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1976 J. Phys. A: Math. Gen. 9 651

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## On the equivalence of the Yvon-Born-Green and Kirkwood hierarchies in polymers

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Received 20 August 1975, in final form 25 November 1975

**Abstract.** The lowest members of the Yvon-Born-Green and Kirkwood hierarchies lead, in the SCF approximation in polymers, to physically non-equivalent consequences: Kirkwood's equation describes Reiss's SCF and so it is equivalent to Reiss's variation principle, whereas the Yvon-Born-Green equation is not. In addition, assuming the existence of a spherically symmetric distribution of the polymer chain about the origin then both the Yvon-Born-Green and Kirkwood equations are equivalent to Edwards' probability approach.

The discrepancy in the consequences of both types of equations in the SCF approximation is obviously due to the use of this approximation. The situation, as described here, is analogous to the situation in the theory of liquids and imperfect gases where the use of Kirkwood's superposition approximation leads to different physical consequences in both types of equation.

### 1. Introduction

It is well known that in the theory of liquids and imperfect gases two systems (hierarchies) of integro-differential equations derived by differentiating the distribution function of these physical systems with respect to the charging parameter (the Kirkwood system) and the position coordinate (the Yvon-Born-Green (YBG) system), are strictly equivalent, i.e. it is possible to mathematically transform one system of these equations to another (Hill 1956, Rice and Gray 1965). Because of mathematical difficulties, so called closure approximations are introduced into the lowest members of these equations by which the hierarchy is truncated. In liquids and imperfect gases Kirkwood's superposition approximation of distribution functions is used and its inclusion into the second member of both hierarchies violates the equivalence already mentioned of the integral equations derived thus (Hill 1956, Rice and Gray 1965).

In describing a polymer chain employing the Kirkwood and YBG systems, a situation occurs similar to the above mentioned case. The lowest members of both hierarchies are again (i.e. without the use of any approximation) precisely equivalent (Kyselka 1974, unpublished). In contrast to the theory of liquids and imperfect gases it is in general not possible to use Kirkwood's superposition approximation. The essence of the usual Kirkwood approximation is the neglect of indirect correlation among a subset of particles in a fluid and other particles of fluid. This neglect is generally not permitted in systems not showing translational invariance. Just such a system is a polymer in which pair-wise interactions between monomer units were replaced according to Reiss (1967) and Edwards (1965), by unknown self-consistent fields (SCF approximation). Because it is necessary to introduce the origin of SCF, the translational

symmetry of space is destroyed, and, therefore, in polymers in the SCF approximation the neglect of indirect correlation including effects transmitted along the backbone of the chain is not justified. In Freed and Gillis (1971) and Freed (1971) the use of Kirkwood's superposition approximation for deriving Reiss's SCF (Yamakawa 1971) was well criticized. These works also showed the incompatibility of the use of this superposition approximation with the introduction of SCF. Now the question arises, if the introduction of the SCF closure approximation in polymers into the lowest members of the YBG and Kirkwood hierarchies leads to a similar situation as that in liquids and imperfect gases, i.e. to violation of their equivalence, or, if the SCF approximation leads, in both hierarchies in polymers, to the same conclusions.

The proper way to investigate the consequences of the SCF approximations of Reiss and Edwards within the framework of the YBG and Kirkwood systems is to introduce into the lowest members of both hierarchies physical assumptions (closure approximations) corresponding to those of Edwards and Reiss. In Kyselka (1973) the equivalence of the lowest member of the YBG hierarchy to Reiss's variational principle was proved on the basis of Reiss's SCF closure approximation (i.e. without the use of the superposition approximation). The mathematical error involved in Kyselka (1973), however, changes this conclusion, and the result is that as in the theory of liquids and non-ideal gases in the SCF approximation of distribution functions of a chain, the lowest members of the YBG and Kirkwood hierarchies are not physically equivalent (i.e. lead to various types of SCF). Our conclusion is in contradiction with the result of Whittington and Dunfield (1973) where Reiss's SCF was obtained by using superposition and then Markovian closure approximations.

The aim of this work is to correct the result of Kyselka (1973) and to show that the use of only Reiss's SCF approximation in Whittington and Dunfield (1973) leads to a conclusion identical to ours.

## 2. The Yvon-Born-Green system

The lowest member of the YBG hierarchy has the form (Whittington and Dunfield 1973)

$$\begin{aligned}
 & -kT \nabla_n p(\mathbf{r}_n, n) \\
 &= \int p_2(\mathbf{r}_{n-1}, n-1; \mathbf{r}_n, n) \nabla_n R(\mathbf{r}_n - \mathbf{r}_{n-1}) d\mathbf{r}_{n-1} \\
 &+ \sum_{i=0}^{n-2} \int p_2(\mathbf{r}_i, i; \mathbf{r}_n, n) \nabla_n U(\mathbf{r}_n - \mathbf{r}_i) d\mathbf{r}_i, \quad (1)
 \end{aligned}$$

where

$$p(\mathbf{r}_n, n) = \frac{1}{Z} \int \exp\left(-\frac{1}{kT} \sum_{i=1}^n R(\mathbf{r}_i - \mathbf{r}_{i-1}) - \frac{1}{kT} \sum_{\substack{0 \leq i < j \leq n \\ j \neq i+1}} U(\mathbf{r}_j - \mathbf{r}_i)\right) \delta(\mathbf{r}_0) d\mathbf{r}_0 \dots d\mathbf{r}_{n-1} \quad (2)$$

$$\begin{aligned}
 p_2(\mathbf{r}_i, i; \mathbf{r}_n, n) &= \frac{1}{Z} \int \exp\left(-\frac{1}{kT} \sum_{i=1}^n R(\mathbf{r}_i - \mathbf{r}_{i-1})\right) \\
 &- \frac{1}{kT} \sum_{\substack{0 \leq i < j \leq n \\ j \neq i+1}} U(\mathbf{r}_j - \mathbf{r}_i) \delta(\mathbf{r}_0) d\mathbf{r}_0 \dots d\mathbf{r}_{i-1} d\mathbf{r}_{i+1} \dots d\mathbf{r}_{n-1}
 \end{aligned}$$

are singlet and pair distribution functions of a polymer.  $\delta(\mathbf{r}_0)$  on the right-hand side of equation (2) means that one end of the polymer chain was chosen as the origin, i.e.  $\mathbf{r}_0 = \mathbf{0}$ . The term  $R(\mathbf{r}_i - \mathbf{r}_{i-1})$  means the bond energy and  $U(\mathbf{r}_i - \mathbf{r}_j)$  includes long-range interactions resulting in the effect of excluded volume.

The SCF approximation of the distribution function of a polymer obeys exactly the diffusion equation (Rosenblatt 1951):

$$\left( \frac{\partial}{\partial n} - \frac{l}{6} \nabla_r^2 + \frac{\phi(\mathbf{r}, n)}{kT} + \frac{\partial Z(n)/\partial n}{Z(n)} \right) p_{\text{SCF}}(\mathbf{r}, n; [\phi]) = \Theta \tag{3}$$

and therefore cannot in general simultaneously obey Markovian approximations of first members of the YBG or Kirkwood systems. However, if such an unknown SCF  $\phi(\mathbf{r}, n)$ —call it  $\phi_0(\mathbf{r}, n)$ —exists, which obeys identically the Markovian approximation of equation (1), i.e.

$$\begin{aligned} & -kT \nabla_r p_{\text{SCF}}(\mathbf{r}, n; [\phi_0]) \\ &= \int p_{2\text{SCF}}(\mathbf{s}, n-1; \mathbf{r}, n; [\phi_0]) \nabla_r R(\mathbf{r}-\mathbf{s}) \, d\mathbf{s} \\ & \quad + \sum_{i=0}^{n-2} \int p_{2\text{SCF}}(\mathbf{s}, i; \mathbf{r}, n; [\phi_0]) \nabla_r U(\mathbf{r}-\mathbf{s}) \, d\mathbf{s}, \end{aligned} \tag{1'}$$

then the function  $p_{\text{SCF}}(\mathbf{r}_n, n; [\phi_0])$  automatically satisfies equation (3) for  $\phi = \phi_0$  and is therefore the solution of our problem. The unknown field  $\phi_0(\mathbf{r})$  is then obtained by direct substitution of the SCF approximation of the distribution function of a polymer into equation (1) and by performing the required operations.

We note now that the unknown field  $\phi_0(\mathbf{r})$  can be obtained by using the Ornstein-Uhlenbeck stationary Gaussian Markovian process of random fields for the distribution function  $p(\mathbf{r}, n)$  of a polymer (Freed 1971, Edwards 1965 and Kac 1968). The relation of this approach with our method will be explained in a further paper.

*The following theorem holds:* Assuming that equation (1) is satisfied by distribution functions of a polymer in the SCF approximation (Reiss's assumption) the unknown field  $\phi_0(\mathbf{r}_n, n)$  is given by the following equation:

$$p_{\text{SCF}}(\mathbf{r}_n, n; [\phi_0]) \nabla_n \phi_0(\mathbf{r}_n, n) = \sum_{i=0}^{n-2} \int p_{2\text{SCF}}(\mathbf{r}_i, i; \mathbf{r}_n, n; [\phi_0]) \nabla_n U(\mathbf{r}_n - \mathbf{r}_i) \, d\mathbf{r}_i. \tag{4}$$

This statement can easily be proved by substituting in equation (2)

$$\sum_{\substack{0 \leq i < j \leq n \\ j \neq i+1}} U(\mathbf{r}_j - \mathbf{r}_i) \approx \sum_{i=1}^n \phi(\mathbf{r}_i)$$

and then by inserting it in equation (1) and by comparing the explicitly expressed left-hand side with the right-hand side of equation (1). Note that by letting  $\phi(\mathbf{0}) = \Theta$  the translational symmetry of space is violated. Equation (4) by no means leads to Reiss's SCF. In Kyselka (1973) it was assumed erroneously that for the hard-sphere potential  $U(\mathbf{r}) = kT\beta\delta(\mathbf{r})$  it is possible to consider the function  $p_{2\text{SCF}}(\mathbf{r}_i, i; \mathbf{r}_n, n) / p_{\text{SCF}}(\mathbf{r}_n, n)$  as basic and then the left-hand side of equation (4) would be the total differential. This condition is not achieved on the boundary of the integration region of the integral on the right-hand side of equation (4) with respect to the limiting properties of this function.

Let us now assume the existence of a spherically symmetric probability distribution of a polymer about the point  $\mathbf{r}_0 \equiv \mathbf{0}$  (Edwards' assumption). In that case it is possible according to Yamakawa (1971), Freed and Gillis (1971), and Freed (1971) to use the superposition approximation on the right-hand side of equation (4) and then the spherically symmetric field, which already is not explicitly dependent on the index  $n$ , will be Edwards' SCF:

$$\phi(\mathbf{r}_n) = \sum_{i=0}^{n-2} \int U(\mathbf{r}_n - \mathbf{r}_i) p_{\text{SCF}}(\mathbf{r}_i, i) d\mathbf{r}_i \quad (5)$$

which is precisely the result (33) in Freed and Gillis (1971). Note that Edwards' original assumption was the Markovian approximation of the distribution functions of a polymer chain. By introducing 'Green functions'

$$G_{\text{SCF}}(\mathbf{r}_i, \mathbf{r}_j; j-i) = \int \exp\left(-\frac{1}{kT} \sum_{l=i+1}^j R(\mathbf{r}_l - \mathbf{r}_{l-1}) - \frac{1}{kT} \sum_{l=i+1}^j \phi(\mathbf{r}_l)\right) d\mathbf{r}_{i+1} \dots d\mathbf{r}_{j-1}, \quad (6)$$

with  $j > i$ , it can easily be seen that

$$p_{2\text{SCF}}(\mathbf{r}_i, i; \mathbf{r}_n, n) = \frac{1}{Z_{\text{SCF}}} G_{\text{SCF}}(\mathbf{0}, \mathbf{r}_i; i) G_{\text{SCF}}(\mathbf{r}_i, \mathbf{r}_n; n-i)$$

i.e. the SCF approximation of distribution functions is identical, except for a constant factor, with the Markovian closure (Freed and Gillis 1971, de Gennes 1969). Note that the Markovian approximation to equation (1) is now

$$\begin{aligned} & -kT \nabla_n G_{\text{SCF}}(\mathbf{0}, \mathbf{r}_n; n; [\phi]) \\ &= \int G_{\text{SCF}}(\mathbf{0}, \mathbf{r}_{n-1}; n-1; [\phi]) G_{\text{SCF}}(\mathbf{r}_{n-1}, \mathbf{r}_n; 1; [\phi]) \nabla_n R(\mathbf{r}_n - \mathbf{r}_{n-1}) d\mathbf{r}_{n-1} \\ &+ \sum_{i=0}^{n-2} \int G_{\text{SCF}}(\mathbf{0}, \mathbf{r}_i; i; [\phi]) G_{\text{SCF}}(\mathbf{r}_i, \mathbf{r}_n; n-i; [\phi]) \nabla_n U(\mathbf{r}_n - \mathbf{r}_i) d\mathbf{r}_i \quad (1') \end{aligned}$$

which is strictly equation (13) of Whittington and Dunfield (1973) and the Edwards field now has form

$$\phi(\mathbf{r}) = \frac{1}{Z_{\text{SCF}}} \sum_{i=0}^{n-2} \int ds U(\mathbf{r} - \mathbf{s}) G_{\text{SCF}}(\mathbf{0}, \mathbf{s}; i; [\phi]) \int d\mathbf{r} G_{\text{SCF}}(\mathbf{s}, \mathbf{r}; n-i; [\phi]) \quad (5')$$

which is precisely equation (2.27) of Freed (1971).

### 3. Kirkwood's system

The lowest member of Kirkwood's hierarchy has the form (Naghizadeh 1967)

$$\begin{aligned} & kT \frac{\partial p(\mathbf{r}_n, n; \xi)}{\partial \xi} \\ &= p(\mathbf{r}_n, n; \xi) \sum_{i=0}^{n-2} \iint U(\mathbf{r}_n - \mathbf{r}_i) p_2(\mathbf{r}_i, i; \mathbf{r}_n, n; \xi) d\mathbf{r}_i d\mathbf{r}_n \\ &- \sum_{i=0}^{n-2} \int U(\mathbf{r}_n - \mathbf{r}_i) p_2(\mathbf{r}_i, i; \mathbf{r}_n, n; \xi) d\mathbf{r}_i \quad (7) \end{aligned}$$

where the charging parameter  $\xi$  is connected to the  $n$ th monomer of a polymer.

### 3.1. Reiss's field

Let equation (7) be satisfied in the same way as in the preceding paragraph by the SCF distribution functions (albeit Markovian type). By inserting the corresponding expressions for the distribution functions of the polymer into (7), differentiating with respect to the charging parameter  $\xi$  on left-hand side of equation (7) and letting  $\xi = 1$  we get

$$\begin{aligned} & \frac{1}{kT} p_{\text{SCF}}(\mathbf{r}_n, n) \int \phi(\mathbf{r}_n, n) p_{\text{SCF}}(\mathbf{r}_n, n) d\mathbf{r}_n - \frac{\phi(\mathbf{r}_n, n)}{kT} p_{\text{SCF}}(\mathbf{r}_n, n) \\ &= \frac{1}{kT} p_{\text{SCF}}(\mathbf{r}_n, n) \sum_{i=0}^{n-2} \iint U(\mathbf{r}_n - \mathbf{r}_i) p_{2\text{SCF}}(\mathbf{r}_i, i; \mathbf{r}_n, n) d\mathbf{r}_i d\mathbf{r}_n \\ & \quad - \frac{1}{kT} \sum_{i=0}^{n-2} \int U(\mathbf{r}_n - \mathbf{r}_i) p_{2\text{SCF}}(\mathbf{r}_i, i; \mathbf{r}_n, n) d\mathbf{r}_i \end{aligned} \tag{8}$$

and by comparing terms in (8) we get

$$\phi(\mathbf{r}_n, n) = \sum_{i=0}^{n-2} \int U(\mathbf{r}_n - \mathbf{r}_i) \frac{p_{2\text{SCF}}(\mathbf{r}_i, i; \mathbf{r}_n, n; [\phi])}{p_{\text{SCF}}(\mathbf{r}_n, n; [\phi])} d\mathbf{r}_i \tag{9}$$

which is the well-known Reiss field. This result, based on approximations which are analogous to Reiss's method, was also obtained by Naghizadeh (1967) which confirms the equivalence of the first member of Kirkwood's hierarchy to Reiss's variational principle. The method of random fields used in Freed's and Edwards' works applied to the functional integral representation of the distribution function  $p(\mathbf{r}_n, n; \xi)$ , however, leads in the case of Kirkwood's equation only to an Edwards-type field. The reason for this discrepancy is probably in the basis of the method used.

### 3.2. Edwards' field

Assuming the spherically symmetric distribution function of a polymer about the origin it is possible to use the superposition approximation (Edwards 1965),  $p_{2\text{SCF}}(\mathbf{r}_i, i; \mathbf{r}_n, n) \approx p_{\text{SCF}}(\mathbf{r}_i, i) p_{\text{SCF}}(\mathbf{r}_n, n)$  (see also Yamakawa 1971, Freed and Gillis 1971 and Freed 1971). Note that in Yamakawa (1971) the superposition approximation was used even in the case of Reiss's SCF which was criticized by Freed and Gillis (1971) and Freed (1971) as mentioned above. Then equation (9) again leads to Edwards' SCF.

## 4. Remark on the derivation of Reiss's SCF in Whittington and Dunfield

In the derivation of Reiss's differential equation, Whittington and Dunfield (1973) used in their work our equation (1) written in the superposition closure approximation:

$$\begin{aligned} & -kT \nabla_r p(\mathbf{r}, n) \\ &= \int ds p(s, n-1) p(\mathbf{r}, n) \nabla_r R(\mathbf{r}-s) + \sum_{i=0}^{n-2} \int ds p(s, i) p(\mathbf{r}, n) \nabla_r U(\mathbf{r}-s). \end{aligned} \tag{10}$$

This equation, for  $n = 1$  and boundary condition  $p(\mathbf{r}, 0) = \delta(\mathbf{r})$ , gives

$$R(\mathbf{r}-s) = -kT \ln p(\mathbf{r}-s; 1). \tag{11}$$

Reiss's differential equation is related to the Green function  $G_{\text{SCF}}(\mathbf{r}_i, \mathbf{r}_j; j-i)$  (see equation (6)) and therefore it is necessary to insert relation (11) into our equation (17):

$$\begin{aligned} \nabla_r G_{\text{SCF}}(\mathbf{0}, \mathbf{r}; n) &= \int d\mathbf{s} G_{\text{SCF}}(\mathbf{0}, \mathbf{s}; n-1) \frac{G_{\text{SCF}}(\mathbf{r}, \mathbf{s}; 1)}{p(\mathbf{r}, \mathbf{s}; 1)} \nabla_r p(\mathbf{r}, \mathbf{s}; 1) \\ &+ \sum_{i=0}^{n-2} \int d\mathbf{s} G_{\text{SCF}}(\mathbf{0}, \mathbf{s}; i) G_{\text{SCF}}(\mathbf{r}, \mathbf{s}; n-i) \nabla_r U(\mathbf{r}-\mathbf{s}). \end{aligned} \quad (12)$$

However, because Reiss's SCF is of such a nature that  $G_{\text{SCF}}(\mathbf{r}, \mathbf{s}; 1) \neq Zp(\mathbf{r}, \mathbf{s}; 1)$ , with regard to incompatibility of the superposition approximation with the introduction of SCF in polymers, it is impossible to perform the integration in equation (12) not even by changing the physical interactions  $U(\mathbf{r}-\mathbf{s})$  to a hard-sphere potential in the second term on the right-hand side. Therefore, in contradiction to the result of Whittington and Dunfield (1973), the first member of the YBG hierarchy is not equivalent to Reiss's differential equation (see equation (25) in Yamakawa 1971).

Edwards' assumption of a spherically symmetrical field in a polymer with one end fixed at the origin and other end free (the end-to-end distance of the chain is not fixed) leads to the relation  $G_{\text{SCF}}(\mathbf{r}, \mathbf{s}; 1) = Zp(\mathbf{r}, \mathbf{s}; 1)$ . For  $U(\mathbf{r}) = kT\beta\delta(\mathbf{r})$ , the result of our work is then the same as the result of Whittington and Dunfield (1973). However, our method is more general because it leads to Edwards' SCF in the case of a general type of physical pair interaction  $U(\mathbf{r}-\mathbf{s})$ .

We note now that it is possible to substitute the approximation (11) by introducing an assumption of constant bond length:

$$\exp\left(-\frac{1}{kT}R(\mathbf{r}-\mathbf{s})\right) \sim \frac{\delta(|\mathbf{r}-\mathbf{s}|-l)}{4\pi l^2} = G_{\text{SCF}}(\mathbf{r}, \mathbf{s}; 1)$$

which would make it possible in the case of a hard-sphere potential to derive Reiss's SCF equation without the use of the superposition approximation. However, the method mentioned above shows that approximation we have used is equivalent to the superposition approximation, incompatible with Reiss's SCF.

## 5. Discussion

The initial point of Reiss's and Edwards' SCF theory of the excluded volume effect in polymers is the decoupling of the many-body problem by substitution of pair-wise interactions of the excluded volume  $U(\mathbf{r}_i - \mathbf{r}_j)$  in the distribution functions of a polymer, by unknown fields  $\phi(\mathbf{r}_j)$ , which depend on the coordinate of a single monomer only.

Reiss's and Edwards' definitions stem from different physical principles adequately elucidated by Freed and Gillis (1971) and Freed (1971): Reiss's scheme stems from the variational principle requiring a minimum of the free energy of a polymer defined by an appropriate choice of an unknown field  $\phi(\mathbf{r}_j)$ , whereas Edwards' scheme stems from probability ideas. Whereas the physical nature of Edwards' approach is less clear than Reiss's, Edwards' system is strictly self-consistent while Reiss's is not (see also Gillis and Freed 1974).

For these reasons both approaches lead to different types of SCF: Edwards' leads to a field which is spherically symmetrical about the origin whereas Reiss's leads to a field

which takes into account not only the presence of the first monomer at the origin but also the presence of the  $n$ th monomer at the considered point. This represents a significant improvement over Edwards' field (de Gennes 1969). In other words, Reiss's field expresses an SCF potential dependent on 'time'.

In Freed (1971) the incompatibility of Kirkwood's superposition approximation with the SCF (albeit Markovian) approximation in polymers was stated. If we accept that this principle is valid only for the more perfect Reiss SCF, then Reiss's assumption is the closure approximation SCF of the distribution functions, whereas Edwards' assumption is the SCF approximation + the superposition approximation (see also Reiss 1967). Under these assumptions the YBG equation is equivalent to Edwards' probability approach whereas Kirkwood's equation is equivalent to Reiss's variational method and, at the same time, to Edwards' approach which is a situation analogous to the insertion of Kirkwood's superposition approximation into the integro-differential systems in liquids and imperfect gases already mentioned.

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