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Kirkwood–Born–Green treatment of polymers with excluded volume

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Abstract. It has been proved that the first member of the hierarchy of the Kirkwood–Born–Green integro-differential equations which give the relation among the distribution functions of the polymer chain with excluded volume is equivalent to the Reiss variational method. If we suppose that the joint probability density function of a polymer chain fulfils the superposition closure approximation then the first member of the Kirkwood–Born–Green hierarchy is equivalent to the Edwards method of the self-consistent field.

1. Introduction

It is well known in classical statistics that the lowest member of the hierarchy of the Born–Green–Yvon type equations describes the behaviour of liquids and imperfect gases as the lowest member of the Kirkwood–Born–Green type equations (Hill 1956). This raises the question: are these systems equivalent even when a polymer chain is described? Recently Whittington and Dunfield (1973) proved that the first member of the Born–Green–Yvon hierarchy involves the Edwards and Reiss self-consistent field (SCF) equations (Edwards 1965, Reiss 1967). In this connection Naghizadeh (1967) was the first to study the Kirkwood–Born–Green type equation. Although his correlation function strongly resembles the Reiss SCF potential the noted equivalence of the first member of the Kirkwood–Born–Green hierarchy to the Reiss method was not proved explicitly in his work. Obviously this was caused by his special choice of model (ring polymer) and the Gauss approximation to correlation functions in the integrand of the lowest member of the Kirkwood–Born–Green hierarchy.

2. Model and derivation of the equations

If the variable charge ξ , which determines the extent of the long-range interaction resulting in the excluded volume effect in a polymer chain, is joined only to the n th monomer unit of the chain, then the lowest member of the Kirkwood–Born–Green hierarchy is given in the form (Naghizadeh 1967)

$$kT \frac{\partial p(\mathbf{r}_n, n; \xi)}{\partial \xi} = p(\mathbf{r}_n, n, \xi) \sum_{i=0}^{n-2} \iint U(\mathbf{r}_n - \mathbf{r}_i) p_2(\mathbf{r}_i, i; \mathbf{r}_n, n; \xi) d\mathbf{r}_i d\mathbf{r}_n - \sum_{i=0}^{n-2} \int U(\mathbf{r}_n - \mathbf{r}_i) p_2(\mathbf{r}_i, i; \mathbf{r}_n, n; \xi) d\mathbf{r}_i. \quad (1)$$

Here $p(\mathbf{r}_n, n; \xi)$ and $p(\mathbf{r}_i, i; \mathbf{r}_n, n; \xi)$ are the probability density for the n th link of the chain to appear at the point \mathbf{r}_n and the joint probability density for the i th link to appear at point \mathbf{r}_i and the n th link at point \mathbf{r}_n , respectively. $U(\mathbf{r}_n - \mathbf{r}_i)$ is the long-range interaction energy. Choosing an interaction potential in (1) (Fixman 1955)

$$U(r) = kT\beta\delta(r) \quad (2)$$

we get

$$\frac{\partial p(\mathbf{r}_n, n, \xi)}{\partial \xi} = \beta p(\mathbf{r}_n, n; \xi) \sum_{i=0}^{n-2} p_2(\mathbf{r}_n, i; \mathbf{r}_n, n; \xi) - \beta \sum_{i=0}^{n-2} p_2(\mathbf{r}_n, i; \mathbf{r}_n, n; \xi) \quad (3)$$

where β is the volume excluded by a monomer.

3. Closure approximation and results

Now we shall prove the following theorem.

Let equation (3) be valid for

$$p(\mathbf{r}_n, n; \xi) \simeq p_{\text{SCF}}(\mathbf{r}_n, n; \xi) \quad \text{and} \quad p_2(\mathbf{r}_n, i; \mathbf{r}_n, n; \xi) \simeq p_{2\text{SCF}}(\mathbf{r}_n, i; \mathbf{r}_n, n; \xi),$$

ie let (3) be valid in the SCF approximation identical with the markovian closure approximation (Reiss 1967, Freed and Gillis 1971):

$$\begin{aligned} p_{\text{SCF}}(\mathbf{r}_n, n; \xi) &= \frac{1}{Z_{\text{SCF}}(\xi)} \int \prod_{i=1}^n \exp\left(-\frac{R(\mathbf{r}_i - \mathbf{r}_{i-1})}{kT}\right) \exp\left(-\frac{1}{kT} \sum_{i=1}^{n-1} \phi(\mathbf{r}_i)\right) \\ &\quad \times \exp\left(-\frac{\xi}{kT} \phi(\mathbf{r}_n)\right) d\mathbf{r}_0 \dots d\mathbf{r}_{n-1} \end{aligned} \quad (4)$$

$$\begin{aligned} p_{2\text{SCF}}(\mathbf{r}_i, i; \mathbf{r}_n, n; \xi) &= \frac{1}{Z_{\text{SCF}}(\xi)} \int \prod_{i=1}^n \exp\left(-\frac{R(\mathbf{r}_i - \mathbf{r}_{i-1})}{kT}\right) \exp\left(-\frac{1}{kT} \sum_{i=1}^{n-1} \phi(\mathbf{r}_i)\right) \\ &\quad \times \exp\left(-\frac{\xi}{kT} \phi(\mathbf{r}_n)\right) d\mathbf{r}_0 \dots d\mathbf{r}_{i-1} d\mathbf{r}_{i+1} \dots d\mathbf{r}_{n-1} \end{aligned} \quad (5)$$

$$Z_{\text{SCF}}(\xi) = \int \prod_{i=1}^n \exp\left(-\frac{R(\mathbf{r}_i - \mathbf{r}_{i-1})}{kT}\right) \exp\left(-\frac{1}{kT} \sum_{i=1}^{n-1} \phi(\mathbf{r}_i)\right) \exp\left(-\frac{\xi}{kT} \phi(\mathbf{r}_n)\right) d\mathbf{r}_0 \dots d\mathbf{r}_n. \quad (6)$$

$R(\mathbf{r}_i - \mathbf{r}_{i-1})$ is a function of the energy of the polymer and defines a bond. Then the self-consistent potential $\phi(\mathbf{r}, n)$ in (3) is expressed by the following relation:

$$\begin{aligned} \phi(\mathbf{r}, n) &= kT\beta \sum_i \frac{p_{2\text{SCF}}(\mathbf{r}, i; \mathbf{r}, n)}{p_{\text{SCF}}(\mathbf{r}, n)} \\ \phi(\mathbf{0}, 0) &\equiv 0. \end{aligned} \quad (7)$$

In fact, differentiating relation (4) with respect to ξ , inserting in (3) and allowing $\xi = 1$ we get

$$\begin{aligned} -\frac{\phi(\mathbf{r}, n)}{kT} p_{\text{SCF}}(\mathbf{r}, n) + \frac{1}{kT} p_{\text{SCF}}(\mathbf{r}, n) \int \phi(\mathbf{r}, n) p_{\text{SCF}}(\mathbf{r}, n) d\mathbf{r} \\ = \beta p_{\text{SCF}}(\mathbf{r}, n) \sum_i \int p_{2\text{SCF}}(\mathbf{r}, i; \mathbf{r}, n) d\mathbf{r} - \beta \sum_i p_{2\text{SCF}}(\mathbf{r}, i; \mathbf{r}, n). \end{aligned} \quad (8)$$

If $p_{\text{SCF}}(\mathbf{r}, n) \neq 0$, the equation (8) is fulfilled identically by relation (7). The self-consistency conditions are identical with the markovian closure approximation for the joint probability function of $p_2(\mathbf{r}_n, i; \mathbf{r}_n, n; \xi)$, but are not compatible with the superposition closure approximation (Freed and Gillis 1971). So $\phi(\mathbf{r}, n)$ in the form of (7) describes the Reiss SCF. If we allow for the existence of a polymer distribution $\sum_i p(\mathbf{r}, i)$, which is spherically symmetric around the point $\mathbf{r}_0 = \mathbf{0}$, then the joint probability density $p_2(\mathbf{r}, i, \mathbf{r}, n)$ fulfils the superposition closure approximation, ie

$$p_2(\mathbf{r}, i; \mathbf{r}, n) = p(\mathbf{r}, i)p(\mathbf{r}, n) \quad (9)$$

and equation (7) then describes the Edwards SCF

$$\phi(\mathbf{r}) = kT\beta \sum_i p(\mathbf{r}, i) = kT\beta \tilde{p}(\mathbf{r}) \quad (10)$$

where $\tilde{p}(\mathbf{r})$ is the total density of monomers at the point \mathbf{r} .

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