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Bond−Vector Correlation Functions in Dense Polymer Systems

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ABSTRACT: It is well-known that homopolymer chains do not exactly follow the Gaussian statistics even in the melt state. In particular, orientations of two bonds l_1 and l_2 of the same chain in a concentrated polymer system are always correlated even when they are separated by a long segment of $s \gg 1$ units: $\langle \underline{l}_1 \cdot \underline{l}_2 \rangle_s = C(s) \sim 1/s^{3/2}$. It is important to know how these orientational correlations are distributed in space, i.e. how $\langle \underline{l}_1 \cdot \underline{l}_2 \rangle$ depends on the distance $\underline{r}$ between the bonds.[1] An unexpected feature is revealed in the present paper: it is shown that the distance-dependent bond-vector correlation function $K(r) = \langle \underline{l}_1 \cdot \underline{l}_2 \rangle_r$ is extremely sensitive to the definition of $\underline{r}$. Depending on the definition, $K(r)$ for $r \gg b$ (b is the monomer size) can be either significantly lower, or significantly higher than the position-averaged correlator $C(s)$ with $s \sim r^2/b^2$ corresponding to a given distance r. We propose an "invariant" definition of the intrachain orientational correlation function and show that it is related to the formfactor of a single chain. A quantitative link between the orientational and positional correlations in polymer melts is thus discovered. We also have found a quantitative relationship between the intrachain and interchain correlation functions. It is shown that the *inter*-chain orientational correlation function (for bonds of *different* chains) is long-range and follows the $1/r^4$ scaling law in the case of infinite chains.

1. Introduction

The classical view on the equilibrium structure of concentrated homopolymer fluids (solutions or melts of flexible polymers) implies that all correlations are short-range:[2−5] the correlation functions of bond concentration, density or orientation are screened at length-scales r beyond the static correlation length ξ which is typically comparable to one or a few monomer sizes b.

This classical concept was amended rather recently:[6−11,1,12] it was shown that correlation functions of physical quantities like local monomer concentration or bond orientation do not vanish exponentially at large distances $r \gg \xi$ but rather exhibit some weak power-law tails.

The long-range corrections concern both the collective and the single-chain properties. It was shown that the conformational distribution of a single chain in a polymer melt is not exactly Gaussian.[8] The deviations from the ideal-chain (Gaussian) statistics in a polymer melt can be illustrated by the bond-vector correlation function $C(s) = \langle \underline{l}_1 \cdot \underline{l}_2 \rangle_s$ where two bonds $\underline{l}_1$, $\underline{l}_2$ belong to the same polymer chain and are separated by a segment of s units (see Figure 1a): The function $C(s)$ shows the following characteristic long-range power-law decrease[8]

$$C(s) \sim (c_1 b)^{-1} s^{-3/2}, \quad s \gg 1 \tag{1}$$

in contrast with the exponential decay of the orientational correlations ($C(s) \propto e^{-\mathrm{const}\ s^3}$) predicted for an *ideal* chain (here c_1 is the mean concentration of monomer units in the system).

The orientational correlations in polymer melts were recently considered from a different point of view in terms of the real-space distance (r) dependence of the bond-vector correlation function $K(r) = \langle l_1 \cdot l_2 \rangle_r$ (see Figure 1b).[1] In the case of infinite chains it was shown that

$$K(r) \sim (b^2/c_1) r^{-3}, \quad r \gg b \tag{2}$$

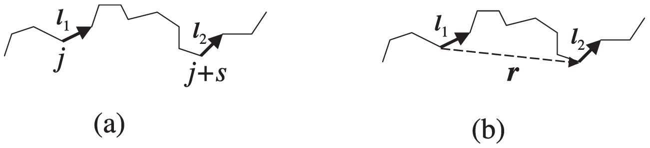

Figure 1. (a) Bond−bond correlation function $C(s) = \langle \underline{l}_1 \cdot \underline{l}_2 \rangle_s$. The bonds l_1 and l_2 are separated by a chain segment of s bonds (of arc-length sl, where l is the bond length). (b) $K(r) = \langle \underline{l}_1 \cdot \underline{l}_2 \rangle_r$ is the intrachain bond-vector correlation function depending on the distance r between the bonds (the vector $\underline{r}$ connects the initial points of the bonds l_1 and l_2). s is treated as a free variable in part b: $\langle ... \rangle$ means both the ensemble average and the average with respect to the arc-length between the bonds.

It was therefore concluded that orientational correlations are *delocalized* in the real space.[1]

The two predictions, eqs 1, 2, are in agreement: $K(r) \sim C(s)$ for the typical $r \sim s^{1/2} b$ corresponding to a given $s \gg 1$. This notion, however, may give a wrong impression about the universality of the law, $K(r) \propto r^{-3}$. There are two problems with the latter result: First, it turns out that the distance-dependent correlation function $K(r)$ is very sensitive to the definition of the bond−bond distance r (see sections 3.1, 3.3, and 3.4 below). The three possible definitions illustrated in Figure 2 (see Appendix D.a) yield three different correlation functions $K_a(r)$, $K_b(r)$, and $K_c(r)$. It may seem natural to anticipate that all the three correlation functions must be close to each other for $r \gg b$ since the three ways to define the bond−bond distance r lead to nearly coinciding distances (for $r \gg b$). It turns out, however, that this is not the case: the functions $K_{a,b,c}$ are not even similar. It is shown below that they can be drastically different, in particular, for the "soft melt" model adopted in ref 1 (see sections 3.1, 3.2, and 3.3): With definitions (a) or (c) the long-range orientational correlations are absent for ∞-long chains: both $K_a(r)$ and $K_c(r)$ are localized near $r \sim b$. This is in drastic contrast with the long-range behavior of $K_b(r) \propto r^{-3}$ for $r \gg b$ predicted in ref 1; see eq 2 (note that it is the second definition of the bond−bond distance r that was adopted in ref 1; cf. Figures 2b and 1b). So, naturally, the question arises

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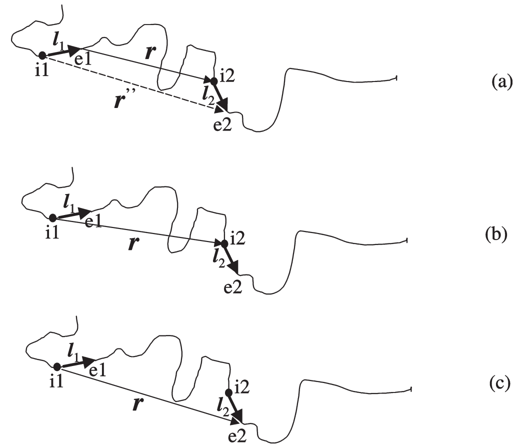

Figure 2. Illustrations of three definitions of the bond−bond distance $\underline{r}$. Two bond vectors $\underline{l}_1 = \underline{r}_{e1} - \underline{r}_{i1}$ and $\underline{l}_2 = \underline{r}_{e2} - \underline{r}_{i2}$ are separated by a segment of s bonds. (a) $\underline{r}$ is the vector connecting the end of the first bond with the initial point of the second bond, $\underline{r} = \underline{r}_a \equiv \underline{r}_{i2} - \underline{r}_{e1}$; (b) $\underline{r} = \underline{r}_b \equiv \underline{r}_{i2} - \underline{r}_{i1}$; (c) $\underline{r} = \underline{r}_c \equiv \underline{r}_{e2} - \underline{r}_{i1}$.

whether the orientational correlations are actually localized in the real space or are long-range.

Another problem arises as we turn to the case of long but finite chains (with the mean polymerization degree $\overline{N} \gg 1$). It is natural to expect that the infinite-chain behavior $K_b(r) \propto r^{-3}$ must persist for r up to the typical coil size $R \sim \overline{N}^{1/2}b$, hence $K_b \propto \overline{N}^{-3/2}$ for $r \sim R$. However, a much stronger orientational correlation $K_b(r) \sim 1/\overline{N}$ was predicted for large $r \sim R$.[1] The question is: what is the physical origin of this mismatch?

One of the aims of the present paper is to clarify the issues mentioned above. To elucidate the connection between the s-dependent and r-dependent bond−bond correlations I calculate the generalized correlation functions $K(r,s)$ depending on both real-space and curvilinear distances (see sections 3.1, 3.2, and 3.3). Another important generalization concerns collective bond−bond correlations. So far only intrachain (single-chain) correlation functions were considered.[1,8,11] What about the orientational correlations for bonds of *different* chains? To clarify the point I define the distance-dependent cross-chain correlation function $K_{inter}(r)$ which is essentially independent of the bond−bond distance definition: all three ways to define r (see Figure 2) lead to the same correlation function (apart from a trivial change of the sign). The same definition, as applied to intrachain bond−bond correlations, yields the invariant single-chain correlation function $K_{intra}(r)$. I show that the cross-chain and single-chain correlation functions are related. I also show that both functions are connected to the polymer chain formfactor (the single-chain scattering function) whose Fourier transform gives the intrachain bead−bead correlation function $G_{intra}(r)$. A physical interpretation of the r-behaviors of the bond-vector correlation functions is provided based on these relationships.

All the results discussed in this paper are equally applicable to any isotropic dense amorphous polymer system like a polymer melt or a concentrated polymer solution. Such systems are referred to below as just polymer melts for simplicity.

2. Background

2.1. Effective Interactions in a Polymer Melt. Consider a dense system (melt) of long flexible polymer chains. The mean concentration of repeat chain units (which are also called "beads" below) is c_1. The beads interact with each other. It is useful to distinguish between three types of pairwise bead−bead interactions. On the microscopic level, the total interaction energy is the sum of contributions $v_d(r_1 - r_2)$ from each pair of beads r_1 and r_2 (the beads can belong to the same chain or to different chains). It is well-known that these direct interactions are effectively screened out due to the low compressibility of the system. The screened interactions arise as we get to monitor the conformational distribution of one single (marked) chain formally considering all other (surrounding) chains as invisible: To a good approximation the marked chain behaves as an isolated chain with some effective (screened) pairwise interactions $v(r_1 - r_2)$ between its beads. Generally, the screened interactions are rather weak; they only slightly perturb the ideal-polymer (Gaussian) conformational statistics at long length-scale $r \gg b$, where b is the chain statistical segment.

The screened interaction potential $v(r)$ depends on the direct function $v_d(r)$ and other parameters. The mean-field prediction for a system of infinite chains ($\overline{N} \to \infty$) reads:[4,7,13]

$$v(q) \simeq \frac{v_1 q^2 a^2}{2c_1 v_1 + q^2 a^2} \tag{3}$$

where $v(q)$ is the Fourier transform of $v(r)$, q is the wave-vector, $a^2 = b^2/6$, and v_1 is the effective monomer volume depending on the direct potential $v_d(r)$. v_1 is related to the bulk compressibility of the system:[14]

$$v_1 = \frac{1}{c_1}\frac{\partial \Pi}{\partial c_1}$$

Π is the pressure (polymer osmotic pressure in the case of a polymer solution). Equation 3 can be rewritten as $v(q) \simeq v_1(q\xi)^2/[1 + (q\xi)^2]$, where

$$\xi \simeq a/\sqrt{2c_1 v_1}$$

is the static correlation length. Strictly speaking, eq 3 is valid for $c_1 v_1 \ll 1$, $qa \ll 1$. Note, however, that in the most important asymptotic regime $q\xi \ll 1$, $v(q) \simeq q^2a^2/(2c_1)$ is independent of the monomer interactions.

To introduce the bead−bead interaction potential of the third type, let us consider invisible all the beads except just two beads, $\underline{r}_1$ and $\underline{r}_2$, belonging to different chains. The distribution of $\underline{r} = \underline{r}_2 - \underline{r}_1$ can be expressed in terms of the energy potential $U(r)$ of effective interactions between the two beads: the distribution density $\rho(r) = \text{const}\exp(-U(r))$. To obtain $U(r)$ it is therefore sufficient to get $\rho(r)$. The distribution $\rho(r)$ for $r \gg \xi$ is discussed below. Suppose the bead $\underline{r}_1$ is located at the origin ($r_1 = 0$). The chain involving the $\underline{r}_1$-bead is marked as "white". The concentration profile of the white beads $c_w(r)$ coincides with the intrachain correlation function $c_w(r) = G_{intra}(r)$. This function can be easily found recalling that the white chain is infinite and is nearly Gaussian (for $r \gg \xi$): $c_w(r) \sim 1/(rb^2)$. The mean concentration $c_d(r)$ of all the beads of other chains (except the white chain) must be proportional to $\rho(r)$ since all such beads are equivalent to the r_2-bead: $c_d(r) = \text{const}\,\rho(r)$. Next, note that $c_d(r) + c_w(r) \simeq c_1$ since the polymer melt is virtually incompressible at length-scales $r \gg \xi$.

Using the above equations one finds

$$U(r) \sim c_w(r)/c_1 \sim 1/(c_1 b^2 r) \tag{4}$$

(note that $c_w \ll c_1$ and $U \ll 1$ for large $r \gg \xi$; hence, $e^{-U} \simeq 1 - U$). Thus, there is a weak but long-range effective repulsion between the beads. The effective potential $U(r)$ is significantly different from the direct bead−bead interaction potential $v_d(r)$ and the screened potential $v(r)$ (for example, both v_d and v are normally attractive at large r rather than repulsive). $U(r)$ is the excess free energy of the *whole* system considered as a function of $\underline{r} = \underline{r}_2 - \underline{r}_1$. The effective potential $U(r)$ was estimated before using a similar argument.[7,13]

The repulsive potential $U(r)$ works also for the distant beads of the same (white) chain. It therefore affects the distribution of white beads (around a white bead fixed at the origin) inducing a slight depletion (that increases at smaller r) on the top of the Gaussian-chain distribution $\sim 1/(rb^2)$: $c_w(r) \sim 1/(rb^2)[1 - \text{const } U(r)]$. The intrachain correlation function in the melt of infinite chains therefore reads:[13]

$$G_{intra}(r) \sim 1/(rb^2) - \text{const}/(c_1 b^4 r^2) \qquad (5)$$

The second term here is the interaction-induced correction. A more precise result for $G_{intra}(r)$ (including the proper numerical factors) was obtained in ref 13. A more general result valid for a polydisperse polymer system with Flory distribution of chain length is also derived in Appendix C (see eq C4).

2.2. The Bond−Vector Correlation Functions. Consider two bonds l_1 and l_2 belonging to the same chain and connected by the chain-segment of s bonds, $s \gg 1$. The three different definitions of the distance $\underline{r}$ between the bonds are illustrated in Figure 2a−c. All three distances are close to each other if $r \gg b$, so it may seem that it does not matter which definition to adopt. It turns out, however, that the distinction between the definitions a−c is important as long as the correlations of bond orientations, $\underline{l}_1$ and $\underline{l}_2$, for a given $\underline{r}$ are concerned (see sections 3.1, 3.2, and 3.3).

The distance and arc-length dependent bond-vector orientational correlation function is $K(r,s) = \langle \underline{l}_1 \cdot \underline{l}_2 \rangle_{r,s}$, where $\langle ... \rangle$ means the ensemble average over the equilibrium distribution of polymer states for a given distance r between the two bonds separated by s main-chain units (the arc-length is sl, where l is the bond length). The relations between $K(r,s)$ and other correlation functions are considered in Appendix D. It is shown there that the single-variable distance-dependent bond-vector correlation function $K(r) = \langle \underline{l}_1 \cdot \underline{l}_2 \rangle_r$ is

$$K(r) = 2Q(r)/G_{intra}(r) \qquad (6)$$

where

$$Q(r) = \int_0^\infty K(r,s) G(r,s) w(s)\, \mathrm{d}s,$$
$$\frac{1}{2} G_{intra}(r) = \int_0^\infty G(r,s) w(s)\, \mathrm{d}s \qquad (7)$$

Here $G(r,s)$ is the single-chain bead−bead correlation function and $w(s)$ is the probability that an arbitrarily chosen bead is more than s units away from the end of the same chain; $w(s) \equiv 1$ for infinite chains; $w(s) = e^{-\mu s}$ in the case of Flory molecular-weight distribution with the mean polymerization degree $\overline{N} = 1/\mu$ (see Appendix D). In polymer melts $G(r,s)$ can be well-approximated by the Gaussian distribution

$$G(r,s) \simeq (2\pi s b^{*2}/3)^{-3/2} \exp\left(-\frac{3r^2}{2sb^{*2}}\right), \quad r \gg b^* \qquad (8)$$

where b^* is the (renormalized) statistical segment of polymer chains. Therefore

$$\frac{1}{2} G_{intra}(r) \simeq \frac{3}{2\pi b^{*2} r} \exp(-r/R),$$
$$R \equiv b^* \sqrt{\overline{N}/6}, \quad r \gg b^* \qquad (9)$$

(compare with more precise results, eqs 41 and 42).

The arc-length dependent orientation correlation function $C(s) \equiv \langle \underline{l}_1 \cdot \underline{l}_2 \rangle_s$ is also related with $K(r,s)$ (see Appendix D, eq D8)

$$C(s) = \int K(r,s) G(r,s)\, \mathrm{d}^3 r \qquad (10)$$

3. The Intrachain Orientational Correlation Functions

In this section, we analyze the distance-dependent bond-vector correlation functions considering the effective (screened) monomer interaction potential $v = v(r)$ as a perturbation. It is shown that the correlations depend very significantly on the definition of the bond-to-bond distance vector $\underline{r}$.

3.1. Orientational Correlations: Definition a. Let us adopt the first definition (a), Figure 2a, of the bond-to-bond distance and analyze the correlation function $K(r,s) = K_a(r,s)$. There are no orientational correlations for an unperturbed Gaussian chain: $K_a \equiv 0$ in the zeroeth order approximation. Hence, it is necessary to take into account the deviations from the Gaussian statistics related to the monomer interactions $v(r)$. We consider first a scaling argument applicable to a system of *infinite* chains. The bond vectors $\underline{l}_1 = \underline{r}_{e1} - \underline{r}_{i1}$ and $\underline{l}_2 = \underline{r}_{e2} - \underline{r}_{i2}$ are sketched in Figure 2a. Suppose the beads $e1$ and $i2$ are located at $\underline{r}_{e1} = 0$ and $\underline{r}_{i2} = \underline{r}$. Variations of bond orientations $\underline{l}_1$ and $\underline{l}_2$ for a fixed $\underline{r}$ then lead to variations of the distance $\underline{r}'' = \underline{r} + \underline{l}_1 + \underline{l}_2$ between the beads $i1$ and $e2$ (see Figure 2a). The energy of effective interaction between the tails adjacent to these beads is $W(l_1,l_2) \sim U(r'')$, where $U(r)$ is defined in eq 4. Hence $W \simeq \text{const}/(c_1 b^2 r'')$.

The probability density $\rho(\underline{l}_1,\underline{l}_2) = \rho(\underline{l}_1,\underline{l}_2,\underline{r}|s)$ is proportional to e^{-W} (see Appendix D.a). For $W \ll 1$, the correlation function $K = \langle \underline{l}_1 \cdot \underline{l}_2 \rangle$ can be approximated as (see eqs D1 and D2)

$$K \simeq -\langle l_1 \cdot l_2 W \rangle_0$$

where $\langle ... \rangle_0$ means average with the ideal-chain (Gaussian) statistics. Performing an expansion of W as a series in $\underline{l}_1$, $\underline{l}_2$ and taking into account that

$$\langle l_{i\alpha} l_{j\beta} \rangle_0 = \frac{1}{3} b^2 \delta_{ij} \delta_{\alpha\beta}$$

where $i, j = 1, 2$ point to one of the two bonds (l_1 or l_2) and α, β are the Cartesian components, one gets

$$K(r,s) \simeq -\frac{1}{9} b^4 \nabla^2 W(\underline{r}) = \text{const} \frac{b^2}{c_1} \delta(\underline{r}) \qquad (11)$$

A quantitative derivation of $K(r,s) = K_a(r,s)$ using the diagram technique treating the interaction potential $v(q)$ as a perturbation is given in Appendix A (see Figure 3 and eqs A4, A8). The result obtained in the first-order approximation coincides with eq 11 with const $= {}^1/_3$:

$$K_a(r,s) \simeq \frac{b^2}{3c_1} \delta(\underline{r}) \qquad (12)$$

Equations 11 and A8 show that the orientational correlation function $K_a(r,s)$ does not depend on the arc-length between the bonds but only on the distance r between them. The arc-length dependent correlation function $C(s)$ can be then obtained in a remarkably simple way using eqs 10, 8, and 12:

$$C(s) \simeq \frac{b^2}{3c_1} G(0,s) = \frac{2\sqrt{6}}{c_1} \frac{s^{-3/2}}{(4\pi)^{3/2} b}, \quad s \gg 1 \qquad (13)$$

Thus, $C(s)$ is proportional to the probability density $P_{over} = G(0, s)$ that an s-segment forms a loop, i.e. that the

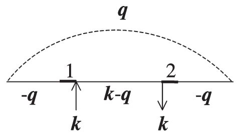

Figure 3. First-order perturbation diagram for $Q = Q_a(k)$. All solid and dashed lines have default orientation from the left to the right. The inserted wave-vector $\underline{k}$ (see upward and downward arrows) is conjugated to the distance $\underline{r}$ between the bonds l_1 and l_2. Thin solid lines represent the Fourier-Laplace transformed Green functions G (see eqs A1, A10). The dashed line brings in the factor $-v(q)$. Bold short segments represent the two bonds l_1 and l_2; they bring in the factor $\mathscr{L}(\underline{k}_1, \underline{k}_2) = -4a^4\underline{k}_1\cdot\underline{k}_2$, where $\underline{k}_1$ and $\underline{k}_2$ are the wave-vectors corresponding to the bonds.

two bonds l_1 and l_2 meet each other (the overlap probability). Note that eq 13 is in agreement with the results of ref 8. The reduced correlator is $\overline{C}(s) = \langle\cos\theta\rangle \simeq C(s)/l^2$ (θ is the angle between $\underline{l}_1$ and $\underline{l}_2$, l is the bond length). For flexible chains $l \sim b$, so eq 13 leads to $\overline{C}(s) \sim C(s)/b^2 \sim s^{-3/2}/(c_1b^3)$ for $s \gg 1$. Therefore, the effective perturbation parameter defining the long-range orientational correlations is $p = 1/(c_1b^3)$.

Is it possible to generalize eq 13 taking into account higher-order perturbation corrections? To this end let us make use of the freedom to change the definition of a monomer unit and consider a group of g consecutive units as a superunit. The concentration of such superunits is $c_g = c_1/g$. The rescaled statistical segment is

$$b_g^* = b^*\sqrt{g}$$

where b^* is the genuine statistical segment of the original chains defined in eq D4. Therefore, the perturbation parameter for superunits is $p_g = 1/(c_gb_g^{*3}) = g^{-1/2}/(c_1b^{*3})$. The parameter p_g has a simple physical meaning: it is proportional to the effective interaction energy of two overlapping g-blobs in a dense polymer system (a simple way to estimate this energy is described in ref 7). In simple geometrical terms, p_g is *inversely* proportional to the number ν of overlapping superunits in a region of size b_g^*: $p_g \sim 1/\nu$. Equation 13 as applied to superbonds reads

$$C^{(g)}(s) \simeq \frac{b_g^{*2}}{3c_g}P_{over} = \frac{g^2b^{*2}}{3c_1}P_{over} \qquad (14)$$

where

$$P_{over} \simeq \left(\frac{6}{4\pi b^{*2}}\right)^{3/2}s^{-3/2} \qquad (15)$$

is the probability density of an encounter between the two superbonds, and s is the number of original bonds between them.

It is remarkable that the perturbation parameter vanishes for large g: $p_g \to 0$ as $g \to \infty$. Therefore, eq 14 becomes asymptotically exact in the limit of large g (the first-order perturbation approximation and the "soft melt" model become exactly valid in this limit). Taking into account that $C^{(g)}(s) \simeq g^2C(s)$ for $s \gg g$, we obtain the desired generalization of eq 13:

$$C(s) \simeq \frac{b^{*2}}{3c_1}P_{over} \simeq \frac{b^{*2}}{3c_1}\left(\frac{6}{4\pi b^{*2}}\right)^{3/2}s^{-3/2} \qquad (16)$$

Thus, the effect of monomer interactions on the orientational correlation function $C(s)$ is adsorbed in the single measurable parameter, the renormalized statistical segment b^*. This statement is valid in all orders of the perturbation theory.[15]

To resume, the orientational correlation function $K_a(r,s)$ for a system of infinite chains is localized in real-space, and, moreover, it does not depend on the reduced arc-length s. The relation $C(s) \propto P_{over}$ naturally follows from the localized $\delta(\underline{r})$ form of $K_a(r,s)$ which comes as a rigorous result of the first order perturbation theory. The relation between $C(s)$ and the bond overlap probability is therefore not a simple coincidence (cf. refs 1 and 16). Note, however, that the localized $K(r)$, eq A4, has nothing to do with the direct interactions of the overlapping bonds: the direct interactions do not contribute to $\langle\underline{l}_1\cdot\underline{l}_2\rangle$ since they do not distinguish between parallel and antiparallel orientations of the bonds.

The orientational correlation function $K_a(r,s)$ was also calculated for a system of finite polydisperse chains with Flory molecular-weight distribution. The result is (see eq A12)

$$K_a(r,s) \simeq K_a(r) \simeq \frac{2}{c_1}\left[\delta(\underline{r}) - \frac{1}{4\pi rR^2}\mathrm{e}^{-r/R}\right] \qquad (17)$$

where

$$R = a\sqrt{\overline{N}} = a/\sqrt{\mu}$$

There are therefore two contributions in the orientational correlation function: one positive term localized at $r = 0$ and another negative term spread over the typical polymer coil size R. For $r \gg a$ the δ-term is not effective, so $K_a(r)$ is negative (anticorrelation of bonds) scaling as $1/r$ for $a \ll r \ll R$.

The two contributions compensate each other integrally:

$$\int K_a(r)\,\mathrm{d}^3r = 0 \qquad (18)$$

The physical meaning of this property is simple. The function $K_a(r)$ is equally applicable to both intrachain and interchain bond–bond correlations. $\langle\underline{l}_1\cdot\underline{l}_2\rangle$ averaged over all l_2-bonds unconnected with l_1 must be identically zero since $\underline{l}_2$ and $-\underline{l}_2$ are physically equivalent. Therefore, $\int K_a(r)c_2(r)\,\mathrm{d}^3r = 0$, where $c_2(r)$ defines the distribution of l_2-bonds. Finally we recall that l_2 bonds are nearly uniformly distributed in space around l_1 bond, i.e., $c_2 \simeq$ const leading to eq 18.

The arc-length dependent correlation function can be obtained using eqs 10 and 17:

$$C(s) = \frac{2}{(4\pi)^{3/2}c_1a}\left(s^{-3/2} - \overline{N}^{-3/2}f\left(\sqrt{s/\overline{N}}\right)\right) \qquad (19)$$

where

$$f(x) = 2/x - 2\sqrt{\pi}e^{x^2}\,\mathrm{erfc}(x)$$

$$\mathrm{erfc}(x) = \frac{2}{\sqrt{\pi}}\int_x^{\infty} e^{-t^2}\,\mathrm{d}t$$

For $s \ll \overline{N} = 1/\mu$, the second term in eq 19 can be neglected and we return to the infinite chain result, eq 13. A faster decay of $C(s)$ is found for larger s:

$$C(s) \propto s^{-5/2}, \quad s \gg \overline{N}$$

This faster decay is formally related to the integral property, eq 18, of the correlation function $K_a(r)$. Physically this behavior of $C(s)$ is due to the fact that the dominant contribution to $C(s)$ for $s \gg \overline{N}$ comes mainly from correlations of the bonds located near the opposite ends of long chains.

3.2. The Orientational Correlation Function $K_b(r,s)$. The correlation function $K = K_b(r,s)$, defined as illustrated in Figure 2b, is calculated in Appendix B (using the diagram technique in the first-order approximation). The main results

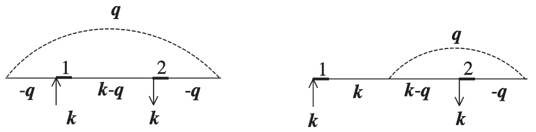

Figure 4. Two first-order perturbation diagrams contributing to $Q_b(k)$. Essentially the same diagrams can be found in Figure 1b of ref 1. All solid and dashed lines have default orientation from the left to the right. The inserted wave-vector $\underline{k}$ (see upward and downward arrows) is conjugated to the distance $\underline{r}$ between the bonds l_1 and l_2 (bold horizontal segments).

are summarized and discussed below. There are basically two first-order contributions (see the diagrams in Figure 4): $K_b(r,s) \simeq K_{b1}(r,s) + K_{b2}(r,s)$,

$$K_{b1}(r,s) \simeq \frac{b^2}{6c_1 s}\left(1+\frac{r}{b}\sqrt{6\mu}\right)G(r), \quad K_{b2}(r,s) \simeq J_{21}\frac{1}{s}\left(-b^2+\frac{r^2}{s}\right) \tag{20}$$

where the ideal-chain Green function $G(r)$ is defined in eq 35 and the constant J_{21} is defined in eq B4.

The physical meaning of the two contributions is clarified below for the case of infinite chains. The K_{b1} term is due to the effective repulsion between two tail parts of the chain (the tail to the left of l_1 and the second tail to right of l_2 in Figure 2b). The energy of this repulsion $U = U(r')$ depends on $\underline{r}' = \underline{r} + \underline{l}_2$. It induces an alignment of $\underline{l}_2$ along the gradient of $U(r)$:

$$\langle \underline{l}_2 \rangle \simeq -\frac{1}{3} b^2 \nabla U(r)$$

On the other hand, $\underline{l}_1$ is oriented along $\underline{r}$ due to the ideal-chain effect: $\langle \underline{l}_1 \rangle = \underline{r}/s$. Invoking eq 4 then leads to

$$\langle \underline{l}_1 \cdot \underline{l}_2 \rangle \simeq \langle \underline{l}_1 \rangle \cdot \langle \underline{l}_2 \rangle \sim \frac{1}{c_1 r s}$$

in agreement with $K_{b1}(r,s)$, eq 20. Turning to the physical meaning of the second term, $K_{b2}(r,s)$, note that the bond vector $\underline{l}_1$ must be correlated with the bond vector $\underline{l}'$ at the opposite end of the internal *s*-segment bounded by the points *i*1 and *i*2 (see Figure 5), in particular, since both vectors must be aligned along $\underline{r}$ for large *r*. This ideal-chain elastic effect is considered in section 3.3 (see eq 33 and the paragraph below it):

$$\langle \underline{l}_1 \cdot \underline{l}' \rangle \simeq \frac{1}{s}\left(-b^2+\frac{r^2}{s}\right), \quad s \gg 1 \tag{21}$$

The bonds l_2 and l' are neighbors on the chain; hence, they must be correlated due to their local interactions:

$$\langle \underline{l}_2 \rangle \simeq \mathrm{const}\, \underline{l}'$$

where the average is taken for a given orientation of the bond vector $\underline{l}'$. Therefore

$$\langle \underline{l}_1 \cdot \underline{l}_2 \rangle \simeq \mathrm{const}\frac{1}{s}\left(-b^2+\frac{r^2}{s}\right) \tag{22}$$

where const must be identified with J_{21}. The obtained $\langle \underline{l}_1 \cdot \underline{l}_2 \rangle$ then agrees with $K_{b2}(r,s)$, eq 20. Thus, K_{b2} is basically due to the ideal-chain alignment of the bonds of the *s*-segment modulated by the local orientational correlation effect.

Equation B4 defining the prefactor J_{21} for $K_{b2}(r,s)$ is approximate: it is valid in the first-order perturbation approximation, i.e., for weak interaction potential of beads, $v(r) \ll 1$, corresponding to $\xi \gg b$ (the "soft-melt" regime,[1]). In addition, it was assumed that an unperturbed ideal polymer is a Gaussian chain with totally uncorrelated bond vectors. Real polymer chains always have some local stiffness; even ideal polymers are non-Gaussian locally. Thus, generally the bonds *j* and $j + m$ neighboring on a chain are correlated due to both the local chain stiffness and the local interaction effects:

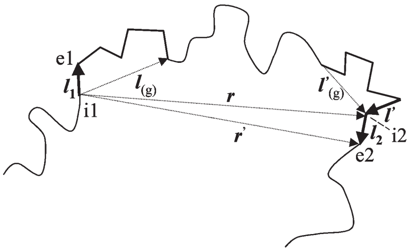

Figure 5. Initial points *i*1, *i*2 of the bonds l_1 and l_2, which are connected by the chain segment of *s* bonds (the *s*-segment). $\underline{r} = \underline{r}_{i2} - \underline{r}_{i1}$; $\underline{r}' = \underline{r}_{e2} - \underline{r}_{i1}$. The terminal bonds of the *s*-segment are $\underline{l}_1$ and $\underline{l}'$. The bond $\underline{l}'$ is adjacent to the bond l_2. The *s*-segment can be also viewed as a sequence of *s*/*g* superbonds. The terminal superbonds are denoted as $l_{(g)}$ and $l'_{(g)}$; they contain, respectively, the primary bonds l_1 and l' (the superbond size is $g = 6$ in the figure).

$$\langle \underline{l}_j \cdot \underline{l}_{j+m} \rangle = C(m)$$

(the correlation function *C* was introduced above eq 1). It is useful to note that

$$C(0) = l^2, b^{*2} = l^2 + 2\sum_{m=1}^{\infty} C(m) \tag{23}$$

where l^2 is the mean-square bond length.

Using the general argument presented just above eq 22, it is possible to find J_{21} more precisely lifting both approximations. We employ again the idea of superunits (groups of *g* beads). The chain of superunits with $g \gg 1$ is (almost) Gaussian since orientational correlations between superbonds are weak (they decay as $1/\sqrt{g}$; see section 3.1). Consider two superbonds, $\underline{l}_{(g)}$ and $\underline{l}'_{(g)}$, at the opposite ends of an *s*-segment (see Figure 5; note that the bonds $\underline{l}_1$ and $\underline{l}'$ are parts of $\underline{l}_{(g)}$ and $\underline{l}'_{(g)}$, respectively; it is assumed that $1 \ll g \ll s$). The vectors $\underline{l}_{(g)}$ and $\underline{l}'_{(g)}$ are correlated according to eq 21, where *s* and b^2 must be replaced by the rescaled quantities, $s \to s/g$, $b^2 \to gb^{*2}$:

$$\langle \underline{l}_{(g)} \cdot \underline{l}_{(g)}' \rangle \simeq \frac{g}{s}\left(-gb^{*2}+\frac{r^2}{s/g}\right) \tag{24}$$

Next we notice that the bond $\underline{l}_1$ must be aligned with the superbond $\underline{l}_{(g)}$ due to the local chain stiffness and local interaction effects:

$$\langle \underline{l}_1 \rangle \simeq C_1 \underline{l}_{(g)}$$

where $\langle \underline{l}_1 \rangle$ is the mean vector $\underline{l}_1$ for a given superbond vector $\underline{l}_{(g)}$. The constant C_1 can be easily found using the linear response theory ($\langle \underline{l}_{(g)}^2 \rangle = b^{*2} g$):

$$C_1 = \frac{1}{b^{*2} g}\sum_{m=0}^{g-1} C(m) \tag{25}$$

The vectors $\underline{l}_2$ and $\underline{l}'_{(g)}$ are connected in a similar manner: $\langle \underline{l}_2 \rangle \simeq C_2 \underline{l}'_{(g)}$ with

$$C_2 = \frac{1}{b^{*2} g} \sum_{m=1}^{g} C(m) \qquad (26)$$

Therefore, $\langle \underline{l}_1 \cdot \underline{l}_2 \rangle \simeq C_1 C_2 \langle \underline{l}_{(g)} \cdot \underline{l}'_{(g)} \rangle$. This equation defines the second contribution, $\langle \underline{l}_1 \cdot \underline{l}_2 \rangle = K_{b2}$, to the correlation function. Using also eqs 24 and 23 and the definitions of C_1 and C_2, eqs 25 and 26 with $g \gg 1$, we get

$$K_{b2}(r, s) \simeq J_{21} \frac{1}{s} \left(-b^{*2} + \frac{r^2}{s} \right) \qquad (27)$$

with

$$J_{21} = \frac{1}{4}\left(1 - (l/b^*)^4\right) \qquad (28)$$

The general eqs 27 and 28 are in agreement with the second eq 20 and eq B4 in the case of "soft melts" with weak bare excluded-volume interactions. This can be easily verified noting that in this case $l = b$ and b^*/b is close to 1, more precisely[17]

$$b^{*2} \simeq b^2 \left(1 + \frac{12 v_1 \xi}{\pi b^4} \right)$$

In a similar manner, one can find a generalization of the first eq 20:

$$K_{b1}(r, s) \simeq \frac{1 + (l/b^*)^4}{8 \pi c_1 s r} \left(1 + \frac{r}{R} \right) \exp(-r/R) \qquad (29)$$

where

$$R = b^* \sqrt{\overline{N}/6}$$

is the typical coil size.

The obtained results, eqs 29 and 27, are sufficient to get the distance-dependent correlation function $K_b(r) = 2Q(r)/G_{intra}(r)$ (see eqs 6, 7, and 9). In particular

$$Q(r) \simeq \int_0^\infty K(r, s) G(r, s) \mathrm{e}^{-s/\overline{N}} \, \mathrm{d}s$$

where $G(r,s)$ is approximately defined in eq 8. After some algebra we get

$$K_b(r) = K_{b1}(r) + K_{b2}(r) \simeq \frac{b^{*2} + l^4/b^{*2}}{24 \pi c_1 r^3} \left(1 + \frac{r}{R} \right)^2 \mathrm{e}^{-r/R} + \frac{1}{9} b^{*4} J_{21}/R^2 \qquad (30)$$

For $b^* \simeq l$, eq 30 is in agreement with the first-order perturbation result, eq B5 (see Appendix B), which essentially coincides with the correlation function $K = K_b(r)$ obtained in ref 1.

The two terms in the rhs of the above equation correspond to $K_{b1}(r,s)$ and $K_{b2}(r,s)$, respectively. It is interesting that while $K_{b2}(r,s)$ generally dominates over $K_{b1}(r,s)$, $|K_{b1}(r,s)/K_{b2}(r,s)| \sim \xi/r \ll 1$, this relationship does not hold for the integral functions $K_{b1}(r)$ and $K_{b2}(r)$: $K_{b2}(r) \gg K_{b1}(r)$ for $r \gtrsim R$, but $K_{b1}(r)$ dominates for small enough r. The $K_{b1}(r)$ contribution is important only for $r \ll R$; hence, it can be approximated as

$$K_{b1}(r) \simeq \frac{b^{*2} + l^4/b^{*2}}{24 \pi c_1 r^3}, \qquad r \ll R$$

(the factor $(1+r/R)^2 e^{-r/R}$ is omitted for simplicity). Hence

$$K_b(r) \simeq \frac{b^{*2} + l^4/b^{*2}}{24 \pi c_1 r^3} + \frac{2}{3} b^{*2} J_{21}/\overline{N} \qquad (31)$$

The two terms in the rhs of the above equation (referred to as K_{b1} and K_{b2}) are significantly different for $r \sim R$: $K_{b1} \sim 1/R^3$, while $K_{b2} \sim 1/R^2$. This difference is not surprising in view of the entirely different physical nature of these terms discussed above: the first term is due to the weak effective *long-range interactions* of the chain tails, while the second term comes from the *ideal-chain* correlation effect simply modulated by the *local* interactions between the bonds (the last point was made in ref 1).

For infinitely long chains, $\overline{N} \rightarrow \infty$, eq 30 simplifies as

$$K_b(r) \simeq \frac{b^{*2} + l^4/b^{*2}}{24 \pi c_1 r^3}$$

Thus, $K = K_b(r)$ shows nonlocal (long-range) bond−bond correlations.

3.3. The Correlation Function $K_c(r,s)$. Let us turn to the correlation function $Q = Q_c(r,s)$ (cf. Figure 2c). Its Fourier transform, $Q(k,s)$, does not vanish even for ideal chains. The dominant term in $Q(k,s)$ (corresponding to the zeroeth perturbation order) corresponds to the first diagram in Figure 8a:

$$Q(k, s) \simeq -4 a^4 k^2 G_s(k)$$

Hence

$$Q(r, s) \simeq 4 a^4 \nabla^2 G_s(r) = \frac{1}{s} \left(-b^2 + \frac{r^2}{s} \right) G_s(r) \qquad (32)$$

Here the functions $G_s(r)$ and $G_s(k)$ are defined in eqs D3 and A5, respectively. The corresponding bond-vector correlation function is (see eq D1)

$$K_c(r, s) \simeq \frac{1}{s} \left(-b^2 + \frac{r^2}{s} \right) \qquad (33)$$

The zero-order correlation function therefore changes its sign: K_c is negative for $r < R_s$ and positive for $r > R_s$, where $R_s = s^{1/2} b$ is the root-mean-square distance between two bonds connected by the s-segment. The physical meaning of this behavior is simple. For small r the s-segment is close to a cycle. Any pair of different bond vectors in an ideal cycle are anticorrelated since the sum of bond vectors is close to 0. On the other hand, for large r both bonds l_1 and l_2 are aligned along $\underline{r}$: $\langle \underline{l}_1 \rangle = \langle \underline{l}_2 \rangle = \underline{r}/s$ and $\langle \underline{l}_1 \cdot \underline{l}_2 \rangle \simeq \langle \underline{l}_1 \rangle \cdot \langle \underline{l}_2 \rangle \simeq r^2/s^2$ in accord with the second term in eq 33.

The ideal-chain correlations reflected in eqs 32 and 33 disappear after averaging over either r or s: $\int Q(r,s) \, \mathrm{d}^3 r = 0$ and $\int Q(r,s) \, \mathrm{d}s = 0$ for $r \neq 0$. The r-dependent bond-vector correlation function $K(r) = 2Q(r)/G_{intra}(r)$ is localized for a system of infinite chains since

$$Q(r) = \int Q(r, s) \, \mathrm{d}s \simeq 4 a^4 \nabla^2 G(r) \simeq -4 a^2 \delta(\underline{r}) \qquad (34)$$

(cf. eq D7). The first-order perturbation calculation of $K_c(r)$ is presented in Appendix C. The first-order result confirms the conclusion that $K_c(r)$ is localized for $\overline{N} = \infty$. For finite chains with Flory molecular-weight distribution the long-range part of $K_c(r)$ is dominated by the 0-th order term (see Appendix C for details):

$$K_c(r) \simeq Q(r)/G(r)$$

where

$$Q(r) = \int Q(r,s)\mathrm{e}^{-\mu s}\,\mathrm{d}s \simeq 4a^4\nabla^2 G(r)$$

(see eq 32) $\mu = 1/\overline{N}$ (see eq D9) and the ideal-chain Green function

$$G(r) = G^{(\mu)}(r) \equiv \int G_s(r)\mathrm{e}^{-\mu s}\,\mathrm{d}s \simeq \frac{1}{4\pi r a^2}\mathrm{e}^{-\sqrt{\mu}r/a} \qquad (35)$$

satisfies the equation

$$a^2\nabla^2 G - \mu G = -\delta(\underline{r})$$

Hence

$$K_c(r) \simeq 4\mu a^2 \simeq 4a^2/\overline{N}, \qquad r \gg \xi \qquad (36)$$

The bond-vector correlation function $K_c(r)$ for polydisperse chains is therefore constant at large distance r; K_c is positive and is inversely proportional to the mean chain length in this regime. Concurrently $K_c(r)$ is localized in the case of infinite chains.

The latter feature is characteristic also for $K_a(r)$, but it is in contrast with the behavior of the correlation function $K_b(r)$ which is nonlocal for $\overline{N} = \infty$. On the other hand, both the r-dependence and the order of magnitude of $K_c(r)$ and $K_a(r)$ are drastically different ($K_a(r) \propto 1/R^3 \propto 1/\overline{N}^{3/2}$ while $K_c(r) \propto 1/R^2 \propto 1/\overline{N}$ for $r \sim R$). The r-dependent bond−bond correlations therefore strongly depend on the definition of the bond-to-bond vector $\underline{r}$. The origin of the distinctions between K_a, K_b, and K_c is connected with the fact that although the differences between $\underline{r}_a$, $\underline{r}_b$, and $\underline{r}_c$ are small, these differences are correlated with the bond vectors $\underline{l}_1$, $\underline{l}_2$. These couplings together with correlations between $\underline{l}_1$, $\underline{l}_2$, and $\underline{r}$ generate significant new terms as the definition of r is changed.

4. The Invariant Single-Chain and Cross-Chain Bond Vector Correlation Functions K_{intra} and K_{inter}

The natural questions arising at this point are as follows: which definition of bond−bond distance should be used? Are the distance-dependent bond−bond correlation functions *actually* local or long-range?

There are reasons to favor the first definition, Figure 2a, as it leads to the simplest correlation function $K = K_a(r)$ which is local for $\overline{N} = \infty$. It is also convenient that $K_a(r,s)$ does not depend on s. It turns out, however, that these nice properties of $K_a(r)$, derived above using the first order perturbation theory, do not stand the higher-order corrections (see point 6 of the Discussion). One therefore has to look for more physical arguments as discussed below.

So far we considered orientational correlations for bonds of the *same* chain. What about correlations of bond vectors of different chains? At the first glance it may seem that such *interchain* bond−bond correlations are absent since any physical bond can be associated with two opposite bond vectors (backward and forward along the chain). This feature indeed ensures that $\langle \underline{l}_1 \cdot \underline{l}_2 \rangle$ vanishes on the *average* if l_1 and l_2 belong to different chains. However, the correlator does not vanish if the bond-to-bond vector $\underline{r}$ is fixed (see below).

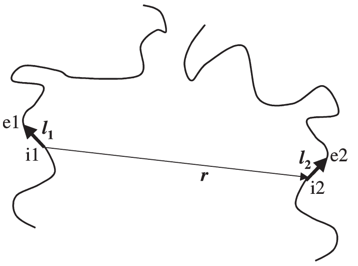

Figure 6. Two bonds l_1 and l_2 belonging to different chains. $\underline{l}_1 = \underline{r}_{e1} - \underline{r}_{i1}$, $\underline{l}_2 = \underline{r}_{e2} - \underline{r}_{i2}$. The bond−bond distance is $\underline{r} = \underline{r}_{i2} - \underline{r}_{i1}$.

The following natural definition of the interchain bond-vector correlation function $K_{inter}(r)$ is adopted: Consider two beads $i1$ and $i2$ of different chains located at $\underline{r}_{i1} = 0$ and $\underline{r}_{i2} = \underline{r}$. The bead $i1$ is bonded with two neighbors (unless it is positioned at the chain end; the end effects can be neglected since the chains are long). Let us choose randomly one of the neighbors, $e1$. In the same way we choose a neighbor $e2$ of the bead $i2$. The two bond vectors thus chosen are $\underline{l}_1 = \underline{r}_{e1} - \underline{r}_{i1}$ and $\underline{l}_2 = \underline{r}_{e2} - {}_{i2}$ (see Figure 2). The interchain bond-vector correlation function then is

$$K_{inter}(r) = \langle \underline{l}_1 \cdot \underline{l}_2 \rangle_r \qquad (37)$$

where the averaging is taken for a fixed $\underline{r} = \underline{r}_{i2} - \underline{r}_{i1}$.

It is worth noting that the correlation function $K_{inter}(r)$ defined above depends trivially on the definition of the bond−bond distance vector $\underline{r}$. In Figure 6 $\underline{r}$ is defined as the vector connecting the initial points of the bond vectors (the beads $i1$ and $i2$). Defining r as the vector connecting the terminal beads $e1$ and $e2$ leads to the same correlation function $K_{inter}(r)$; K_{inter} just changes sign if $\underline{r}$ is defined as $\underline{r} = \underline{r}_{e2} - \underline{r}_{i1}$ or $\underline{r} = \underline{r}_{e1} - \underline{r}_{i2}$.

4.1. The First-Order Approximations. The first-order perturbation calculation of K_{inter} is simple. In this approximation the correlation of $\underline{l}_1$ and $\underline{l}_2$ is due to the interaction of two tails adjacent to beads $e1$ and $e2$ (see Figure 6). Exactly the same interaction defines the single-chain correlation function $K_a(r)$: In the first-order approximation the interactions of the polymer s-segment connecting the bonds with the tails do not contribute to K_a. That is why it does not matter if the two bonds belong to the same chain or to different chains. Hence

$$K_{inter}(r) \simeq -K_a(r)$$

where the "−" sign comes from the trivial difference of the direction of the first bond (compare Figures 6 and 2a). Using eq 17 we get

$$K_{inter}(r) \simeq \frac{2}{c_1}\frac{a^2}{4\pi r R^2}\mathrm{e}^{-r/R}, \qquad r \gg \xi \qquad (38)$$

where $R = a\sqrt{N}$ and the strongly localized $\delta(\underline{r})$ term is omitted.

The above definition of the interchain bond−bond correlations is independent of the choice of local direction along the chain. As such, this definition can be applied also to the bonds of the same chain. The corresponding intrachain bond-vector correlation function, $K_{intra}(r)$, is invariant with respect to both a reversal of the local direction along the chain and a change of the definition of the bond-to-bond vector $\underline{r}$;. $K_{intra}(r)$ is obviously related to the correlation functions introduced before:

$$K_{intra}(r) = [2K_b(r) - K_a(r) - K_c(r)]/4 \tag{39}$$

The function $K_{intra}(r)$ is calculated in Appendix C in the first-order approximation. The result can be expressed in terms of the intrachain correlation function $G_{intra}(r)$, eq D5 (which is also calculated in Appendix C):

$$K_{intra}(r) \simeq -\frac{a^4\nabla^2 G_{intra}(r)}{G_{intra}(r)}, \quad r \gg \xi \tag{40}$$

where

$$G_{intra}(r) \simeq 2\left[G^*(r) - \frac{1}{2c_1}G^*(r)^2\right] \tag{41}$$

$$G^*(r) = \frac{1}{4\pi r a^{*2}} e^{-\sqrt{\mu^*}r/a^*} \tag{42}$$

G^* is the renormalized ideal-chain Green function, a^* is related to the effective statistical segment, $a^{*2} = b^{*2}/6$, and μ^* is the renormalized parameter of the molecular weight distribution (the mean polymerization degree $\overline{N} \simeq 1/\mu^*$).[18]

4.2. Generalizations. Equation 41 was derived in the first-order perturbation approximation valid for “soft melts” of Gaussian chains. It obviously agrees with the result for G_{intra}, eq 5, obtained using simple physical arguments. On the basis of these arguments it is possible to anticipate that the expression for G_{intra} in terms of the renormalized Green function G^* (see eq 41) is valid more generally: eq 41 is also valid for chains with some rigidity of the backbone, and in all perturbation orders provided that a and μ are properly renormalized and apart from small corrections to the last term in the rhs (for small ξ/r, ξ/R).

Turning to eq 40, it is important to clarify if it is applicable outside the soft-melt regime. To provide a tentative answer, let us try and find a simple way to derive a relationship between K_{intra} and G_{intra} avoiding lengthy calculations. Equation 39 can be rewritten as

$$K_{intra}(r) = Q_{intra}(r)/G_{intra}(r) \tag{43}$$

where

$$Q_{intra}(r) = \frac{1}{2}[2Q_b(r) - Q_a(r) - Q_c(r)] \tag{44}$$

The Fourier transform of $Q_{intra}(r)$ is

$$Q_{intra}(k) = \frac{1}{4\overline{N}}\left\langle \sum_{l_1, l_2} (e^{i\underline{k}\cdot\underline{r}_{e1}} - e^{i\underline{k}\cdot\underline{r}_{i1}})(e^{-i\underline{k}\cdot\underline{r}_{e2}} - e^{-i\underline{k}\cdot\underline{r}_{i2}})\,\underline{l}_1\cdot\underline{l}_2\right\rangle \tag{45}$$

where $\underline{l}_1 = \underline{r}_{e1} - \underline{r}_{i1}$, $\underline{l}_2 = \underline{r}_{e2} - \underline{r}_{i2}$, the summation is taken over all pairs of bonds l_1, l_2 of one chain, and the sum is averaged with respect to the chain conformations, and finally over all the chains. We are interested in the long-range behavior of Q_{intra} corresponding to the regime of small k. In this case the first factor in brackets can be approximated as

$$e^{i\underline{k}\cdot\underline{r}_{e1}} - e^{i\underline{k}\cdot\underline{r}_{i1}} \simeq \frac{1}{2}(e^{i\underline{k}\cdot\underline{r}_{e1}} + e^{i\underline{k}\cdot\underline{r}_{i1}})\,i\underline{k}\cdot\underline{l}_1 \tag{46}$$

Using a similar approximation for the factor in the second brackets in eq 45, and noting that

$$\langle l_{1\alpha} l_{2\alpha} l_{1\beta} l_{2\beta'}\rangle \simeq \langle l_{1\alpha} l_{1\beta}\rangle\langle l_{2\alpha} l_{2\beta'}\rangle \simeq \frac{1}{3}l^2\delta_{\alpha\beta}\frac{1}{3}l^2\delta_{\alpha\beta'} \tag{47}$$

where α, β, β' denote Cartesian components, we transform eq 45 as:

$$Q_{intra}(k) \simeq \frac{l^4}{36}\frac{1}{4\overline{N}}\left\langle k^2 \sum_{l_1, l_2}(e^{i\underline{k}\cdot\underline{r}_{e1}} + e^{i\underline{k}\cdot\underline{r}_{i1}}) (e^{-i\underline{k}\cdot\underline{r}_{e2}} + e^{-i\underline{k}\cdot\underline{r}_{i2}})\right\rangle \tag{48}$$

The Fourier image of $G_{intra}(r)$ is the single-chain formfactor which can be defined as

$$G_{intra}(k) = \frac{1}{\overline{N}}\left\langle \sum_{b1, b2} e^{i\underline{k}\cdot(\underline{r}_{b1} - \underline{r}_{b2})}\right\rangle$$

where the summation is taken over all pairs of beads ($b1$, $b2$) of the same chain. The sum, $\sum_{b1,b2}$, in the last equation equals to one-fourth of the sum, $\sum_{l_1,l_2}$, in eq 48 (end effects providing weak corrections of relative order $\sim 1/\overline{N}$ are neglected in this argument); hence

$$Q_{intra}(k) \simeq \frac{l^4}{36}k^2 G_{intra}(k)$$

In real space, the above relation converts to

$$Q_{intra}(r) \simeq -\frac{l^4}{36}\nabla^2 G_{intra}(r)$$

The latter result together with eq 43 leads to

$$K_{intra}(r) \simeq -\frac{l^4}{36}\frac{\nabla^2 G_{intra}(r)}{G_{intra}(r)}, \quad r \gg \xi \tag{49}$$

in agreement with eq 40 (since $a^2 \simeq l^2/6$ for “soft melts”). Thus, in the general case, the invariant intrachain bond-vector correlation function K_{intra} is defined in eq 49 with the intrachain correlation function $G_{intra}(r)$ defined in eqs 41, 42. For a system of infinite chains these equations give

$$K_{intra}(r) \simeq \frac{l^4}{24\pi b^{*2}}\frac{1}{c_1}\frac{1}{r^3}, \quad r \gg \xi \tag{50}$$

i.e., K_{intra} shows positive correlations decaying as $1/r^3$, the behavior similar to that of $K_b(r)$, although with a different prefactor. In view of the relation between K_{intra} and G_{intra}, the rhs of eq 50 can be traced back to the effective $1/r$ repulsion between two polymer tails generating the last term ($\propto 1/r^2$) in eq 5.

The general result for finite $\overline{N}$ reads (for $r \gg \xi$):

$$K_{intra}(r) \simeq \frac{l^4}{6b^{*2}}\left[-\frac{1}{\overline{N}} + \frac{1}{4\pi}\frac{1}{c_1 r^3}e^{-r/R}\left(1 + \frac{2r}{R} + \frac{3r^2}{2R^2}\right)\right] \tag{51}$$

where

$$R = b^*\sqrt{\overline{N}/6}$$

The first negative term here comes from the ideal (Gaussian) chain form factor, while the second positive term represents the genuine effect of interactions between polymer segments.

4.3. The Second-Order Approximation for K_{inter}. It is useful to define the *collective* bond-vector correlation function in analogy with eq 37

$$K_{coll}(r) \equiv \langle \underline{l}_1 \cdot \underline{l}_2\rangle_r$$

where the averaging is performed for *all* pairs of bonds whose initial points are separated by $\underline{r}$: l_1 and l_2 may belong to different chains or to the same chain. Obviously, K_{coll} is related to intra- and interchain correlation functions:

$$K_{coll}(r) = \frac{G_{intra}(r)}{G_{coll}(r)}K_{intra}(r) + \left[1 - \frac{G_{intra}(r)}{G_{coll}(r)}\right]K_{inter}(r) \qquad (52)$$

Here

$$G_{coll}(r) = \frac{1}{c_1}\langle c(0)c(\underline{r})\rangle$$

where $c(\underline{r})$ is the local concentration of beads at the point $\underline{r}$. Thus, $G_{coll}(r) = c_1 + \mathscr{G}(r)$, where $\mathscr{G}(r)$ is the correlation function of concentration fluctuations in the system. $G_{coll}(r)$ is very close to c_1 for large r since $\mathscr{G}(r)$ is small for $r \gg \xi$ (see below). The small correction ($\mathscr{G}(r) \ll c_1$ for $r \gg \xi$) is disregarded in what follows since the terms it generates in K_{coll} are totally negligible for $r \gg \xi$ (when compared with the first term in the rhs of eq 52). Hence, the approximation $G_{coll} \simeq c_1$ is adopted below.

The collective correlation function $K_{coll}(r)$ is related to fluctuations of the following vector order parameter field:

$$\eta_\alpha(r) = \frac{1}{2c_1}\sum_l [\delta(\underline{r} - \underline{r}_i) - \delta(\underline{r} - \underline{r}_e)]l_\alpha$$

where $\underline{l} = \underline{r}_e - \underline{r}_i$ is a bond vector ($\underline{r}_i$ and $\underline{r}_e$ are the positions of the initial and terminal points of a bond, respectively), α is a Cartesian component, and the sum is taken over all bonds (l) of all chains. Note that η_α is invariant with respect to the choice of a bond direction. Obviously $\langle\eta_\alpha(r)\rangle = 0$ due to the macroscopic isotropy of the system. The following relation comes directly from the definitions of K_{coll} and η_α:

$$K_{coll}(r)\frac{G_{coll}(r)}{c_1} = \langle\eta_\alpha(0)\eta_\alpha(r)\rangle \equiv \mathscr{Y}(r)$$

where the summation over α is assumed. Therefore

$$K_{coll}(r) \simeq \mathscr{Y}(r)$$

The correlation function $\mathscr{Y}(r)$ is essentially localized near $r = 0$; $\mathscr{Y}(r)$ is very small for large r (like the concentration correlation function $\mathscr{G}(r) = G_{coll}(r) - c_1$). In the mean-field approximation both correlation functions, $\mathscr{G}(r)$ and $\mathscr{Y}(r)$, decay exponentially at $r \gg \xi$ since neither $c(r)$ nor $\eta_\alpha(r)$ show any soft fluctuation modes. It was shown, however, that the very effective Hamiltonian H_{eff} of a concentrated polymer system is weakly nonlocal (H_{eff} is the free energy considered as a functional of the order parameters like $c(r)$ and $\eta_\alpha(r)$).[9,10] This property leads to a long-range power-law tail in the concentration correlation function: $\mathscr{G}(r) \propto 1/r^6$ for $R \gg r \gg \xi$.[9,10] This weak tail can be considered as a fluctuation effect of a special type which was analyzed using the perturbation approach;[10] it is related to the anti-Casimir repulsive interactions generated in a polymer matrix.[9] The bond orientation correlation function can be obtained using a similar approach; the fluctuation effects lead to a weak power-law tail: $\mathscr{Y}(r) \propto 1/r^8$ for $R \gg r \gg \xi$. It is interesting that this result can be easily confirmed using the approximate relation between $\eta_\alpha(r)$ and $c(r)$ considered below.

Indeed, using the approximations which are similar in spirit to eqs 46, 47, it is easy to show that

$$\eta_\alpha(r) \simeq \frac{l^2}{6c_1}\frac{\partial c(r)}{\partial r_\alpha}$$

Therefore

$$\langle\eta_\alpha(r)\eta_\alpha(r')\rangle \simeq \frac{1}{c_1^2}\left(\frac{l^2}{6}\right)^2 \frac{\partial}{\partial r_\alpha}\frac{\partial}{\partial r'_\alpha}\langle c(r)c(r')\rangle$$

leading to

$$\mathscr{Y}(r) \simeq -\frac{1}{{c_1}^2}\left(\frac{l^2}{6}\right)^2 \nabla^2\mathscr{G}(r)$$

The resultant collective bond orientation correlation function, $\mathscr{Y}(r) \propto 1/r^8$, can be neglected for $r \gg \xi$ as long as we are interested in the dominant terms in the interchain correlation function $K_{inter}(r)$. The latter approximation can be expressed simply as $\mathscr{Y}(r) \simeq 0$ for $r \gg \xi$. Then, using eqs 52, 50 we get for *infinite* chains and $r \gg \xi$:

$$K_{inter}(r) \simeq -\frac{G_{intra}(r)}{c_1}K_{intra}(r) \simeq -\frac{1}{8\pi^2}\frac{l^4}{b^{*4}c_1^2}\frac{1}{r^4} \qquad (53)$$

The more general result valid for polymers with Flory molecular weight distribution reads

$$\begin{aligned} K_{inter}(r) &\simeq \frac{l^4}{36}\frac{1}{c_1}\frac{\nabla^2 G_{intra}(r)}{1 - G_{intra}(r)/c_1} \\ &\simeq \frac{l^4}{36}\frac{2}{c_1}\left(1 - \frac{2G^*(r)}{c_1}\right)^{-1}\nabla^2\left(G^*(r) - \frac{1}{2c_1}G^*(r)^2\right) \\ &\simeq \frac{l^4}{2\pi c_1 b^{*4} r}\mathrm{e}^{-r/R}\left[\frac{1}{\overline{N}} - \frac{1}{4\pi}\frac{1}{c_1 r^3}\mathrm{e}^{-r/R}\left(1 + \frac{2r}{R}\right)\right] \end{aligned} \qquad (54)$$

The first term ($\propto 1/\overline{N}$) in the rhs of this equation agrees with eq 38 obtained above in a more direct way. Equation 38 is derived as a first-order approximation for a small effective interaction parameter, which is proportional to $1/c_1$; that is why the second term in square brackets in eq 54, which formally represents the *second*-order perturbation effect, is absent in eq 38.

For large $r \gtrsim R$ the second term in square brackets is negligible, so the function $K_{inter}(r)$ simplifies as

$$K_{inter} \propto \frac{1}{r\overline{N}}\mathrm{e}^{-r/R}, \quad r \gtrsim R$$

The correlation function K_{inter} therefore gets exponentially small beyond the coil size, for $r \gg R$.

5. Discussion and Conclusions

1. The distance-dependent correlations of bond orientations in concentrated polymer systems are considered in this paper. It is found that both intrachain and cross-chain orientational correlation functions, $K_{intra}(r)$ and $K_{inter}(r)$, are related to the single-chain bead−bead correlation function $G_{intra}(r)$. Thus, it appears that orientational correlations in polymer systems are essentially guided by the concentration fluctuations.

2. The intrachain correlation function $K_{intra}(r)$ is defined in eq 39. Its definition ensures a close relationship between the functions $K_{intra}(r)$ and $K_{inter}(r)$ (see section 4.1). The general result for $K_{intra}(r)$, eq 51, can be simplified as

$$K_{intra}(r) \simeq \frac{1}{6}\frac{l^4}{b^{*2}}\left[-\frac{1}{\overline{N}} + \frac{1}{4\pi c_1 r^3}\right] \qquad (55)$$

The second term in square brackets is approximately valid for $\xi \ll r \ll R$, where $R \sim b^*\sqrt{N}$ is the coil size (note that this term is

Figure 7. Two extremely distant bonds l_1, l_2 of the same chain are aligned antiparallel on the average.

anyway subdominant for $r \gtrsim R$). Thus, K_{intra} involves two main contributions:[19]

(i) The first term is negative and is proportional to $1/\overline{N}$. It is related to the *ideal-chain alignment* of the bonds by the chain tension. The same effect leads to a similar behavior of $K_c(r)$, see eq 36 (apart from a trivial difference in the sign). The physical origin of this effect is clarified in section 3.3. This ideal-chain elastic effect averages out for infinite chains (due to the compensation of the negative contribution coming from the stretched s-segments connecting the bonds and the positive contribution arising when the s-segment nearly forms a closed loop).

(ii) The second term is positive and is proportional to $1/r^3$. This term is due to the effective repulsion (nearly following the $1/r$ law) of the chain tails adjacent to the two bonds. Alternatively, the $1/r^3$ term can be interpreted in the framework of the general relationship between K_{intra} and G_{intra} (see eq 49): the $1/r^3$ term is generated by the interaction-induced correction (which scales as $-1/r^2$) in $G_{intra}(r)$. The correction can be traced back to the same physical effect: the effective $1/r$ repulsion of the chain tails (see section 2.1, eq 5).

For large distances, $r \gg R$, the function $K_{intra}(r) \simeq -l^4/(6\overline{N}b^{*2})$ is dominated by the first negative term. The physical meaning of this behavior can be clarified as follows: Typically, the distance between the bonds of the same chain is $r \lesssim R$. The fraction of more distant bonds with $r \gg R$ is exponentially small. Such distant bonds are mostly located at the opposite ends of untypically long chains with $N \gg \overline{N}$ (see Figure 7). Moreover, the chains have to stretch in order to span the long distance r. The probability of a stretched conformation for a given N is $p_1 \propto \exp(-3r^2/(2Nb^{*2}))$, while, by virtue of the Flory distribution, the probability of a large N is $p_2 \propto \exp(-N/\overline{N})$. Minimization of $p = p_1 p_2$ with respect to N gives: $N = r(6\overline{N})^{1/2}/(2b^*)$Thus, $N \propto r$, and the chain tension is independent of r; hence, the bonds l_1 and l_2 are oriented oppositely on the average: $\langle \underline{l}_1 \rangle = -\langle \underline{l}_2 \rangle = \underline{r}/N$ (see Figure 7; note that it is the K_c contribution in K_{intra} that dominates in this regime). Therefore

$$\langle l_1 \cdot l_2 \rangle \sim -\left(\frac{r}{N}\right)^2 \sim -\frac{b^{*2}}{\overline{N}}$$

in qualitative agreement with eq 51.

3. Both correlation functions $K_{intra}(r)$ and $K_{inter}(r)$, eq 54, change their sign in the region $r \gg R$: K_{inter} is positive and K_{intra} is negative for $r < r^*$, but $K_{inter} < 0$, $K_{intra} > 0$ for larger $r > r^*$, where

$$r^* \simeq \left(\frac{1}{4\pi}\frac{\overline{N}}{c_1}\right)^{1/3} \tag{56}$$

$r^* \ll R$ since $c_1 b^{*3} \gg \overline{N}^{-1/2}$.[20] The length r^* emerges as a result of a competition between the two main contributions in K_{inter} corresponding to the first-order and the second-order interaction effects. Turning to K_{intra}, it is possible to interpret the length r^* in a different way, in terms of the competition between the negative contribution to K_{intra} related to the Gaussian chain formfactor and the positive contribution due to the first-order monomer interaction effects. The two interpretations underpin the fact that the effective monomer interactions in polymer melts are intimately related to nearly Gaussian conformations of chains there.

From a more formal point of view r^* corresponds to the distance where the Laplacian of $G_{intra}(r)$ is zero. Another formal (almost mnemonic) rule relates r^* to the size of a globule formed by a single polymer chain in a poor solvent.

4. The bond vector correlations significantly depend on the definition of the bond−bond distance $\underline{r}$: The three definitions illustrated in Figure 2a,b,c yield three essentially different correlation functions $K_a(r)$, $K_b(r)$, and $K_c(r)$. The first-order "soft-melt" approximation yields (see eqs A3, 17, 31, and 36):

$$K_a(r) \simeq \frac{v_1}{\pi r}\mathrm{e}^{-r/\xi} - \frac{1}{2\pi c_1 \overline{N} r}\mathrm{e}^{-r/R}$$

$$K_b(r) \simeq \frac{b^2}{12\pi c_1 r^3} + \frac{2b^2 J_{21}}{3\overline{N}}, \quad K_c(r) \simeq \frac{2b^2}{3\overline{N}}, \quad r \gg \xi \tag{57}$$

where

$$\xi \simeq b/\sqrt{12 c_1 v_1}$$

$$R = b\sqrt{\overline{N}/6}$$

$$J_{21} \simeq \frac{3\sqrt{2}}{\pi}\frac{1}{b^3}\left(\frac{v_1}{c_1}\right)^{1/2}$$

$R \gg \xi$.[21] Therefore, $K_a(r)$ and $K_b(r)$ have opposite signs and $|K_a(r)| \ll K_b(r)$ for $r \gg \xi$. On the other hand, $K_c(r) \gg K_b(r)$ for $r \gg r^*$ since $J_{21} \ll 1$ in the "soft-melt" regime (r^* is defined in eq 56).

For length scales longer than ξ the function $K_a(r)$ can be simplified (see eq 17):

$$K_a(r) \simeq \frac{b^2}{3c_1}\delta(\underline{r}) - \frac{1}{2\pi c_1 \overline{N} r}\mathrm{e}^{-r/R}$$

This equation remains valid also for superbonds defined as groups of g original bonds. The grouping implying the following changes: $c_1 \to c_1/g$, $\overline{N} \to \overline{N}/g$, $a^2 \to g a^2$, $K \to g^2 K$, leaves the above equation invariant.

5. The correlation functions $K_i(r,s)$, $i = a, b, c$, which depend on both the real-space and curvilinear distances between the bonds, are calculated as well. It is shown that in the first-order "soft-melt" approximation the function $K_a(r,s) \simeq K_a(r)$ is independent of the curvilinear distance $\propto s$ (see eq A8). On the other hand, the other two functions $K_b(r,s)$ and $K_c(r,s)$ significantly depend on s (see eqs 20 and 33).

6. Let us turn to the effects of chain stiffness. Both orientational correlation terms discussed in the point 2 above are also involved in the correlation function $K_b(r)$ obtained in section 3.2, see eq 31. On the other hand, only the first term (const $\sim 1/\overline{N}$) enters $K_c(r)$ and neither term is involved in $K_a(r)$ (see sections 3.3 and 3.1). It is important, however, that these conclusions are based on the "soft-melt" approximations involving the first-order perturbation theory and the assumption that the chains are totally flexible (very weak interactions between neighboring units on the chains). The results are different in the case of polymer chains with some local stiffness. Such stiffness may be inherent in ideal polymer chains (for example, in chains with fixed bond angle), or it can be induced by effective interactions of monomer units (generally, the stiffness effects always arise in the higher-order perturbation theory). In any case the local stiffness implies that the genuine (effective) statistical segment b^* is larger than the bond length, $b^* > l$. It turns out that the local stiffness effectively transmits both correlation effects (yielding the two correlation terms, $\sim 1/\overline{N}$ and $\sim 1/r^3$) to all the correlation functions (K_i, $i = a,b,c$). Using an argument similar to that presented in section 3.2 (above eq 28), we find the following general long-range behavior of the functions K_i

$$K_i(r) \simeq \frac{b^{*2}}{6}\left[\frac{\kappa_{1i}}{4\pi c_1 r^3} + \frac{\kappa_{2i}}{\overline{N}}\right] \tag{58}$$

where

$$\kappa_{1a} = \kappa_{1c} = \kappa_{2b} = 1-\frac{l^4}{b^{*4}}, \quad \kappa_{1b} = 1+\frac{l^4}{b^{*4}},$$
$$\kappa_{2a} = \left(1-\frac{l^2}{b^{*2}}\right)^2, \quad \kappa_{2c} = \left(1+\frac{l^2}{b^{*2}}\right)^2 \tag{59}$$

Equations 55 and 58 are valid asymptotically for large $r \gg b^*$ and large $\overline{N} \gg 1$. On the other hand, their validity is not restricted by the first-order perturbation approximation: the effect of all perturbation orders is captured there (it is adsorbed in the effective statistical segment b^*; the bond-length l can be affected by the monomer interactions as well).

It is instructive to consider the following two limiting cases:

(i) Flexible chains, $b^* \simeq l$. This regime is accessible for any concentrated polymer system as long as correlations of superbonds are considered: it is always applicable to decimated chains of large enough superunits (g-blobs, with $g \gg 1$). The decimated chains are characterized by the rescaled parameters: c_1 must be replaced by $c_g = c_1/g$, l by the superbond size

$$l_{(g)} \sim l\sqrt{g}$$

and b^* by

$$b_g^* = b^*\sqrt{g}$$

It is obvious that the difference $b_g^{*\,2} - l_{(g)}{}^2 \sim g^2C(g)$, where $C(s)$ is defined in eq 13.

More precisely, using the relation,[8]

$$\frac{\partial^2}{\partial g^2}(b_g^{*2} - l_{(g)}^2) = -2C(g)$$

and eq 16 leads to

$$b_g^{*2}/l_{(g)}{}^2 - 1 \simeq \frac{2\sqrt{6}}{\pi^{3/2}}\,\frac{1}{g^{1/2}c_1b^{*3}} = \frac{2\sqrt{6}}{\pi^{3/2}}\,\frac{1}{c_gb_g^{*3}} \tag{60}$$

Therefore, indeed $b_g^* \simeq l_{(g)}$ since

$$c_gb_g^{*3} \sim \sqrt{g} \gg 1$$

Replacing $c_1, l, b^*, \overline{N}$ by $c_g, l_{(g)}, b_g^*, \overline{N}/g$ in eqs 58 and 59, and using eq 60, we get the correlation functions of the superbonds (for $r \gg b_g^*$):

$$K_a^{(g)}(r) \simeq \frac{b_g^{*2}}{6}\,\frac{1}{c_g^2b_g^{*6}}\left[\frac{\sqrt{6}}{\pi^{5/2}}\,\frac{b_g^{*3}}{r^3} + \frac{24}{\pi^3}\,\frac{g}{\overline{N}}\right] \tag{61}$$

$$K_b^{(g)}(r) \simeq \frac{b_g^{*2}}{6}\,\frac{1}{c_gb_g^{*3}}\left[\frac{b_g^{*3}}{2\pi r^3} + \frac{4\sqrt{6}}{\pi^{3/2}}\,\frac{g}{\overline{N}}\right] \tag{62}$$

$$K_c^{(g)}(r) \simeq \frac{b_g^{*2}}{6}\left[\frac{\sqrt{6}}{\pi^{5/2}}\,\frac{1}{c_g{}^2b_g^{*3}r^3} + \frac{4g}{\overline{N}}\right] \tag{63}$$

The correlation functions $K_i^{(g)}(r)$ can be compared with the analogous s-dependent correlation function $C^{(g)}(s)$ defined in eqs 14 and 15:

$$C^{(g)}(s) \sim \frac{b_g^{*2}}{c_g}\,\frac{1}{R_s^3}$$

where $R_s = s^{1/2}b^*$ is the typical size of an s-segment. Demanding $r \sim R_s$, we get the reference correlation function

$$C_{ref}(r) \equiv C^{(g)}(s) \sim \frac{b_g^{*2}}{c_g}r^{-3}$$

A comparison of the $1/\overline{N}$ terms in eqs 61, 62, and 63 with C_{ref} does not make much sense since their nature is entirely different: the $1/\overline{N}$ terms are related to the ideal-chain conformational statistics, while C_{ref} is due to interactions of monomer units. So, let us compare $K_i^{(g)}$ with C_{ref} for long chains, $\overline{N} \to \infty$. In this case

$$K_a^{(g)}(r)/C_{ref} \simeq K_c^{(g)}(r)/C_{ref} \sim \frac{1}{c_gb_g^{*3}} \ll 1$$

and $K_b^{(g)}(r)/C_{ref} \sim 1$ for $r \gg b_g^*$. Therefore, the functions $K_a(r)$ and $K_c(r)$ are quasi-localized in this regime (since they are small for large r compared with the reference level), while $K_b(r)$ is essentially nonlocal.

(ii) Stiff chains, $b^* \gg l$. All the constants κ_{ji} approach 1 in this case, so all the functions $K_i(r)$, $i = a,b,c$, show almost the same r-dependence for $r \gg \xi$

$$K_i(r) \simeq \frac{b^{*2}}{6}\left[\frac{1}{4\pi c_1r^3} + \frac{1}{\overline{N}}\right] \tag{64}$$

The important special case of a stiff polymer is a persistent chain whose local orientation is defined by the tangential unit vector $\underline{n}$. The r-dependent intrachain correlation function of tangential vectors in an isotropic system of persistent chains (in this case one could think of a concentrated solution rather than a melt) can be easily derived from eq 64:

$$\langle \underline{n}_1 \cdot \underline{n}_2 \rangle \simeq \frac{l_K}{6}\left[\frac{1}{4\pi c_Lr^3} + \frac{1}{\overline{L}}\right] \tag{65}$$

where $l_K \simeq 2\tilde{l}$ is the chain Kuhn segment ($\tilde{l}$, the persistence length), $\overline{L}$ is the mean chain contour length, and c_L, the average total contour length per unit volume.[22,23]

To resume, the qualitative distinctions between K_a, K_b, and K_c established in sections 3.1, 3.2, and 3.3 are valid for "soft melts" in the first-order perturbation approximation (i.e., when unperturbed chains are Gaussian, $\xi \gg l$ and, consequently, b^* is close to l). The effects of local chains stiffness (both ideal-chain and induced by local interactions) render these correlation functions less dissimilar,[24] although significant quantitative differences still remain in the general case (cf. eqs 58 and 59).

7. The cross-chain bond-vector correlation function $K_{inter}(r)$ in the case of *infinite chains* is defined in eq 53. $K_{inter} < 0$; hence, the bonds of different chains are anticorrelated. This effect compensates for the positive orientational correlations of bonds belonging to the same chain. The interchain correlation function decays as $1/r^4$ with the distance between the bonds. This correlation behavior is due to effective interactions between polymer chains. There are two ways to physically interpret it. The first approach is to employ the general relation between $K_{inter}(r)$ and $G_{intra}(r)$ derived in section 4.3, eq 54:

$$K_{inter}(r) \simeq \frac{l^4}{36c_1}\nabla^2G_{intra}(r), \quad r \gg \xi \tag{66}$$

(here we take into account that $G_{intra}(r)/c_1 \ll 1$ for $r \gg \xi$). In view of eq 66, the source of the $1/r^4$ interchain correlation term can be traced back to the interaction-induced contribution in the intrachain correlation function (the term proportional to $-1/r^2$ in eq 5).

The second interpretation of eq 53 is more direct. The physical origin of the interchain bond–bond correlation is the effective repulsion of the tails adjacent to the terminal points ($e1$ and $e2$) of the two bonds (see Figure 6). The repulsion drives the beads $e1$ and $e2$ away from each other. The effective force on the bead $e2$ is $f \simeq -\partial U(r)/\partial r$, where $U(r) \sim 1/(c_1 b^2 r)$ (see eq 4). The force f induces some alignment of the l_2-bond along $\underline{r}$: $\langle \underline{l}_2 \rangle \simeq (l^2/3) f \underline{r}/r$. The first bond is aligned in the opposite way by the force $-f$: $\langle \underline{l}_1 \rangle = -\langle \underline{l}_2 \rangle$. Then, assuming that fluctuations of l_1 and l_2 are independent, we get

$$K_{inter} = \langle \underline{l}_1 \cdot \underline{l}_2 \rangle \simeq \langle \underline{l}_1 \rangle \cdot \langle \underline{l}_2 \rangle \simeq -\frac{l^4}{9} f^2 \sim -\frac{l^4}{b^4} \frac{1}{c_1^2 r^4}$$

in agreement with eq 53. Both the negative sign and the $1/r^4$ power law are explained by this argument.

8. The correlation function K_{inter} also significantly depends on the chain stiffness: K_{inter} decreases for more rigid chains as $1/b^{*4}$. A more universal result emerges if we recall the idea of superunits (groups of g units) and consider correlations between superbonds. For $g \gg 1$ these correlations are weak at all length-scales, so the superbond length $l_{(g)}$ and the corresponding statistical segment b_g^* are nearly equal, $l_{(g)} \simeq b_g^*$, leading to the following correlation function of the superbonds

$$K_{inter}^{(g)}(r) \simeq -\frac{1}{8\pi^2} \frac{1}{c_g^2 r^4}$$

where $c_g = c_1/g$ is the mean concentration of superbonds. The generalization of this universal result (which is valid for $r \gg l_{(g)}$) to a d-dimensional system is simple:

$$K_{inter}^{(g)}(r) \simeq -\text{const}\ c_g{}^{-2} r^{2-2d}$$

The case $d = 2$ corresponds to a thin polymer layer; in this case $K_{inter} \propto r^{-2}$.

6. Summary

1. We reveal a *strong coupling* between correlations of *positions* and of *orientations* of the main-chain bonds in concentrated polymer systems. The expression of this coupling is 2-fold:

(i) On one hand, it is reflected in the strong sensitivity of the distance-dependent bond-vector correlation function $K(r) = \langle \underline{l}_1 \cdot \underline{l}_2 \rangle$ to the particular definition of the bond-to-bond distance vector $\underline{r}$ (see section 3).

(ii) On the other hand, it is reflected in the quantitative relationship (see eq 49) defining the invariant intrachain *orientational* correlation function $K_{intra}(r)$ in terms of the intrachain correlation function of monomer *positions*, $G_{intra}(r)$, related to the single-chain formfactor.

2. We show that correlations of bond orientations are generally long-range and are related to the *effective repulsion* between two polymer chains (tails): the range of this repulsion is comparable with the polymer coil size R (in the limit of infinite molecular weight the effective repulsion potential scales as $1/r$ with the distance r between the terminal points of the tails, see section 2.1, eq 4).

3. A quantitative relationship between the intrachain and interchain bond-vector correlation functions, $K_{intra}(r)$ and $K_{inter}(r)$, is derived and elucidated. The interchain correlations are negative (anticorrelation) and are long-range following a universal scaling law, $K_{inter} \propto 1/r^4$ (see eq 53), in the case of infinite chains. $K_{inter} \propto 1/r^2$ in the two-dimensional systems.

4. We found that orientational correlation functions show nontrivial and significant dependence on the local chain stiffness: while the direct correlation functions $K_a(r)$, $K_b(r)$, $K_c(r)$ increase with the chain rigidity, the invariantly defined correlation functions $K_{intra}(r)$ and $K_{inter}(r)$ gets weaker for more rigid chains (see eqs 50, 53, and 58).

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Appendix A: Perturbation Calculation of $K_a(r)$, $K_a(r,s)$

Let us consider the distance-dependent bond-vector correlation functions corresponding to the first definition of the bond–bond distance, $\underline{r} = \underline{r}_a$ (see Figure 2a). We start with the case of infinite chains. In view of eq 6, the first task is to calculate the intrachain correlation functions $G_{intra}(r)$ and $Q(r)$. The interaction potential $v(q)$, eq 3, is considered as the perturbation parameter. To get the first-order results for the bond-vector correlation functions it is sufficient to find $G_{intra}(r)$ in the 0-th order:

$$\frac{1}{2} G_{intra}(r) \simeq G(r) \equiv \int_0^\infty G_s(r)\, \mathrm{d}s = \frac{1}{4\pi r}$$

where $G_s(r)$ is defined in eq D3. Here and below we set the monomer length $a = 1$ (a is restored in the more final equations in the main text).

The 0-order contribution to $Q = Q_a$ is absent. The only relevant first-order term contributing to $Q(k) = \int Q(r) e^{-ik\cdot r} d^3 r$ is represented by the diagram of Figure 3 (we omit the subscript "a" here and below). Each thin solid line in the diagram represents $G(k_i)$, where k_i is the relevant wave-vector and

$$G(k) = \int G(r) \mathrm{e}^{-ik\cdot r}\, \mathrm{d}^3 r = \frac{1}{k^2} \qquad \text{(A1)}$$

The dashed line is associated with the factor $-v(q)$. Thick short lines represent the two bonds l_1 and l_2; they bring in the factor $\mathscr{L} = \underline{l}_1 \cdot \underline{l}_2$. The distribution density for, e.g., $\underline{l}_1$ is $G_1(\underline{l}_1)$ (see eq D3), so that $\partial G_1/\partial_1 = -0.5 \underline{l}_1 G_1$; hence, we can identify $\underline{l}_1$ with

$$-2 \frac{\partial}{\partial \underline{l}_1} = -2i\underline{k}_1$$

Therefore

$$\mathscr{L}(\underline{k}_1, \underline{k}_2) = -4 \underline{k}_1 \cdot \underline{k}_2$$

where $\underline{k}_1$ and $\underline{k}_2$ are the wave-vectors corresponding to the bonds l_1 and $\overline{l}_2$. (An analogous equation was used in ref 1) The diagram of Figure 3 therefore reads

$$Q(k) \simeq 4 \int_q q^2 G(q)^2 G(k-q) v(q) \qquad \text{(A2)}$$

where

$$\int_q \equiv \int \frac{\mathrm{d}^3 q}{(2\pi)^3}$$

Noting that the above integral is a convolution and rewriting eq A2 in real-space gives

$$Q(r) \simeq K(r) G(r)$$

where

$$K(r) \simeq 4 \int_q q^2 G(q)^2 v(q) \mathrm{e}^{i\underline{q}\cdot\underline{r}} = \frac{4 v_1}{4\pi r} \mathrm{e}^{-r/\xi} \qquad \text{(A3)}$$

where

$$\xi = a/\sqrt{2c_1 v_1}$$

is the mean-field correlation length. The correlation function is therefore localized, it vanishes exponentially at $r \gg \xi$. It can be represented as a δ-function for large length-scales ($\gg\xi$):

$$K(\underline{r}) \simeq \frac{2}{c_1}\delta(\underline{r}) \tag{A4}$$

Let us turn to the (r,s)-dependent correlation functions. To get $Q(k, s) = \int Q(r, s)\mathrm{e}^{-ik\cdot r}\,\mathrm{d}^3r$ it is sufficient to replace the $G(k - q)$ factor corresponding to the segment between the marked bonds by $G_s(k - q)$, where

$$G_s(k) = \int G_s(r)\mathrm{e}^{-i\underline{k}\cdot\underline{r}}\,\mathrm{d}^3r = \mathrm{e}^{-sk^2} \tag{A5}$$

Hence (cf. eq A2)

$$Q(k,s) \simeq 4\int_q q^2 G(q)^2 G_s(k-q)v(q) \tag{A6}$$

leading to

$$Q(r,s) \simeq K(r)G_s(r) \tag{A7}$$

and yielding the bond-vector correlation function (see eqs D1, D3)

$$K(r,s) \equiv \frac{Q(r,s)}{G(r,s)} \simeq \frac{Q(r,s)}{G_s(r)} \simeq K(r) \tag{A8}$$

The above equation is obviously in agreement with eq 11.

The results obtained above can be generalized to a polydisperse system of linear polymers with the Flory molecular-mass distribution: The number concentration n_N of chains with exactly N units is proportional to $\mathrm{e}^{-N/\overline{N}}$, where $\overline{N}$ is the mean number of units per chain. In this case the effective potential $v(q)$ and the function $G(q)$ in eq A6 must be defined as[13]

$$v(q) = \frac{v_1(\mu + q^2a^2)}{2c_1v_1 + \mu + q^2a^2} \tag{A9}$$

$$G(q) = G^{(\mu)}(q) \equiv \int G_s(q)\mathrm{e}^{-\mu s}\,\mathrm{d}s = \frac{1}{\mu + q^2a^2} \tag{A10}$$

where $\mu = 1/\overline{N}$. Note that

$$G(q)v(q) \simeq \frac{1}{2c_1} \tag{A11}$$

for small $q \ll 1/\xi$ (provided that $\overline{N}c_1v_1 \gg 1$). Equations A7 and A8 defining $Q(r, s)$ and $K(r, s)$ stay valid with

$$K(r) = 4\int_q q^2G(q)^2v(q)\mathrm{e}^{\mathrm{i}q\cdot r} \simeq \frac{2}{c_1}\left[\delta(\underline{r}) - \frac{1}{4\pi rR^2}\mathrm{e}^{-r/R}\right] \tag{A12}$$

where

$$R = a\sqrt{\overline{N}} = a/\sqrt{\mu}$$

Appendix B: First-Order Perturbative Calculation of $K_b(r)$, $K_b(r,s)$

Let us consider a system of polydisperse chains with exponential molecular weight distribution and the mean polymerization degree $\overline{N} = 1/\mu$. As before we adopt the "soft-melt" approximation (eqs A9). The length a is treated as the unit length in this section.

There are two first-order diagrams (involving one dashed line associated with the factor $-v(q)$) contributing to $Q_b(k) = Q_{b1}(k) + Q_{b2}(k)$ (see Figure 4). The first diagram reads

$$Q_{b1}(k) = -4\int_q (\underline{k} - \underline{\mathrm{q}})\cdot\underline{\mathrm{q}}G(q)^2v(q)G(k-q) \tag{B1}$$

where $G(q) = G^{(\mu)}(q)$ is defined in eq A10 and $v(q)$, eq A9. On using eq A11 the last equation gives Q_{b1} in real space:

$$Q_{b1}(r) \simeq \frac{2}{c_1}(\nabla G(r))^2 = \frac{2}{c_1}\left(\frac{1}{r} + \sqrt{\mu}\right)^2\frac{1}{(4\pi r)^2}\mathrm{e}^{-2r\sqrt{\mu}}, \quad r \gg \xi$$

where $G(r)$ is defined in eq 35.

The second diagram reads:

$$Q_{b2}(k) = -4G(k)\underline{k}\cdot\int_q \underline{\mathrm{q}}G(k-q)G(q)v(q) \tag{B2}$$

The $\int_q$ above is a regular function of k. The most interesting long-range regime corresponds to $r \gg \xi$ and $k \ll 1/\xi$. Hence it is sensible to expand $\int_q$ for small k. It is enough to keep the linear term only (higher-order terms can be neglected):

$$\int_q \underline{\mathrm{q}}G(k-q)G(q)v(q) \simeq J_{21}\underline{k} \tag{B3}$$

$$J_{21} = -\frac{1}{3}\int_q \underline{\mathrm{q}}\cdot\frac{\partial G(q)}{\partial\underline{\mathrm{q}}}G(q)v(q) \simeq \frac{\sqrt{2}}{12\pi}\left(\frac{v_1}{c_1}\right)^{1/2} - \frac{1}{8\pi}\frac{\sqrt{\mu}}{c_1} \tag{B4}$$

Note that the second term in the rhs is a small correction of the relative order

$$\propto \sqrt{\mu} \simeq 1/\sqrt{N}$$

Such corrections are omitted in section 3.2. Higher-order corrections $\propto \mu$ are omitted in eq B4. Hence

$$Q_{b2}(k) \simeq -4J_{21}k^2G(k)$$

and

$$Q_{b2}(r) \simeq 4J_{21}\nabla^2G(r) = 4J_{21}\mu G(r) = 4J_{21}\frac{\mu}{4\pi r}\mathrm{e}^{-\sqrt{\mu}r}$$

The bond-vector correlation function $K_b(r)$ is proportional to $Q_b(r) = Q_{b1}(r) + Q_{b2}(r)$:

$$K_b(r) \simeq \frac{Q_b(r)}{G(r)} \simeq \frac{2}{c_1}\left(\frac{1}{r} + \sqrt{\mu}\right)^2\frac{1}{4\pi r}\mathrm{e}^{-r\sqrt{\mu}} + 4J_{21}\mu \tag{B5}$$

This equation is in agreement with the results of ref 1.

Turning to the (r,s)-dependent correlation function $Q_b(r,s)$, it is useful to introduce its Fourier−Laplace transform

$$Q_b(k,\alpha) = \int_0^\infty Q_b(k,s)\mathrm{e}^{-\alpha s}\,\mathrm{d}s$$

The function $Q_b(k, \alpha)$ is defined by the same diagrams of Figure 4 with one amendment: each Green function G corresponding to the segment between the vertical arrows must be replaced by $G^{(\alpha)}$ (defined in eq A10 with μ replaced by α). Thus

$$Q_{b1}(k,\alpha) = -4\int_q (\underline{k}-\underline{q})\cdot\underline{q}\,G(q)^2 v(q) G^{(\alpha)}(k-q)$$

$$Q_{b2}(k,\alpha) = -4G^{(\alpha)}(k)\underline{k}\cdot\int_q \underline{q}\,G^{(\alpha)}(k-q)G(q)v(q)$$

where

$$G(q) = \frac{1}{\mu+q^2}, \quad G^{(\alpha)}(k) = \frac{1}{\alpha+k^2}$$

In real-space (r,s) variables these equations give for large s ($s \gg \xi^2/a^2$)

$$Q_{b1}(r,s) \simeq \frac{2}{c_1}\nabla G_s(r)\cdot\nabla G(r)$$

$$Q_{b2}(r,s) \simeq 4J_{21}\nabla^2 G_s(r)$$

where $G_s(r)$ is defined in eq D3 (the corrections to $Q_{b2}(r,s)$ of relative order

$$\frac{\xi}{r} \sim \frac{1}{\sqrt{s}}$$

are neglected here). Using the above equations we find the bond-vector correlation function $K_b(r, s) \simeq Q_b(r, s)/G_s(r) = Q_{b1}(r, s)/G_s(r) + Q_{b2}(r, s)/G_s(r)$ (see eq D1):

$$K_b(r,s) = K_{b1}(r,s) + K_{b2}(r,s)$$

$$K_{b1}(r,s) \simeq \frac{1}{c_1 s}(1+r\sqrt{\mu})\frac{1}{4\pi r}e^{-\sqrt{\mu}r} \tag{B6}$$

$$K_{b2}(r,s) \simeq 4J_{21}\frac{1}{2s}\left(-3+\frac{r^2}{2s}\right) \tag{B7}$$

where J_{21} is defined in eq B4 with $\mu = 0$ (corrections of the relative order ξ/r are omitted in eq B7). The first term $K_{b1}(r, s)$ corresponding to the first diagram in Figure 4 is generally subdominant since $r \gg \xi$.

Appendix C: The Correlation Functions $G_{intra}(r)$, $K_c(r)$, and $K_{intra}(r)$

The correlation function Q_c (in contrast to the functions Q_a and Q_b considered above) does not vanish in the zeroeth order, i.e., in the case of no interactions (see the first diagram in Figure 8a).[25]

There are three first-order diagrams contributing to Q_c (see Figure 8a). The analogous diagrams for the single-chain form-factor $G_{intra}(k)$ are shown in Figure 8b. An important point has to be invoked here: in the general case the perturbation series represented by the interaction diagrams define the quantities that are *proportional* to the correlation functions. In particular,

$$G_{intra}(k) = \frac{2}{A}\mathscr{D}_G$$

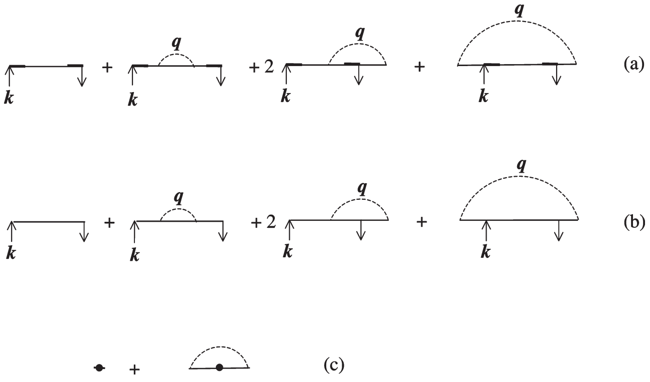

Figure 8. (a) Perturbation series $\mathscr{D}_Q$ (including the diagrams of the zeroeth and the first order) for the function $Q_c(k)$; (b) the analogous series $\mathscr{D}_G$ for the single-chain scattering function $G_{intra}(k)$; (c) the series $\mathscr{D}_c$ for monomer concentration. The factor 1 is associated with the bold dot.

and

$$Q(k) = \frac{1}{A}\mathscr{D}_Q$$

where $\mathscr{D}_G$, $\mathscr{D}_Q$ are the corresponding diagram series, and A is the relevant normalization factor. The same normalization factor must be applied to the concentration of bonds (beads), which is formally equal to $(c_1/A)\mathscr{D}_c$, where the diagrams $\mathscr{D}_c$ are shown in Figure 8c ($\mathscr{D}_c$ is proportional to the partition function of a polymer chain with an arbitrary chosen marked unit). Hence

$$A = \mathscr{D}_c$$

(The zeroeth order approximation $A \simeq 1$ was used so far.)

Let us start with the simplest series of Figure 8c. It reads

$$A \simeq 1 - J_{10}$$

$$J_{10} = \int_q G(q)^2 v(q) \sim \sqrt{\frac{v_1}{c_1}}$$

The single-chain formfactor is defined by the series of Figure 8b:

$$\frac{A}{2}G_{intra}(k) \simeq G(k) - G(k)^2 J_0(k) - 2G(k)J_1(k) - J_3(k) \tag{C1}$$

where the auxiliary functions $J_{0,1,3}(k)$ are

$$J_0(k) \equiv \int_q v(\underline{q})G(\underline{k}-\underline{q}) \simeq J_{00} + J_{01}k^2,$$

$$J_{00} = \int_q G(q)v(q),$$

$$J_{01} = \frac{-1}{6}\int_q \frac{\partial v(q)}{\partial \underline{q}}\cdot\frac{\partial G(q)}{\partial \underline{q}}$$

$$J_1(k) \equiv \int_q v(\underline{q})G(\underline{q})G(\underline{k}-\underline{q}) \simeq J_{10} + J_{11}k^2,$$

$$J_{11} = -\frac{1}{6}\int_q \frac{\partial[v(q)G(q)]}{\partial \underline{q}}\cdot\frac{\partial G(q)}{\partial \underline{q}} = -\frac{J_{01}}{2v_1 c_1}$$

$$J_3(k) \equiv \int_q v(\underline{q})G(\underline{q})^2 G(\underline{k}-\underline{q}) \simeq \frac{1}{2c_1}\int_q G(\underline{q})G(\underline{k}-\underline{q})$$

Using the equations above, we get, after simple transformations:

$$\frac{1}{2}G_{intra}(k) \simeq G^*(k) - \frac{1}{2c_1}\int_q G(\underline{q})G(\underline{k}-\underline{q}) + \text{const} \tag{C2}$$

Here

$$G^*(q) \simeq \frac{1}{k^2 a^{*2} + \mu^*}$$

is the renormalized Green function with

$$a^{*2} \simeq a^2(1 + J_{10} + J_{01} - 2J_{11}\mu), \quad \mu^* \simeq J_{00} + \mu(1 + J_{10}) - 2J_{11}\mu^2 \tag{C3}$$

The first of eqs C3 defines the renormalized (genuine) statistical segment

$$b^* = \sqrt{6}a^*$$

For $\mu = 0$, it agrees with the pioneering result of Edwards,[17] which was later confirmed by several authors.[26,13] The renormalized parameter μ^* defines the mean chain length, $\overline{N} \simeq 1/\mu^*$.

Transforming eq C2 in real space variables one gets the intrachain correlation function (the last constant term in this equation, which transforms into the $\delta(\underline{r})$-function, is omitted):

$$\frac{1}{2}G_{intra}(r) \simeq G^*(r) - \frac{1}{2c_1}G^{*2}(r), \quad r \gg \xi \tag{C4}$$

where $G^*(r)$ is the real-space image of $G^*(k)$:

$$G^*(r) = \frac{1}{4\pi r a^{*2}} e^{-\sqrt{\mu^*}r/a^*}$$

(based on physical grounds, see section 2.1, the bare Green function $G(r)$ in the second term in eq C4 is replaced by the renormalized function $G^*(r)$).

Let us turn to the orientational correlation function $Q_c(k)$. On the basis of the graphs shown in Figure 8a we write

$$AQ_c(k) \simeq -4k^2G(k) + 4k^2G(k)^2J_0(k) + \Delta_2(k) + \Delta_3(k) \tag{C5}$$

where

$$\begin{aligned}\Delta_2(k) &\equiv 8G(k)\int_q \underline{k}\cdot(\underline{k}-\underline{q})v(\underline{q})G(\underline{q})G(\underline{k}-\underline{q}) \\ &= 8k^2G(k)J_1(k) - 8G(k)J_2(k)\end{aligned} \tag{C6}$$

$$J_2(k) \equiv \int_q \underline{k}\cdot\underline{q}v(q)G(q)G(\underline{k}-\underline{q}) \simeq J_{21}k^2$$

(see eqs B3 and B4; note that $2J_{21} = J_{10} + J_{01}$) and

$$\begin{aligned}\Delta_3(k) &\equiv 4\int_q v(q)G(q)^2G(\underline{k}-\underline{q})(\underline{k}-\underline{q})^2 \\ &= \text{const} - 4\mu J_3(k)\end{aligned} \tag{C7}$$

After some algebra we get (omitting small $\mathcal{O}(\mu^2)$ corrections)

$$Q_c(k) \simeq 2\mu^* G_{intra}(k) + \text{const}$$

Hence $Q_c(r) \simeq 2\mu^* G_{intra}(r)$, $r \gg \xi$; the corresponding bond-vector correlation function is

$$K_c(r) = \frac{Q_c(r)}{0.5G_{intra}(r)} \simeq 4a^2\mu^* \simeq 4a^2/\overline{N}, \quad r \gg \xi$$

Let us now turn to the invariant intrachain bond-vector correlation functions $Q_{intra}(r)$ and $K_{intra}(r)$ defined in eqs 39, 43, and 44. In particular

$$Q_{intra}(k) = \frac{1}{2}(2Q_b(k) - Q_a(k) - Q_c(k))$$

Here $Q_a(k)$ is defined in eq A2 which, after a simple algebra, can be rewritten as

$$AQ_a(k) \simeq \text{const} - 4\mu J_3(k)$$

where const stands for the terms that are nearly constant for small $k \ll 1/\xi$. Using eqs B1 and B2, we obtain in a similar way

$$AQ_b(k) \simeq \text{const} - 2(k^2 + 2\mu)J_3(k) - 4G(k)J_2(k)$$

The function $Q_c(k)$ is defined in eqs C5, C6, and C7. On using the above equations and eq C1, we obtain

$$Q_{intra}(k) \simeq k^2 G_{intra}(k) + \text{const} \tag{C8}$$

Hence

$$Q_{intra}(r) \simeq -\nabla^2 G_{intra}(r), \quad r \gg \xi$$

(the localized contribution generated in real space by the const term in eq C8 is omitted). Finally we obtain the intrachain bond-vector correlation function:

$$K_{intra}(r) = Q_{intra}(r)/G_{intra}(r) \simeq -a^2\nabla^2 G_{intra}(r)/G_{intra}(r) \tag{C9}$$

Appendix D: Definitions of the Correlation Functions

a. Infinite Chains. Let $\rho(\underline{l}_1, \underline{l}_2, \underline{r}|s)$ be the distribution density of $\underline{l}_1$, $\underline{l}_2, \underline{r}$ for a given s (see Figure 2). The distance and arc-length dependent bond-vector orientational correlation function $K(r, s) = \langle \underline{l}_1 \cdot \underline{l}_2 \rangle_{r,s}$ can be expressed in terms of ρ as

$$K(r,s) = Q(r,s)/G(r,s) \tag{D1}$$

where

$$\begin{aligned}G(r,s) &= \int \rho(l_1, l_2, r|s)\, d^3l_1\, d^3l_2, \\ Q(r,s) &= \int l_1 \cdot l_2 \rho(l_1, l_2, r|s)\, d^3l_1\, d^3l_2\end{aligned} \tag{D2}$$

$G(r, s)$ is the single-chain bead concentration correlation function. For weak screened interactions $v(r) \ll 1$ (i.e., in the mean-field regime $\xi \gg b$) $G(r, s)$ is dominated by the ideal-chain Gaussian distribution:

$$G(r,s) \simeq G_s(r) \equiv (4\pi s a^2)^{-3/2} \exp\left(-\frac{r^2}{4sa^2}\right) \tag{D3}$$

where $G_s(r)$ is the ideal-chain Green function, $a^2 = b^2/6$ and b is the ideal-chain statistical segment related to the end-to-end distance r_s of an s-segment: the ideal-chain mean-square r_s is $\langle r_s^2\rangle_0 \simeq b^2 s$ for $s \gg 1$. In the general case of arbitrary screened interaction potential eq D3 stays valid for $s \gg 1$, $r \gg \xi$ provided that a is replace by a renormalized quantity $a^* = b^*/\sqrt{6}$, accounting for the local effect of monomer interactions. The renormalized statistical segment b^* defines the actual mean-square end-to-end distance of a long s-segment:

$$b^{*2} = \lim_{s \to \infty} \langle r_s^2 \rangle / s \tag{D4}$$

The overall intra-chain correlation function $G_{intra}(r)$ is defined as follows: Consider a randomly chosen bead located at the origin $r = 0$. Let us mark all the beads of the chain involving the chosen bead. Then $G_{intra}(r)$ is the mean concentration of marked beads. This function is obviously related to $G(r,s)$:

$$G_{intra}(r) = 2\int_0^\infty G(r,s)\,\mathrm{d}s \tag{D5}$$

where the factor 2 accounts for two equivalent chain-tails adjacent to an arbitrary bead. The overall distance-dependent bond-vector correlation function $K(r) = \langle \underline{l}_1 \cdot \underline{l}_2 \rangle_r$ is

$$K(r) = 2Q(r)/G_{intra}(r) \tag{D6}$$

$$Q(r) = \int_0^\infty Q(r,s)\,\mathrm{d}s \tag{D7}$$

Integrating $Q(r,s)$ over $\underline{r}$, we get the overall orientational correlation function of two bonds separated by the reduced arc-length s:

$$C(s) \equiv \langle \underline{l}_1 \cdot \underline{l}_2 \rangle_s = \int Q(r,s)\,\mathrm{d}^3 r \tag{D8}$$

b. Finite Polydisperse Chains. Equations D1, D2, D8, and D6 stay valid in the general case, for a system of polydisperse chains. In this case an averaging is performed over all pairs of bonds (l_1 and l_2) separated by the given reduced arc-length s. As for the functions $G_{intra}(r)$, $Q(r)$, one must take into account that the number of such pairs, $N(s)$, decreases with s. Hence eqs D5, D7 must be modified as

$$G_{intra}(r) = 2\int_0^\infty G(r,s)w(s)\,\mathrm{d}s,$$

$$Q(r) = \int_0^\infty Q(r,s)w(s)\,\mathrm{d}s \tag{D9}$$

where $w(s) = \mathcal{N}(s)/\mathcal{N}(0)$. $w(s) = \mathrm{e}^{-\mu s}$ in the case of Flory molecular weight distribution (cf. eq A10 and the paragraph above it). Hence, in the latter case

$$\frac{1}{2}G_{intra}(r) \simeq \frac{3}{2\pi b^{*2} r}\exp(-r/R), \qquad r \gg b^*$$

where

$$R \equiv b^* \sqrt{\overline{N}/6}$$

is the typical coil size.

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(14) The thermal energy $k_B T$ is considered as the energy unit here and below.
(15) A general equation equivalent to eq. 16 was proposed and used, but not derived, before (see refs 1 and 11 and references therein).
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(18) Note that it is the parameters a^* and μ^* that are measurable, while a and μ are the formal “bare” constants of the model; the relations between a^*, μ^* and a, μ for “soft melts” are defined in eq C3.
(19) Similar terms were originally identified in the correlation function $K_b(r)$.[1] There are, however, important differences (compare eqs 55 and 31): (i) the $1/\overline{N}$ term in K_b is positive, rather than negative; (ii) the prefactor in the $1/r^3$ term in K_b is larger (much larger in the case of stiff chains) than that for the analogous term in K_{intra}.
(20) Note that the length r^* is akin to, but is different from the length r_b^* introduced in ref 1. (r_b^* was denoted simply as r^* in this reference): r_b^* is the crossover length characterizing the behavior of the correlation function $K_b(r)$; r_b^* is *much larger* than r^* for the “soft melt” regime considered in ref 1 (see also the first equation, eq 57).
(21) Note that it is only the function $K = K_b(r)$ that was defined and calculated before in the “soft-melt” regime.[1] The first equation, eq 57, for K_b agrees with the previously obtained results.[1]
(22) An attempt to consider the finite persistence length effects was done in ref 1. The recipe given there is not entirely satisfactory; it leads to incorrect magnitudes of the main contributions in the correlation functions, both generally and in the limiting case of eq. 65.
(23) The prefactor l_K in eq. 65 does not mean that the correlation is strong for stiff chains. On the contrary, the necessary conditions $\overline{L} \gg l_K$ and $r \gg l_K$ ensure that $\langle \underline{n}_1 \cdot \underline{n}_2 \rangle$ is small.
(24) The local monomer interaction effects are extremely important in some polymer systems.[27]
(25) Note that here and below we consider the molecular weight distribution for a living polymer system characterized by the exponential dependence of the intrinsic (“bare”) statistical weight W_N on the number N of chain units: $W_N = \mathrm{e}^{-\mu N}$. The number concentration of chains $n_N \propto W_N$ and $\overline{N} = 1/\mu$ for an ideal living system. However, these relations are approximate for a real living polymer system due to interaction effects. In this case $n_N \propto \mathrm{e}^{-\mu^* N}$ and $\overline{N} \simeq 1/\mu^*$, where μ^* is the renormalized chemical potential of a unit (bead), see the second eq. C3. The distinction between μ and μ^* is not important for the orientational correlation functions K_a and K_b in the first-order perturbation approximation.
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