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Liquids and liquid mixtures—I

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Abstract. An iterational method is presented here to solve the integrodifferential equation of the general theory of the molecular assembly, using Green's function. The first iterational result is the Born-Green and Kirkwood's equation. So the error introduced by the superposition approximation can be minimised with this method.

Keywords. Integrodifferential equation; Green's function; iterational method; radial distribution function.

1. Introduction

The scattering function $i(s)$ of a liquid is the fourier transform of the correlation function $g(r)-1$ where $g(r)$ is the radial distribution function. All the thermodynamical properties are related with the radial distribution function if one represents the interatomic forces as additive pair potential. The theory of the structure of simple fluid is enmeshed in the theory of the equation of state, which can be deduced from the expression of the radial distribution function.

The radial distribution function $g(r)=n_{2(r_0)}/n^2$ is the particular cases for the generalised theory of the molecular assembly and for $h=2$ i.e. the integrodifferential equation, Hill (1956)

$$k\frac{\delta \ln n_h(\mathbf{r}^h)}{\partial \mathbf{r}_i} = -\frac{\delta \phi(\mathbf{r}^h)}{\partial \mathbf{r}_i} - \int \frac{\partial \phi_{i,h+1}}{\partial \mathbf{r}_i}\frac{n_{h+1}}{n_h}\frac{(\mathbf{r}^{h+1})}{(\mathbf{r}^h)}d\mathbf{r}_{h+1} \tag{1}$$

where $\mathbf{r}$ is the radius vector, $\phi(r)$ is the potential energy function, k is Boltzmann constant.

Born and Green (1946) and Kirkwood (1935) applied the superposition approximation to reduce (1) for $h=2$ to a simplified form. But for the calculation of the forth and fifth virial coefficient from the above equation the error is as much as 30% and not negligible (Porter 1964).

An iterative method is presented here to solve (1). Firstly the intergrodifferential equation was changed to a form similar to Poissili's equation. The equation was then solved by Green function and an iterational method.

2. Solution of the integrodifferential equation

Equation (1) can be differentiated with respect to $\mathbf{r}_i$ and get,

$$kT\nabla^2 \ln n_h(\mathbf{r}^h) = -\nabla^2\phi(\mathbf{r}^h) - \frac{\delta}{\partial \mathbf{r}_i}\int \frac{\partial \phi_{i,h+1}}{\partial \mathbf{r}_i}\cdot\frac{n_{h+1}}{n_h}\cdot\frac{(\mathbf{r}^{h+1})}{(\mathbf{r}^h)}d\mathbf{r}_{h+1} \tag{2}$$

or $$kT \nabla^2 \ln n_h(\mathbf{r}^h) + K'^2 \ln n_h(\mathbf{r}^h) = \chi_h(\mathbf{r}^h) \tag{3}$$

where $$K'^2 = \lim_{r \to \infty} \frac{\partial}{\partial \mathbf{r}_i} \int \frac{\partial \phi_{i,h+1}}{\partial \mathbf{r}_i} \frac{n_{h+1}}{n_h} \frac{(\mathbf{r}^{h+1})}{(\mathbf{r}_h)} d\mathbf{r}_{h+1}. \tag{4}$$

and $$\chi(\mathbf{r}^h) = -\nabla^2 \phi(\mathbf{r}^h) - \frac{\partial}{\partial \mathbf{r}_i} \int \frac{\partial \phi_i}{\partial \mathbf{r}_i} \cdot \frac{n_{h+1}}{n_h} \cdot \frac{(\mathbf{r}^{h+1})}{(\mathbf{r}^h)} d\mathbf{r}_{h+1}$$

$$+ K^2 \ln [-n_h(\mathbf{r}^h)]. \tag{5}$$

The obvious solution of (3) is

$$\ln n_h(\mathbf{r}^h) = \int G(\mathbf{r}^h/\mathbf{r}_0{}^h)\, \chi_h(\mathbf{r}_0{}^h)\, d\mathbf{r}_0{}^h \tag{6}$$

where $G(\mathbf{r}^h/\mathbf{r}_0{}^h)$ is the Green's function suitable for the problem.

Equation (6) becomes the obvious solution of the equation which contain n_{h+1} and n_h in the r.h.s. and now the iterational method is to be used.

3. Iterational procedure

From equation (6)

$$n_h = \exp\, [\int G(\mathbf{r}^h/\mathbf{r}_0{}^h)\, \chi_h(\mathbf{r}_0{}^h)\, d\mathbf{r}_0{}^h]. \tag{7}$$

The order of iteration of the expression is

$$n_h^{(n)} = \exp\left[\int G\left(\frac{\mathbf{r}^h}{\mathbf{r}_0{}^h}\right) \chi_h^{(n-1)}(\mathbf{r}_0{}^h)\, d\mathbf{r}_0{}^h\right] \tag{8}$$

where $$\chi_h^{(n-1)} = \frac{\delta}{\delta \mathbf{r}_i} \int \frac{\partial \phi_{i,h+1}}{\partial \mathbf{r}_i} \cdot \frac{n_{h+1}^{(n-2)}}{n_h^{(n-2)}} \cdot \frac{(\mathbf{r}^{h+1})}{(\mathbf{r}^h)} d\mathbf{r}_{h+1}. \tag{9}$$

For the first iteration

$$kT \ln n_h{}^0(\mathbf{r}^h) = -n_1 \phi(\mathbf{r}^h)$$

$$n_h{}^0(\mathbf{r}^h) = n_1 \exp\left(-\frac{\phi(\mathbf{r}^h)}{kT}\right).$$

Similarly

$$n_h^{(1)} = n_1 \exp\left[-\frac{\phi(\mathbf{r}^h)}{kT} + \frac{\partial}{\partial \mathbf{r}_i} \int \frac{\partial \phi_{i,h+1}}{\partial \mathbf{r}_i} \cdot \frac{n_{h+1}^0}{n_h{}^0} \cdot \frac{(\mathbf{r}^{h+1})}{(\mathbf{r}^h)} d\mathbf{r}_{h+1}\right]$$

Thus in (9) the definition of $\chi_h^{(n-1)}$ follows from (5) (Sengupta and Guha 1973). Now (9) can be obtained on considering a trial solution of n_h and proceeding stepwise.
From (2)

$$n_{h+1}^{(n)} = \exp \int G\left(\frac{\mathbf{r}^{h+1}}{\mathbf{r}_0{}^{h+1}}\right) \chi_{h+1}^{(n-1)} (\mathbf{r}_0{}^{h+1})\, d\mathbf{r}_0{}^{h+1}. \tag{10}$$

Therefore

$$\chi_h^{(n)} = \frac{\partial}{\partial \mathbf{r}_i} \int \frac{\partial \phi_{i,\,h+1}}{\partial \mathbf{r}_i} \cdot \frac{n_{h+1}^{(n-1)}}{n_h^{(n-1)}}\, d\mathbf{r}_{h+1} \cdot$$

$$= \frac{\partial}{\partial \mathbf{r}_i} \int \frac{\partial \phi_{i,\,h+1}}{\partial \mathbf{r}_i} \cdot \exp\left[\int G\left(\frac{\mathbf{r}^{h+1}}{\mathbf{r}_0{}^{h+1}}\right) \cdot \chi_{h+1}^{(n-1)} (\mathbf{r}^{h+1}) \right.$$

$$\left. - \int G\left(\frac{\mathbf{r}^h}{\mathbf{r}_0{}^h}\right) \cdot \chi_h{}^{(n-1)} (\mathbf{r}^h)\, d\mathbf{r}^h \right] d\mathbf{r}_{h+1}.$$

So,

$$n_h{}^{(n-1)} = \exp \int G\left(\frac{\mathbf{r}^h}{\mathbf{r}_0{}^h}\right) \left[\frac{\partial}{\partial \mathbf{r}_i} \int \frac{\partial \phi_{i,\,h+1}}{\partial \mathbf{r}_i} \exp \left\{ G\left(\frac{\mathbf{r}^{h+1}}{\mathbf{r}_0{}^{h+1}}\right) \right.\right.$$

$$\left.\left. \chi_{h+1}^{(n-1)} (\mathbf{r}^{h+1})\, d\mathbf{r}_{h+1} - \int G\left(\frac{\mathbf{r}^h}{\mathbf{r}_0{}^h}\right) \cdot \chi_h (\mathbf{r}^h)\, d\mathbf{r}_h \right\} \right] d\mathbf{r}_h. \tag{11}$$

Thus we can proceed to find out $n_h{}^{(n-1)}$ ..., etc. to any order of accuracy.

4. Choice of the Green function

The choice of the Green function essentially depend on the boundary conditions.
We can write (3) as

$$\nabla^2 \psi (\mathbf{r}^h) + K'^2 \psi (\mathbf{r}^h) = \delta (\mathbf{r}^h - \mathbf{r}_0{}^h) \tag{12}$$

Hence one has to satisfy the proper condition at infinity. The condition usually put in the following form must behave as an outgoing wave at infinity.
Now G is so chosen that,

$$\int \left(G \frac{\partial \psi}{\partial r} - \psi \frac{\partial G}{\partial r} \right) dr \to 0 \tag{13}$$

easily satisfied if G is also required to behave as outgoing wave i.e. G is chosen to satisfy the same asymptotic condition as required.

For the development of the liquid state theory one has to take the Green function of the type,

$$\frac{\exp\,[-iK\,(\mathbf{r}^h-\mathbf{r}_0{}^h)]}{(\mathbf{r}^h-\mathbf{r}_0{}^h)}\,, \tag{14}$$

as for the imperfect gases,

$$\frac{\exp\,[K\,(\mathbf{r}^h-\mathbf{r}_0{}^h)]}{(\mathbf{r}^h-\mathbf{r}_0{}^h)}\,, \tag{15}$$

and for the development of the theory of solids an undamped periodic function is to be chosen (Green 1960). Obviously for the transition from the gaseous to the liquid state there is a change of sign of K^2 which is given in (15). Thus we can build up the theory of liquid and gases from this procedure adapted.

5. Explicit results

The trial solution considered is,

$$n_h{}^0 = n_1{}^h \text{ where } n_1 = N/V$$

Therefore $n^0_{h+1}/n_h{}^0 = n_1$

and

$$\chi_h{}^0 = -\nabla^2\phi\,(\mathbf{r}^h) - n_1\frac{\partial}{\partial\mathbf{r}_i}\int\frac{\partial\phi_{i,\,h+1}}{\partial\mathbf{r}_i}\,d\mathbf{r}_{h+1} - K^2\ln n_1{}^h \tag{16}$$

Putting this value in (6)

$$\ln n_h{}^{(1)} = \int\frac{\exp\,[-ik\,(\mathbf{r}^h-\mathbf{r}_0{}^h]}{(\mathbf{r}^h-\mathbf{r}_0{}^h)}\left[-\nabla^2\phi\,(\mathbf{r}^h) - n_1\frac{\partial}{\partial\mathbf{r}_i}\int\frac{\partial\phi_{i,\,h+1}}{\partial\mathbf{r}_i}\,d\mathbf{r}_{h+1}\right.$$

$$\left. - K^2\ln n_1{}^h\right]d\mathbf{r}_h. \tag{17}$$

Therefore $n_h{}^{(1)} = \exp\left[\int\frac{\exp iK\,(\mathbf{r}^h-\mathbf{r}_0{}^h)}{(\mathbf{r}^h-\mathbf{r}_0{}^h)}\left\{-\nabla^2\phi\,(\mathbf{r}^h) - n_1\int\frac{\partial\phi_{i,\,h+1}}{\partial\mathbf{r}_i}\cdot d\mathbf{r}_{h+1}\right.\right.$

$$\left.\left. - K^2\ln n_1{}^h\right\}\right]d\mathbf{r}_{h+1} \tag{18}$$

and $Q_h^{(1)} = \frac{n_{h+1}^{(1)}}{n_h^{(1)}} = \exp\left[\int\frac{\exp\,[-iK\,(\mathbf{r}^h-\mathbf{r}_0{}^h)]}{(\mathbf{r}^h-\mathbf{r}_0{}^h)}\left\{-\nabla^2\phi(\mathbf{r}^h)\right.\right.$

$$-n_1 \int \frac{\partial \phi_{i,h+2}}{\partial \mathbf{r}_i} d\mathbf{r}_{h+2} - K^2 \ln n_1^{h+2} \Big\} \frac{-\exp\,[-ik(r^h - \mathbf{r}_0^h)]}{(\mathbf{r}^h - \mathbf{r}_0^h)}$$

$$\Big\{ -\nabla^2 \phi(\mathbf{r}^h) - n_1 \int \frac{\partial \phi_{i,h+1}}{\partial \mathbf{r}_i} d\mathbf{r}_{h+1} - K^2 \ln n_1^{h+1} \Big\} \Big] d\mathbf{r}_{h+1}. \tag{19}$$

Therefore $$\chi_h^{(1)} = -\nabla^2 \phi(\mathbf{r}^h) - \frac{\partial}{\partial \mathbf{r}_i} \int \frac{\partial \phi_{i,h+1}}{\partial \mathbf{r}_i}(Q_h)\, d\mathbf{r}_{h+1}; \tag{20}$$

$$n_h^{(2)} = \exp \int \frac{\exp\,[-iK(\mathbf{r}^h - r_0^h)]}{(\mathbf{r}^h - \mathbf{r}_0^h)} \cdot \Big[-\nabla^2 \phi(\mathbf{r}^h)$$

$$- \frac{\partial}{\partial \mathbf{r}_i} \int \frac{\partial \phi_{i,h+1}}{\partial \mathbf{r}_i}(Q_h)\, d\mathbf{r}_h \Big] d\mathbf{r}_{h+1} \tag{21}$$

and so on.

Then we see that n_h, the multiple distribution function, can be obtained up to any order of accuracy from this method of iterations.

6. Conclusions

It is obvious from the above formulae that for $h=2$ the first iterational result is the Born-Green and Kirkwood's equation (5). So the superposition approximation which is the source of error in the Born-Green and Kirkwood's equation can be avoided by this iterational method. The virial coefficients are to be calculated and for the second iteration the fourth virial coefficient is same as that obtained by the cluster integral method (Sengupta and Guha 1973).

From the above method the theory of the imperfect gases, liquids and solid state can be developed with proper choice of the Green function.

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