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Green-Function Description of Dense Polymeric Systems

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ABSTRACT: A self-consistent Green-function description of concentrated polymer solutions and dense polymeric melts is presented. The method, which applies to both uniform and nonuniform systems, is used in this work to calculate the static structure factor of a homogeneous fluid of Gaussian model chains. Limiting expressions are obtained analytically for large, intermediate, and small wave vectors. The results conform to the well-known and often used polymer reference interaction site model, and other polymeric liquid-state theories. The advantages of the Green-function description are discussed in relation to other polymer density functional methods, with special reference to the problem of polymer crystallization.

1. Introduction

The properties of macromolecular systems are potentially dictated by a multitude of vastly differing length scales.[1] For example, the interfacial width of a phase-separated polymer mixture can not only greatly exceed the dimensions of the polymer coils but also be significantly sharper than it, depending on how far one is removed from the critical demixing point.[2,3] Polymer crystallization seems to involve a number of length scales, including ones comparable to or even smaller than the Kuhn length of the polymer, which is often seen as the smallest pertinent length scale in the physics of flexible polymers.[4] Most (but not all) of the predominant lengths encountered in inhomogeneous systems present themselves also in the equilibrium structure of the homogeneous fluid state, to which we restrict our discussion. In the discussion, the relevant experimentally accessible quantity is the (static) structure factor, which gauges correlations in spontaneously occurring density and/or composition fluctuations. Numerous theoretical approaches have been devised to approximately calculate the structure factor of a polymeric fluid.[5] To name but a few, we have the single-contact approximation,[6,7] the random phase approximation (RPA),[8] the renormalization group theory,[9] the polymer reference interaction site model (PRISM), and theories related to that.[10−12] Some of these approaches apply to polymers in dilute or semidilute solution, while others are better suited to describe polymers in concentrated solution, or in the dense, molten state.[1] Focusing specifically on very concentrated homopolymeric systems, where a mean-field description is accurate, the structure factor, $S(q)$, can be cast into the following form

$$S(q) = \frac{F(q)}{1 - \bar{\rho}\hat{c}(q)F(q)} \tag{1}$$

at least when the chains are flexible and the long-chain limit holds.[5] Here, $F(q)$ denotes the form factor, q the momentum transfer variable, $\bar{\rho}$ the average number density of segments in the system, and $\hat{c}(q)$ a coupling or effective interaction term with the dimension of volume. The form factor describes positional correlations between segments within a single chain. Short-range correlations between segments on *different* chains enter the structure factor via $\hat{c}(q)$. In (polymer) liquid-state theory, $\hat{c}(q)$ is known as the Fourier transform of the (chain-averaged) direct correlation function of the segments (the “interaction sites”).[13,14]

Because of the screening of self-interactions, polymers behave to all practical purposes ideally in the strongly entangled state, that is, in a sufficiently concentrated solution or in the melt state.[1] An adequate description of the statistical properties of polymer chains is then provided by the Gaussian chain model, provided one focuses on length scales greatly exceeding those of the chemical details of molecules. The form factor of a Gaussian chain consisting of $M \gg 1$ identical and structureless monomeric units or segments is given by[14]

$$F(q) = F(Q) = \frac{1 - f^2 - \frac{2}{M}f + \frac{2}{M}f^{M+1}}{(1-f)^2} \tag{2}$$

where $f = f(Q) \equiv \exp -{}^1\!/_6 Q^2$, and $Q \equiv ql_K$, a dimensionless momentum transfer variable; l_K is the Kuhn length of the chain. Despite its apparent simplicity, the Gaussian model already points at the existence of at least three length scales. On length scales very much smaller than the Kuhn length, that is, in the short-wavelength limit $Q \gg 1$, eq 2 reduces to $F(Q) \sim 1$. This property reflects the lack of microscopic detail of the model in this limit; in reality we would of course be probing the detailed chemical structure of macromolecule at hand. In the opposite limit $Q \ll 1$, correlations are probed that are on scales large compared with the Kuhn length, and consequently also large on the scale of the details of the chemical chain. Two length scales emerge in the low-Q regime: one large compared to the size of the polymer, $M^{1/2}l_K$, and another small on the scale of the polymer coil yet large on the scale of the Kuhn length, l_K. Associated with these lengths is (i) the long wavelength limit $Q \ll M^{-1/2}$ and (ii) the intermediate wavelength regime $M^{-1/2} \lesssim Q \lesssim 1$. In the long-wavelength limit, $F \sim M\,(1 - {}^1\!/_{18}Q^2M)$, while in the intermediate regime, $F^{-1} \sim {}^1\!/_{12}Q^2 + {}^1\!/_2 M^{-1}$.

Additional length scales arise because the chains interact with each other. Let σ tentatively denote the range of the “bare” (direct) interactions between two chain segments, a quantity that must obviously depend

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on the chemical details of the polymers, the presence of solvent and so forth. For uncharged polymers, the interactions are (as a rule) local on the scale of the size of the chains, $\sigma \ll M^{1/2} l_K$. Notions from the theory of simple liquids dictate that the real-space direct correlation function, $c(r)$, must have a similarly short-ranged quality.[13] (See also Fuchs.[15]) Naïvely, this translates into the scaling form $c(r) = c(r/\sigma)$, where r denotes the distance between two segments. However, it is clear that even when chain connectivity does not alter the short-ranged character of the direct correlation function, it must influence its precise form. The reason is that segments linked into chains do not interact with each other in exactly the same way as free, "monomeric" segments.[16] Consequently, the scaling relation as it stands is incomplete, and there must be additional polymer-related quantities that enter the description of the direct correlation function. This complication is usually circumvented by treating σ not merely as a bare interaction range and as a measure of the physical size of the Kuhn segments, but also to assume it incorporates the influence of chain connectivity on the interactions in some way. In practice, $\sigma = O(l_K)$ is often used as an adjustable parameter, varied to optimize agreement with experimentally determined structure factors.[14]

It is clear that any theory set up to describe polymers in congested conditions must be able to deal with hugely differing length scales. An appealing method that we present in this paper is based on an amalgamation of the Green-function description of polymers,[17] and the theory of simple liquids.[13] The objective of our work is 2-fold. First, our aim is to present a description of polymeric liquids that shares with other polymeric liquid-state theories the benefit of being applicable to dense systems, but which is from the outset more clearly based on a self-contained, statistical mechanical description of the macromolecules. Second, our approach aims to connect directly with the density functional description of inhomogeneous polymeric systems, harking back to theories describing the structure of the globular state of collapsed polymers,[18] polymers near interfaces,[19] and polymer liquid crystals.[20] Although our approach is similar in spirit to previous work, it does not in its implementation suffer from the drawbacks that seem to characterize previous attempts, such as requiring input from RPA, restricting the analysis to a particular length scale, or providing only an incomplete description of the connectivity of the (ideal) chains.[21–26] For the Gaussian chains studied in this paper, we find that the structure factor has a form consistent with RPA and, essentially, with the starting point of PRISM theory. It has to be stressed, however, that although similar to RPA for weak density variations, it does go beyond RPA for strong ones. Furthermore, the methodology can be adapted in a straightforward manner to study other types of model chain, and opens up a computationally convenient method for the systematic study of inhomogeneous systems of high molecular weight polymers, including the ordering in a crystalline state. Work in this direction is currently underway.[27]

The remainder of this paper is organized as follows. In section 2, we present a self-consistent field theory for an inhomogeneous system of interacting polymer chains. By applying a weak external field and gauging the response of the segment density field, a formal expression for the structure factor of the polymers is derived. Sections 3–5 are devoted to solving the governing set of equations *analytically* for three different length scales. Section 3 discusses a perturbation theory for the long wavelength limit. Section 4 gives a ground-state analysis valid for intermediate wavelengths, and section 5 provides a similar analysis for very short length scales. The paper concludes with section 6, where the implications and possible applications of the approach are discussed.

2. Self-Consistent Field Theory

A volume V, containing N flexible, Gaussian chains of M segments is considered. The polymer segments interact with each other through an unspecified potential, which includes the effects of a solvent (if present). Within a mean-field ansatz, the multichain partition function, Z, is equal to the product of the single-chain partition functions, Z_M, of the N chains present in the volume

$$Z = Z_M^{\ N} \tag{3}$$

Here, we have ignored the unimportant factor $1/N!$ correcting for the indistinguishability of the chains. The partition function of a single chain can in turn be expressed in terms of a conditional partition function, $Z(\mathbf{r}', \mathbf{r}; M)$, of all configurations of that chain, starting at position $\mathbf{r}'$ and ending at $\mathbf{r}$

$$Z_M = \int \mathrm{d}\mathbf{r} \int \mathrm{d}\mathbf{r}' \, Z(\mathbf{r}', \mathbf{r}; M) \tag{4}$$

where the spatial integrations are as usual implied to be carried out over the entire volume V. The quantity $Z(\mathbf{r}', \mathbf{r}; M)$ is often referred to as the *Green function* of the polymer.[1] It obeys the operator equation[28]

$$\frac{\partial}{\partial M} Z(\mathbf{r}', \mathbf{r}; M) = \left[\exp\left(-U(\mathbf{r}) + \frac{1}{6} l_K^{\ 2} \nabla^2\right) - 1\right] Z(\mathbf{r}', \mathbf{r}; M) \tag{5}$$

at least for sufficiently large $M \gg 1$, when a continuous description of the segment ranking number is possible. As usual, the thermal energy, $k_B T$, is set equal to unity. In eq 5, $U(\mathbf{r})$ denotes an auxiliary field that will below assume the role of the molecular field each polymer experiences from the presence of the others, and

$$\exp\left(\frac{1}{6} l_K^{\ 2} \nabla^2\right) \equiv 1 + \frac{1}{6} l_K^{\ 2} \nabla^2 + \frac{1}{2}\left(\frac{1}{6} l_K^{\ 2} \nabla^2\right)^2 + \ldots \tag{6}$$

a formal representation of the "linear memory" operator, describing the chain connectivity in this case of the Gaussian model. If we were to choose a different polymer model, the memory operator would take a different form.[28] The "initial" condition complementing eq 5 reads

$$\lim_{M \to 0} Z(\mathbf{r}', \mathbf{r}; M) = \delta(\mathbf{r}' - \mathbf{r}) \tag{7}$$

The free energy of our polymeric system is as usual given by

$$F = -\ln Z \tag{8}$$

As such this expression is not very meaningful, for we have yet to specify the molecular field. To obtain a meaningful free energy functional, we follow Lifshitz[18] (and others[20]) and subtract from eq 8 the internal energy of the system

$$F_{\mathrm{conf}} = F - \int \mathrm{d}\mathbf{r}\, U(\mathbf{r})\, \rho(\mathbf{r}) \tag{9}$$

to give the contribution of the configurational entropy to the total free energy. Here, $\rho(\mathbf{r})$ denotes the segment density at position $\mathbf{r}$, summed over all ranking numbers. The segment density itself is a functional of the Green function:

$$\rho(\mathbf{r}) = N\frac{\int_0^M \mathrm{d}s \int \mathrm{d}\mathbf{r}' \int \mathrm{d}\mathbf{r}''\, Z(\mathbf{r}', \mathbf{r}; s) Z(\mathbf{r}, \mathbf{r}''; M - s)}{\int \mathrm{d}\mathbf{r} \int \mathrm{d}\mathbf{r}'\, Z(\mathbf{r}', \mathbf{r}; M)} \tag{10}$$

One may verify by applying the standard properties of Markov chains, that eq 10 obeys the mass-conserving normalization $\int \mathrm{d}\mathbf{r}\, \rho(\mathbf{r}) = \bar{\rho}V = NM$. In keeping with our mean-field description, we now define the relevant free energy functional, $\mathcal{F}$, to be equal to the sum of eq 9 and an excess free energy F_{exc}, accounting for the interactions between the segments, and the coupling of the segments to an externally applied field.

$$\mathcal{F} = F_{\mathrm{conf}} + F_{\mathrm{exc}} \tag{11}$$

The external field we need later to calculate the structure factor of the interacting chains. For the excess free energy we simply put

$$F_{\mathrm{exc}} = -\frac{1}{2}\int \mathrm{d}\mathbf{r} \int \mathrm{d}\mathbf{r}' \rho(\mathbf{r})\, \rho(\mathbf{r}')\, c(\mathbf{r}, \mathbf{r}') + \int \mathrm{d}\mathbf{r}\, \rho(\mathbf{r})\, \phi(\mathbf{r}) \tag{12}$$

with $\phi(\mathbf{r})$ the external field, and $c(\mathbf{r}, \mathbf{r}')$ the earlier mentioned (real-space) direct correlation function. (Implied is a zero-density reference state.[13]) Obviously, by choosing such a chain-averaged description any distinction between segments of different ranking numbers is lost. In a homogeneous fluid, $c(\mathbf{r}, \mathbf{r}') = c(\mathbf{r} - \mathbf{r}')$ due to translational invariance. We do not specify the direct correlation function any further than this, to keep the analysis as generally applicable as possible. At the end of this section ways of fixing c are briefly indicated.

As the system is presumed to be in a state of equilibrium, the segment density must functionally minimize the total free energy, i.e.

$$\frac{\delta}{\delta\rho(\mathbf{r})}\mathcal{F} = \mu \tag{13}$$

with μ the chemical potential of a polymer segment. The chemical potential acts a Lagrange parameter, associated with the conservation of mass. It should now be evident that the auxiliary field, $U(\mathbf{r})$, may be viewed as a self-consistent field, for $Z(\mathbf{r}', \mathbf{r}; M)$ is a function of $U(\mathbf{r})$, and vice versa. Only when they are consistent with each other is the free energy at a minimum. In the following, $U(\mathbf{r})$ will be treated as if it were an external field, although, obviously, it is not.

In the absence of an external field, the equilibrium segment distribution is homogeneous, i.e., for $\phi(\mathbf{r}) = 0$ we have $\rho(\mathbf{r}) = \bar{\rho} \equiv NM/V$. If we switch on the external field, this causes the homogeneous segment distribution to be perturbed. To what extent, and in what way, the segment density is perturbed can, in principle, be calculated from eq 13. It is well-known that the response of a fluid to a external field is intimately related to spontaneous fluctuations that arise in that fluid in absence of the field, and hence to its structure factor. Let $\delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - \bar{\rho}$ be the shift in the density field, resulting from the switching on of the external field. The Yvon equation connects the *linearized* response to *weak* fields, and the structure factor.[29]

In Fourier space, the equation (originally derived for simple liquids, but which trivially extends to polymeric systems) reads

$$\widehat{\delta\rho}(q) = -\bar{\rho}S(q)\hat{\phi}(q) \tag{14}$$

For any *given* direct correlation function $c(\mathbf{r}, \mathbf{r}')$, $S(q)$ can be evaluated explicitly by solving (either numerically, or, if possible, analytically) the set of eqs 3−14.

Next we discuss what to use for the direct correlation function. At the level of an Edwards type theory, aimed at describing *low* polymer densities, a sensible choice is $c(\mathbf{r}, \mathbf{r}') = v\delta(\mathbf{r} - \mathbf{r}')$, with v the excluded volume parameter.[17] Although this is convenient, such a choice is of little use in the dense state, where packing effects are important. When considering dense polymer systems, it is advisable to *calculate* in a self-consistent fashion both the direct correlation function, and a quantity known as the total correlation function.[13] The latter describes pair correlation between segments on different chains, and is related to the structure factor via

$$S(q) = F(q) + \bar{\rho}\hat{h}(q) \tag{15}$$

where $\hat{h}(q)$ denotes the Fourier transform of the total correlation function. This follows by a straightforward separation of segmental density fluctuations in contributions stemming from segments within chains, and those from segments on different chains. The direct and total correlation functions can be obtained by iteratively solving eqs 3−15, given a suitable closure, such as the Percus−Yevick closure.[13] This is quite analogous to standard practice in PRISM theory.[14] If a polymer model is selected for which a closed expression for the form factor is not available, $F(q)$ is obtainable numerically from eqs 3−15, setting $c(\mathbf{r}, \mathbf{r}') = 0$. The reason is (i) that the structure factor and form factor are identical for ideal, noninteracting polymers and (ii) that the polymers in our theory behave ideally even when they do interact, because of the mean-field approximation. Again, this is a valid approximation in the strongly congested state, where the polymers behave ideally (in the statistical sense).[1]

In the remainder of this paper, we attack the equations analytically, and show that the self-consistent field theory presented here is, to lowest order in the magnitude of the density fluctuations, equivalent to RPA and PRISM. The advantages of the Green-function description are discussed in section 6.

3. The Long-Wavelength Limit

Assuming the density gradients as well as the external field to be weak, eq 5 reduces to the well-known Edwards equation[17]

$$\frac{\partial}{\partial M}Z(\mathbf{r}', \mathbf{r}; M) = \left[\frac{1}{6}l_{\mathrm{K}}^{2}\nabla^{2} - U(\mathbf{r})\right] Z(\mathbf{r}', \mathbf{r}; M) \tag{16}$$

describing a Gaussian path in a self-consistent field. Treating U as a known external field, eq 16 can be solved for very small wave vectors $Q \ll M^{-1/2}$. The exact solution in the limit $QM^{1/2} \rightarrow 0$ is

$$Z_0(\mathbf{r}', \mathbf{r}; M) = \delta(\mathbf{r}' - \mathbf{r}) \exp[-U(\mathbf{r})\, M] \tag{17}$$

where the subscript 0 indicates that we are dealing with the limiting solution for a zero wave vector. Notice that eq 17 obeys the initial condition of eq 7. By applying perturbation theory, we get for the first order correction to eq 17

$$Z(\mathbf{r}', \mathbf{r}; M) = Z_0(\mathbf{r}', \mathbf{r}; M) + \frac{1}{6} l_{\mathrm{K}}^2 \int_0^M \mathrm{d}s \exp[-(M - s)\, U(\mathbf{r})] \nabla^2 Z_0(\mathbf{r}', \mathbf{r}; s) + \ldots \tag{18}$$

where the limit $QM^{1/2} \ll 1$ is implied. Inserting eq 18 into eq 8 gives the free energy of the system in terms of the auxiliary field, U. Although useful in itself, in density functional theory we instead aim to express the free energy as a function of the segment density distribution. This can be achieved as follows. First we establish how the segment density varies with the auxiliary field, by substituting eq 18 into eq 10. The functional dependence of the auxiliary field on the segment density field then follows by inversion. The result of the inversion is next inserted in eq 8, to provide the sought-after free energy density functional.

Substituting eq 18 into eq 10, gives, after some algebra

$$\rho(\mathbf{r}) = \frac{NM}{Z_M} \exp[-U(\mathbf{r})\, M] \left\{ 1 + \frac{1}{6} l_{\mathrm{K}}^2 \int_0^M \mathrm{d}s \exp[U(\mathbf{r})\, s] \nabla^2 \exp[-U(\mathbf{r})\, s] + \ldots \right\} \tag{19}$$

This equation can be inverted by successive approximation, yielding

$$U(\mathbf{r}) = -\frac{1}{M} \ln \left(\frac{\rho(\mathbf{r}) Z_M}{MN} \right) + \frac{1}{6} l_{\mathrm{K}}^2 \left\{ \frac{1}{2} \left(\nabla^2 \ln \frac{\rho(\mathbf{r})}{MN} \right) + \frac{1}{3} \left(\nabla \ln \frac{\rho(\mathbf{r})}{MN} \right)^2 \right\} + \ldots \tag{20}$$

which, when inserted into eq 9, gives

$$F_{\mathrm{conf}} = \int \mathrm{d}\mathbf{r} \frac{\rho(\mathbf{r})}{M} \ln \frac{\rho(\mathbf{r})}{MN} - \frac{1}{9} l_{\mathrm{K}}^2 \int \mathrm{d}\mathbf{r}\, \rho^{1/2}(\mathbf{r})\, \nabla^2 \rho^{1/2}(\mathbf{r}) + \ldots \tag{21}$$

where the for our purposes unimportant constant terms have been dropped. Equation 21 applies to situations of very weak gradients in the segment density. The first, leading-order term is a Flory-type ideal entropy of mixing of the polymers, and the second, in effect, a finite-size correction. A similar expression was derived by McMullen[22] and by Tang and Freed,[26] although by different methods.

Next, we perform the minimization of the free energy functional, F, and determine the equilibrium segment density distribution, $\rho(\mathbf{r})$. The outcome of the functional minimization is the following highly nonlinear integro-differential equation

$$\frac{1}{M} \ln \frac{\rho(\mathbf{r})}{MN} - \frac{1}{9} l_{\mathrm{K}}^2 \rho^{-1/2}(\mathbf{r}) \nabla^2 \rho^{1/2}(\mathbf{r}) - \int \mathrm{d}\mathbf{r}' \rho(\mathbf{r}')\, c(\mathbf{r}, \mathbf{r}') + \phi(\mathbf{r}) = \mu \tag{22}$$

if we neglect all but the first order correction in the small parameter $QM^{1/2} \ll 1$. As was advertised in section 2, to calculate from eq 22 the structure factor, we only need to know the linear response of the density field to a weak external field $\phi \ll 1$. Substituting $\delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - \bar{\rho}$, eq 22 reduces to

$$\frac{\delta\rho(\mathbf{r})}{M\bar{\rho}} - \frac{1}{18} l_{\mathrm{K}}^2 \nabla^2 \frac{\delta\rho(\mathbf{r})}{\bar{\rho}} - \int \mathrm{d}\mathbf{r}' \delta\rho(\mathbf{r}')\, c(\mathbf{r} - \mathbf{r}') = -\phi(\mathbf{r}) \tag{23}$$

to linear order in the external field, where we note that $c(\mathbf{r}, \mathbf{r}') = c(\mathbf{r} - \mathbf{r}')$ in the homogeneous (field-free) fluid. The linearized eq 23 is easy to solve in Fourier space

$$\widehat{\delta\rho}(q) = -\frac{\hat{\phi}(q)\bar{\rho}M}{1 + \frac{1}{18} MQ^2 - M\bar{\rho}\hat{c}(q)} \tag{24}$$

Comparison of eq 24 with the Yvon equation, eq 14, shows that the structure factor obeys

$$S(q) = \frac{M\left(1 - \frac{1}{18} Q^2 M\right)}{1 - \bar{\rho} M \left(1 - \frac{1}{18} Q^2 M\right) \hat{c}(q)} \tag{25}$$

in the limit $Q \ll M^{-1/2}$, since $(1 + {}^{1}/_{18}MQ^2)^{-1} = 1 - {}^{1}/_{18}Q^2M$ to first order in Q^2M. This result agrees with eq 1, as $F \sim M\,(1 - {}^{1}/_{18}Q^2M)$ in the same limit of long wavelengths.

4. The Intermediate-Wavelength Regime

The perturbation theory presented in the preceding section is not applicable to the intermediate-wavelength regime $M^{-1/2} \lesssim Q \lesssim 1$, because the gradient term is not small. In the intermediate regime, headway can be made using the following bilinear expansion of the Green function[1]

$$Z(\mathbf{r}', \mathbf{r}; M) = \sum_{n=0}^{\infty} \psi_n^*(\mathbf{r}')\, \psi_n(\mathbf{r}) \exp(-\lambda_n M) \tag{26}$$

given in terms of the eigenfunctions and values of the transfer operator on the right-hand side of eq 16

$$\left[\frac{1}{6} l_{\mathrm{K}}^2 \nabla^2 - U(\mathbf{r}) \right] \psi_n(\mathbf{r}) = -\lambda_n \psi_n(\mathbf{r}) \tag{27}$$

Since the transfer operator is self-adjoint, its eigenvalues λ_n are real, and its eigenfunctions $\psi_n(\mathbf{r}) = \psi_n^*(\mathbf{r})$ are orthogonal. The eigenfunctions can be made ortho*normal*, i.e., can be made to obey the relation $\int \mathrm{d}\mathbf{r}\, \psi_n^*(\mathbf{r})\, \psi_m(\mathbf{r}) = \delta_{n,m}$. Assuming that the eigenvalues are discrete and nondegenerate, we can order them according to their magnitude $0 \leq \lambda_0 < \lambda_1 < \lambda_2 < \ldots$. The assumption of discrete eigenvalues is not too far-fetched considering that the direct correlation function, and therefore also the self-consistent field, is short ranged. (As is well-known, the direct correlation function becomes negligible at distances greater than the bare interaction range $\sigma \simeq l_{\mathrm{K}}$.[14]).

Assuming that the eigenvalues are well separated, we get for the free energy in the long chain limit $M \gg 1$

$$F = \lambda_0 MN - 2N \ln \int \mathrm{d}\mathbf{r}\, \psi_0(\mathbf{r}) - \exp(-(\lambda_1 - \lambda_0)\, M)\left(\frac{\int \mathrm{d}\mathbf{r}\, \psi_0(\mathbf{r})}{\int \mathrm{d}\mathbf{r}\, \psi_1(\mathbf{r})}\right)^2 + ... \quad (28)$$

The question arises under what conditions the third and higher order terms in eq 28 can be neglected. To find this out, let us consider the structure of the polymeric liquid on a length scale Q^{-1}. From what is known about the spectrum of an ideal polymer in a box of size Q^{-1}, we estimate the eigenvalues to obey $\lambda_n \simeq n^2Q^2$.[28] This means that $(\lambda_1 - \lambda_0)\, M = Q^2M \gg 1$ if $Q \gg M^{-1/2}$. In other words, if $Q \gtrsim M^{-1/2}$, all contributions to the free energy *not* stemming from the smallest eigenvalue are exponentially small and can safely be neglected. This is the so-called ground-state approximation, often used in studies of polymers near interfaces, and/or in confined geometries.[1] Within this approximation

$$\rho(\mathbf{r}) = NM\psi_0(\mathbf{r})\, \psi_0^*(\mathbf{r}) \quad (29)$$

as one may verify by inserting $Z(\mathbf{r}', \mathbf{r}; M) = \psi_0^*(\mathbf{r}')\psi_0^*(\mathbf{r})$ $\exp[-\lambda_0 M]$ into eq 10. Since

$$\lambda_0 = -\frac{1}{MN}\int \mathrm{d}\mathbf{r}\, \rho^{1/2}(\mathbf{r}) \left[\frac{1}{6}{l_\mathrm{K}}^2\nabla^2 - U(\mathbf{r})\right] \rho^{1/2}(\mathbf{r}) \quad (30)$$

we conclude from eqs 9, 28, and 30 that the configurational free energy must be given by

$$F_\mathrm{conf} = -\frac{1}{6}{l_\mathrm{K}}^2 \int \mathrm{d}\mathbf{r}\rho^{1/2}(\mathbf{r})\, \nabla^2\rho^{1/2}(\mathbf{r}) - 2N \ln \int \mathrm{d}\mathbf{r} \left(\frac{\rho(\mathbf{r})}{MN}\right)^{1/2} \quad (31)$$

provided conditions are such that the ground-state approximation does indeed hold. The leading order term is a well-known result.[1] Less well-known is the logarithmic (finite-size) correction, first derived in slightly different form for orientationally ordered semiflexible polymers[20] and later also for flexible ones in the vicinity of an interface.[30]

The free energy minimization $\delta F/\delta\rho(\mathbf{r}) = \mu$ now gives for the equilibrium segment distribution

$$-\frac{1}{6}{l_\mathrm{K}}^2\nabla^2\rho^{1/2}(\mathbf{r}) - \rho^{1/2}(\mathbf{r}) \int \mathrm{d}\mathbf{r}'\, \rho\,(\mathbf{r}')\, c(\mathbf{r}, \mathbf{r}') + \phi(\mathbf{r})\, \rho^{1/2}(\mathbf{r}) - \frac{N}{\int \mathrm{d}\mathbf{r}\rho^{1/2}(\mathbf{r})} = \mu\rho^{1/2}(\mathbf{r}) \quad (32)$$

or, equivalently, to linear order in a weak field $\phi \ll 1$

$$-\frac{1}{12}{l_\mathrm{K}}^2\nabla^2\delta\rho(\mathbf{r}) - \bar{\rho} \int \mathrm{d}\mathbf{r}'\, \delta\rho(\mathbf{r}')\, c(\mathbf{r} - \mathbf{r}') + \frac{1}{2M}\delta\rho(\mathbf{r}) = -\bar{\rho}\phi(\mathbf{r}) \quad (33)$$

where we used that in zero field $\mu = -\bar{\rho} \int \mathrm{d}\mathbf{r}'\, c(\mathbf{r} - \mathbf{r}') - M^{-1}$. Following the prescription of the previous section, the linearized equation can be solved exactly by transforming to Fourier space, and combining the result with eq 16. The structure factor thus obtained reads

$$S(q) = \frac{\left(\frac{1}{12}Q^2 + \frac{1}{2}M^{-1}\right)^{-1}}{1 - \bar{\rho}\left(\frac{1}{12}Q^2 + \frac{1}{2}M^{-1}\right)^{-1}\hat{c}(q)} \quad (34)$$

in the regime $M^{-1/2} \lesssim Q \lesssim 1$. Because the relation $F^{-1} \sim {}^1/_{12}Q^2 + {}^1/_2M^{-1}$ holds in the same regime, we have again arrived at a result that is consistent with the general form of eq 1.

5. Very Short Wavelengths

The theory set up in sections 3 and 4 needs to be modified significantly if we are to probe lengths of the order of, or smaller than, the Kuhn length. The reason is that for such small lengths the Green function no longer obeys a Schrödinger-type equation, eq 16, but a much more awkward one, eq 5. One complicating factor is that the (transfer) operator on the right-hand side of eq 5 is not self-adjoint. Fortunately, standard methods from operator theory allow us to overcome complications of this kind. Another, perhaps more important point of concern is that we enter a nonuniversal regime, where the detailed structure of the polymeric model emerges. Indeed, the Gaussian model loses its usefulness at very small scales. (See also section 1.) We investigate the behavior of the Gaussian chain fluid for $Q \gg 1$ regardless, because it helps us to understand the properties of the model.

We again take full advantage of the ground-state approximation discussed in the previous section. The relevant eigenvalue equation now is

$$\left[\exp\left(-U(\mathbf{r}) + \frac{1}{6}{l_\mathrm{K}}^2\nabla^2\right) - 1\right] \psi_0(\mathbf{r}) = -\lambda_0\psi_0(\mathbf{r}) \quad (35)$$

with λ_0 again the smallest eigenvalue. The adjoint eigenvalue equation is given by[28]

$$\left[\exp\left(\frac{1}{6}{l_\mathrm{K}}^2\nabla^2 - U(\mathbf{r})\right) - 1\right] \psi_0^*(\mathbf{r}) = -\lambda_0\psi_0^*(\mathbf{r}) \quad (36)$$

where it has to be kept in mind that the memory operator and the Boltzmann factor do not commute.[19] Equations 35 and 36 imply that

$$\psi_0^*(\mathbf{r}) = \psi_0(\mathbf{r})\, \exp[U(\mathbf{r})] \quad (37)$$

To simplify further analysis, it proves useful to rewrite the linear memory operator as[19]

$$\exp\left(\frac{1}{6}{l_\mathrm{K}}^2\nabla^2\right)(\cdots) = \left(\frac{3}{2\pi {l_\mathrm{K}}^2}\right)^{3/2} \int \mathrm{d}\mathbf{r}' \exp\left(-\frac{3(\mathbf{r} - \mathbf{r}')^2}{2{l_\mathrm{K}}^2}\right)(\cdots) \quad (38)$$

The equivalence of the differential and integral forms of the memory operator is straightforwardly verified in Fourier space.[28] Replacing in eq 5 the differential form by the integral form of the memory operator, we immediately see that $\psi_0(\mathbf{r}) \propto \exp[-U(\mathbf{r})]$ is a solution of the eigenvalue equation eq 35, but only when $U(\mathbf{r})$ is sufficiently short ranged on the scale of the Kuhn length l_K. This condition is realizable theoretically through a suitable choice of the external potential ϕ. It follows that

$$\rho(\mathbf{r}) = NM\frac{\exp[-U(\mathbf{r})]}{\int \mathrm{d}\mathbf{r}\,\exp[-U(\mathbf{r})]} \tag{39}$$

where we have used conservation of mass to fix the eigenvalue λ_0. This in turn implies that

$$U(\mathbf{r}) = -\ln \rho(\mathbf{r}) \tag{40}$$

Finally, inserting eq 40 into the ground-state configurational free energy $F_{\mathrm{conf}} = \int \mathrm{d}\mathbf{r}\ \rho(\mathbf{r})\ (\lambda_0 - U(\mathbf{r}))$ gives

$$F_{\mathrm{conf}} = \int \mathrm{d}\mathbf{r}\ \rho(\mathbf{r})\ (\ln \rho(\mathbf{r}) - 1) + ... \tag{41}$$

apart from uninteresting constant terms, and a finite-size correction of order $M^{-1} \to 0$. This free energy functional applies when the scale of the typical density variations is small compared to the Kuhn length of the chain.

One recognizes in eq 41 an ideal entropy of mixing.[13] Apparently, the connectivity of the chains has lost its relevance to the structure of the fluid when the limit $Q \gg 1$ applies, and the segments behave as if they were free monomers. This has to be expected, of course, because the harmonic (ideal spring) potential, enforcing the connectivity between consecutive beads, is flat on a scale small compared to the root-mean-square step length (itself equal to the Kuhn length). An expression for all practical purposes identical to eq 41 was derived earlier for the configurational free energy of a polymer in an extremely confined state.[18]

The equilibrium segment density $\rho(\mathbf{r})$ we again obtain by functionally minimizing the free energy $F = F_{\mathrm{conf}} + F_{\mathrm{exc}}$. The equilibrium segment density now obeys a nonlinear integral equation

$$\ln \rho(\mathbf{r}) - \int \mathrm{d}\mathbf{r}'\rho(\mathbf{r}')\ c(\mathbf{r}, \mathbf{r}') + \phi(\mathbf{r}) = \mu \tag{42}$$

This expression we use to calculate the structure factor of the polymeric system in the short wavelength limit $Q \gg 1$, following the procedure as discussed in the preceding sections, to give

$$S(q) = \frac{1}{1 - \bar{\rho}\hat{c}(q)} \tag{43}$$

The structure factor of the polymeric fluid in the high Q limit, eq 43, coincides with the structure factor of a simple liquids of unconnected segments.[13] This does not contradict eq 1, for the form factor attains the value of unity in that limit.

6. Discussion and Conclusions

The self-consistent Green-function method, outlined in section 2, provides a natural amalgamation of the statistical theory of polymers, and the density functional theory of simple liquids. The method was used in sections 3−5 to calculate by analytical means the structure factor of a fluid of Gaussian model polymers. Comparison of our results with what is in essence the starting point of the often used PRISM theory, shows that the latter is justifiable within a self-consistent field approximation, at least when we consider flexible, Gaussian chains. (This was also concluded in other work, although based on different theoretical methods.[23,31]) A drawback of PRISM theory as it is normally set up is that it needs significant modification if one is to incorporate the coupling of positional and angular degrees of freedom in the description.[14,32] Although not relevant for the standard Gaussian model, these do become important when studying more realistic polymer models.[33] That this must be so can be inferred from theoretical work on isotropic solutions of polymers with a bending rigidity.[34−36] The cited works show that if angular correlations are present between the chains, the structure factor must have a much more complicated form than given in eq 1. Translation-rotation coupling is of crucial importance when it comes to the structure and stability of liquid-crystalline phases[37] and probably also of solid phases.[38] It must be stressed that translation-rotation coupling is an integral part of the Green-function formalism, provided a suitable polymeric model is selected and the interactions between the chains are not described as purely isotropic. Recently published theoretical work on nonuniform isotropic and liquid-crystalline phases of wormlike chains demonstrate the usefulness of the Green-function description.[39−43] By making the connection with density functional theory of liquid crystals,[44] instead of relying on low-density approximations[41,42] or on a Flory−Huggins approximation combined with a phenomenological description of the anisotropic interactions, if present,[39,40,43] a more realistic description is also within reach for these systems.

As to the configurational free energy of inhomogeneous polymeric material, limiting expressions were obtained for segment density variations of Gaussian chains on large, intermediate and small length scales. Similar expressions have been derived previously in the literature, albeit in quite different contexts.[1,18,22,26,30] Ideally, one would like to find a suitable interpolation between the various limiting expressions, given in eqs 21, 31, and 41. We have not been able to find a interpolation formula that has the correct asymptotic behavior all three regimes. It has been suggested in the literature that the functional

$$F_{\mathrm{conf}} = \int \mathrm{d}\mathbf{r}\frac{\rho(\mathbf{r})}{M} \ln \frac{\rho(\mathbf{r})}{MN} - \kappa {l_{\mathrm{K}}}^2 \int \mathrm{d}\mathbf{r}\ \rho^{1/2}(\mathbf{r})\ \nabla^2\ \rho^{1/2}(\mathbf{r}) \tag{44}$$

provides a valid description of the free energy of inhomogeneous systems of Gaussian polymers, provided we set κ equal to $^1/_9$ for weak density gradients, and $^1/_6$ for strong ones.[8,21,22,26,28] Although not without merit for weak gradients, eq 44 can hardly be called accurate in the opposite limit of strong gradients, even when restricting to the case $Q \ll 1$. See eq 31 of section 4. Indeed, if we accept eq 44 at face value, and use it to calculate the structure factor

$$S(q) = \frac{M}{1 + \frac{1}{2}\kappa M Q^2 - \bar{\rho} M \hat{c}(q)} \tag{45}$$

we find its accuracy wanting for $QM^{1/2} > 1$; cf. eq 34. One should therefore be wary when using eq 44 to describe nonuniform polymer solutions and melts, except when it is absolutely clear that the density gradients are sufficiently weak. An interesting spin-off of our analysis is the configurational free energy for density variations on a very small scale, eq 41. It suggests that the individual segments of a Gaussian chain behave very much like free monomers, if one considers length scales corresponding to $Q \gg 1$. It is tempting to speculate on what consequences this could have for our understanding of polymer crystallization. Let us, for the sake of argument, consider a toy model of hard, Gaussian chains, i.e., Gaussian chains constructed of globular segments that interact via their mutually excluded volumes only. The reader is reminded that in the melt limit such excluded-volume chains behave ideally with regard to their configurational properties, but only in the statistical sense. Since the crystallization of hard spheres involves ordering processes in the high Q range,[45] we expect on the basis of eqs 41 and 43 that our hard-sphere toy polymer must crystallize under very similar conditions. As a consequence, there cannot be a great loss of configurational entropy associated with the crystalline ordering of Gaussian chains.[46] Note that this contrasts with what was concluded elsewhere,[47] in a description where in the crystal phase the microscopic degrees of freedom of the chains were assumed to be completely frozen in. The explanation for this paradox is that although in our model the beads may arrange themselves in regular arrays upon crystallization, the bonds between the beads need not do the same, for they are phantom in nature. The inability of the bonds to order is clearly a pathology of the Gaussian model.[4] Nevertheless, results from the computer simulations of Malanoski and Monson[48] do appear to bear out a conclusion that one might draw on the basis of the foregoing, namely that chain connectivity may well have only a minor influence on the thermodynamics of the crystallization of polymers. The simulation study, which was limited to short chains of $M = 1, ..., 8$ tangent hard spheres, show that the density at which such chains start to crystallize levels off rapidly with increasing degree of polymerization. For $M > 3$, crystallization sets in at a volume fraction of approximately 0.53, which is very close to the value of 0.49 found for $M = 1$, that is, for the free “monomers”.

The slight difference in the crystallization densities of the monomers and the oligomers could be due to a renormalization of the interaction range of the segments when linked into a chain. This is the chain-connectivity effect we alluded to in section 1. Of course, real polymer chains are much more complex and longer than the highly idealized short-chain models studied by Malanoski and Monson. In reality chain stiffening is likely to be an important factor governing the crystallization of polymers[38]—an effect we intend to study using the Green-function description in the near future.[27] Nonetheless, there appears to be a strong case in favor of the idea that the thermodynamics of polymer crystallization is predominantly (but not entirely) determined by local packing effects. For completeness we add that there is no conflict between such a local *thermodynamics*, and the observation that the initial crystallization *kinetics* involve processes on much longer length scales.[49]

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