \times kT \frac{\partial \ln h^{(2)}(w_1 w_2)}{\partial w_1} = - \frac{\partial \varphi_a(r_{12}, w_1 w_2)}{\partial w_1} - \rho \int \frac{\partial \varphi_a(r_{13}, w_1 w_3)}{\partial w_1} \frac{h^{(3)}}{h^{(2)}} dw_3. \end{aligned}$$

The equation gives the solution for $g(r_{12})$

$$g^{(2)}(r_{12}) = \exp[-\varphi_0(r_{12})/kT] [1 + S(r_{12})]. \quad (16)$$

Similarly one can write

$$h^{(2)}(w_1 w_2) = \exp[-\varphi_a(r_{12}, w_1 w_2)/kT] [1 + S(w_1 w_2)],$$

$$\text{so, } g^{(2)}(r_{12}, w_1 w_2) = \exp[-\varphi_0(r_{12})/kT] [1 + S(r_{12})] \exp[-\varphi_a(r_{12}, w_1 w_2)/kT] [1 + S(w_1 w_2)]. \quad (17)$$

$$\text{or, } g^{(2)}(r_{12}, w_1 w_2) = \exp[-\varphi(r_{12}, w_1 w_2)/kT] y(r_{12}, w_1 w_2). \quad (18)$$

$$\text{where } y(r_{12}, w_1 w_2) = 1 + S(r_{12}) + S(w_1 w_2) + S(r_{12}) S(w_1 w_2). \quad (19)$$

4. Discussions

Expression (18) is the same as obtained by Ben-Naim (1971) in the case of liquid water using a point charge model of potential. Ben-Naim (1971) assumed actually the following approximation:

$$y(r_{12}, w_1 w_2) \approx y(r_{12}).$$

Thus we find that the radial part and the angle-dependent part of the potential energy function as well as that of the distribution function can be separated. It is now useful to calculate the angular distribution function. To obtain this we propose to use the Stockmayer potential of the following form

$$\Phi(r_1 w) = \Phi(r) + \Phi(\theta_1 \psi).$$

The first part of the potential energy function is incorporated into the radial distribution function. It is convenient to expand the potential energy function in terms of the products of spherical harmonics of the orientation of the molecules and the intermolecular distance. If we consider (Gray 1978)

$$C(\Lambda m_1 m_2 m) = C(l_1 l_2 l m_1 m_2 m)$$

the Clebsch-Gordon coefficient, the expansion coefficient becomes

$$\Phi(\Lambda) = \sum \epsilon(\Lambda m_1 m_2 r_{12}) C(\Lambda m_1 m_2 m) D_{m_1 n_1}^{l_1}(w_1) D_{m_2 n_2}^{l_2}(w_2) Y_{lm}(w_{12}),$$

where $D_{ml}^l(w) = D_{ml}^l(\theta, \psi)$ is the generalised spherical harmonic for $\Lambda = 001$, $\Phi(\Lambda) = \Phi(r_{12})$, i.e., isotropic potential. In Guha (1978) the method of solving the integro-differential equation has been reported. The method with the inclusion of the angular-dependent parts can be used to calculate the physico-chemical properties of the polyatomic molecules. This work is in progress.

5. References

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