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Torsional fluctuations in columnar DNA assemblies

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Abstract

In columnar assemblies of helical bio-molecules the azimuthal degrees of freedom, i.e. rotations about the long axes of molecules, may be important in determining the structure of the assemblies, especially when the interaction energy between neighbouring molecules explicitly depends on their relative azimuthal orientations. For DNA this leads to a rich variety of mesophases for columnar assemblies, each categorized by a specific azimuthal ordering. In a preceding paper (Wynveen *et al* 2005 *Eur. Phys. J. E* **16** 303) a statistical mechanical theory was developed for the assemblies of torsionally rigid molecules in order to determine how thermal fluctuations influence the structure of these mesophases. Here we extend this theory by including torsional fluctuations of the molecules, where a DNA molecule may twist about its long axis at the cost of torsional elastic energy. Comparing this with the previous study, we find that inclusion of torsional fluctuations further increases the density at which the transition between the hexagonal structure and the predicted rhombic phase occurs and reduces the level of distortion in the rhombic phase. As x-ray diffraction may probe the 2D lattice structure of such assemblies and provide information concerning the underlying interaction between molecules, we have also calculated correlation functions for the azimuthal ordering which are manifest in x-ray scattering intensity profiles.

1. Introduction

Condensed DNA exists in a rich variety of phases and mesophases. Molecular assemblies of DNA are considered to be lyotropic, so much of this rich phase structure may be accessed by changing the concentration of DNA in solution. As the concentration of DNA molecules is increased, the orientations of the molecules evolve from a completely disordered isotropic phase into a liquid crystal phase. Eventually, at large enough densities, long range order is established, and a crystalline state is established [1]. In the liquid crystal phase, various mesophases are observed [2–5]. At relatively low concentrations the DNA molecules form a cholesteric mesophase, whereas at larger concentrations the molecules form columnar

assemblies. We should point out that not only is DNA concentration a parameter in determining what mesophase the DNA is in, but other factors such as monovalent salt concentration, as well as the type and quantity of condensing agent used, are equally important [6, 7]. Hence, any analytical study is necessarily quite involved due to the complexity of the system.

Many of these mesophases have been seen in biological systems [8]. Determining how these mesophases form is important for understanding how DNA packs into viral capsids and sperm heads [6] and may also be relevant in the advancement of gene therapies [9, 10]. The study of x-ray diffraction patterns of such mesophases, as well as an understanding of the statistical physics underlying DNA assemblies, could well elucidate the nature of the forces between such molecules [11]. Furthermore, understanding how properties of these mesophases might depend on the sequence of base pair text of the DNA that forms the mesophase may reveal information concerning the process of homologous recognition of genes [12].

Another question that might be probed in the study of DNA mesophases is whether the interaction between molecules depends on the azimuthal orientations of the DNA about their long axes. The polyelectrolyte model [13–15] assumes that the forces between molecules are independent of the azimuthal orientations of the molecules. This is only valid if the azimuthal dependence of the force is very weak or is completely screened by the solvent and its constituent ions. This model, however, is insufficient to describe the various mesophases. An alternative model [16] was proposed, which took into account the helical nature of the surface charge patterns on the DNA molecule. In this model the interaction energy of a pair of molecules depends strongly on the azimuthal orientation out to separations of $R > 30 \text{ \AA}$. This azimuthal dependence was further enhanced when counter-ions were assumed to be preferentially adsorbed within the grooves of the molecule¹. Such an azimuthal dependence was indeed shown to influence both the structures of columnar [18] and cholesteric assemblies [19].

In [18] it was shown that the variety of states observed in columnar assemblies are intrinsically linked with the azimuthal orientation of the molecules. These states corresponded to different ‘spin’ orderings, i.e. the configuration of the relative azimuthal orientations between neighbouring molecules, of the molecules situated on the two-dimensional lattice of a columnar assembly. For example, there exist ‘ferromagnetic’ and ‘antiferromagnetic’ states, i.e. states corresponding to where all the molecules are azimuthally aligned and to where molecules along a lattice direction have alternating values for their azimuthal orientations. In a later work [20], we extended this ground state calculation [18] to incorporate the effects of thermal fluctuations to build up a full statistical mechanical model of the columnar assemblies. Here, two new transitions were observed for a fixed hexagonal lattice. The first corresponded to a transition from one of two topologically distinct states of a three-spin configuration, where nearest neighbours of a molecule have one of two different azimuthal orientations (referred to as the Potts state), to a more disordered state where both topologies were equally likely in the system. The second was a transition to a Berezinskii–Kosterlitz–Thouless like vortex state². Here, also, it was shown that the antiferromagnetic state was only stable when the two-dimensional hexagonal lattice was distorted. Allowing for these lattice distortions, a phase transition occurring between this rhombic (distorted hexagonal) antiferromagnetic state and the ferromagnetic state is observed. As compared to the ground state calculations, incorporating thermal fluctuations resulted in a decrease in the mean separation between molecules at which this transition occurred, a reduction in the amount the distortion to the hexagonal lattice, and a shift from a second order transition to a first order one. In both of these studies [18, 20], however, the DNA molecules were assumed to be completely rigid.

¹ In [17], Mn^{2+} ions were found to bind to the major groove of the DNA molecule.

² For the range of parameters considered here, the Berezinskii–Kosterlitz–Thouless state would occur at extremely high temperatures.

Torsional flexibility has been considered in a ground state calculation of interacting non-homologous DNA [21] where the reduction of sequence-dependent distortions due to electrostatic interactions between the molecules is observed. This present study, however, considers the effects of thermal excitations of homologous flexible molecules so that torsional fluctuations, in which the azimuthal orientation of the double helix is no longer uniform along the length of the molecule, occur. Such effects may be implemented relatively easily into an energy functional, which forms a starting point for the statistical mechanical treatment. Previously, for rigid molecules, the effect of doubling the length had the same effect as halving the temperature. In flexible molecules, however, length is no longer such a trivial parameter in the theory. Here, shortening the molecules plays a similar role to increasing the torsional rigidity since the free energy cost of twisting a short molecule to the same degree, i.e. the same variation in the azimuthal angle between the ends of the molecule, as that of twisting a longer molecule is much greater. Hence, very short molecules may be assumed to be rigid. Furthermore, as a molecule is lengthened beyond a certain torsional persistence length, the extent of the torsional fluctuations becomes independent of the length of the molecule.

Though formulating the energy functional and partition function for columnar assemblies of flexible molecules is a relatively simple task, calculating the free energy and other thermodynamic quantities is not. Due to the extra degrees of freedom associated with torsional fluctuations, Monte Carlo methods become less reliable and more time consuming. Utilizing self-consistent approximations developed through field theoretical methods, however, we encounter a problem arising from treating molecules of finite length: how to account for the freely fluctuating ends of the molecules in the assembly. Nevertheless, we have managed to incorporate free end effects into the field theoretical calculations and have determined the extent to which they alter the results.

The layout of the paper is as follows. In section 2 we consider the case of finite temperature interactions between two molecules in parallel juxtaposition as a starting point for developing the present calculations since the reliability of these calculations may be tested against the ‘quantum mechanical’ formulation of DNA interactions set out in [22]. In section 3 we summarize the results of the various ground state calculations of the system and then incorporate thermal fluctuations at the harmonic level (Gaussian fluctuations) for the different configurations of the columnar assembly. Here, we determine the free energy of the assembly as well as the correlation function corresponding to the variation of relative azimuthal fluctuations between molecules, which is important in determining the x-ray diffraction patterns of the assemblies [11]. In section 4 we go beyond the harmonic treatment of the interaction, developing a self-consistent approximation for the assembly. This relies on a Hartree approximation for the case where the ends satisfy periodic boundary conditions, i.e. both ends of a molecule have the same azimuthal orientation, and a correction which takes into account independent fluctuations at the ends of each molecule. At this level of the calculation, we demonstrate how torsional fluctuations affect the free energy and correlation functions of the assemblies and compare these results to those of assemblies composed of rigid molecules [20]. We find that the correction accounting for independent fluctuations of the ends of the molecules is quite small, and so in a first approximation may be neglected, demonstrating that the utilization of periodic boundary conditions in the calculation is a reasonable approximation. Finally, in section 5, we discuss our results and possible future developments.

2. How to treat molecules of finite length: the two-body problem

Our primary aim is to develop a field theoretical framework in which to treat the statistical mechanics of flexible molecules condensed in columnar assemblies. As mentioned in the

introduction, we first encounter the problem of how to treat molecules of finite length. If we assume that periodic boundary conditions can be applied to the ends of the molecules, however, we may take advantage of field theoretical techniques that already have been developed³. By assuming periodic boundary conditions we presuppose that both ends of a DNA molecule fluctuate torsionally in phase. In other words, both ends share the same azimuthal orientation, which is not necessarily the case. And so within our statistical mechanical treatment, we also take into account freely fluctuating ends of the molecules.

Before turning our attention to an assembly, we begin by first considering two molecules in parallel. One of the main motivations for doing this is that for the pair interaction, an alternative approach for formulating the statistical mechanics of interactions between flexible molecules, which resembles that of a quantum mechanical problem, may be employed [22]. This, then, provides a check on the reliability of the formulation with which we use to treat the assemblies.

The pair potential is a function of the interaxial separation R and the relative azimuthal angle ϕ between molecules. The relative azimuthal angle is defined as the difference in the azimuthal angles between the two molecules, $\phi = \phi_1 - \phi_2$, where ϕ_i is the angle that a vector, from the centre of the i th molecule to the middle of its minor groove, makes with an axis that lies perpendicular to the long axes of the molecules. This axis is chosen to pass through the centres of both molecules. The pair potential energy per unit length has the form

$$E_{\text{int}}(R, \phi) = \sum_{n=0}^{\infty} (-1)^n a_n(R) \cos(n\phi). \quad (2.1)$$

Equation (2.1) is completely model independent and can be deduced purely from symmetry requirements. The first requirement is that rotation of one of the molecules one whole revolution about its long axis should leave the interaction energy unchanged. Hence we may express E_{int} as a Fourier expansion in terms of the relative azimuthal angle. Secondly, for DNA molecules, helical symmetry dictates that $E_{\text{int}}(R, \phi) = E_{\text{int}}(R, -\phi)$, so only cosine terms in the Fourier series are retained. Finally, provided that $L \gg H$, where H is the helical pitch of the DNA molecule, helical symmetry also ensures that the interaction energy per unit length does not depend on z , where z is the coordinate that runs along the long axis of the molecule.

Before proceeding further, we need to consider the behaviour of the a_n coefficients. We shall use forms for these coefficients obtained within the Kornyshev–Leikin (KL) theory [16] of the electrostatic interactions between helical macromolecules. Such a treatment, grounded in Debye–Huckel theory, neglects important non-local effects [24–26] of the dielectric response of explicit water. However, such a theory can still provide a qualitative picture into the behaviour of our system. Furthermore, this theory should work quite well at sufficiently large separations between molecules and for dilute salt concentrations where Debye–Huckel theory is valid. Explicit forms for the a_n coefficients obtained in such a theory are given in [22]. In the theory, all of the a_n coefficients decay exponentially with large interaxial separations with higher order terms (larger n) decaying at a greater rate. (The inverse decay length κ_n for each these terms is given by $\kappa_n = \sqrt{n^2 g^2 + \kappa_s^2}$ where $g = 2\pi/H$ and κ_s is the inverse Debye screening length calculated in Donnan equilibrium [18, 20, 27].) Because of this, it is sufficient to truncate the series given in equation (2.1) at $n = 2$ [16]. The zeroth-order term a_0 , which describes the interaction between two cylinders with a uniform charge distribution, does not depend on ϕ and therefore need not be considered in the treatment of torsional fluctuations. However, it does play an important role in the positional structure of the assembly. Finally, since a_2 decays

³ Periodic boundary conditions are used regularly in finite-temperature field theory, namely by the Matsubara formalism. To see how such boundary conditions are applied in this context the reader may consult [23] or any other book dealing with finite-temperature field theory or finite size effects.

faster than a_1 , minimizing the interaction energy with respect to ϕ leads to a configuration below a critical value R_* of the interaxial spacing where the preferred value of ϕ is non-zero, whereas above R_* it is zero. Even when including non-local effects, these qualitative features should still be manifest in the interactions.

Upon including thermal fluctuations of the relative twisting of one DNA molecule with respect to another, ϕ now must be assigned a z -dependence. Following from previous work [22], we write down the partition function as a functional or path integral

$$\int \mathcal{D}\phi(z) \exp\left(-\frac{1}{k_B T} \int_{-L/2}^{L/2} dz \left[\frac{C}{4} \left(\frac{d\phi}{dz}\right)^2 - a_1 \cos(\phi) + a_2 \cos(2\phi) \right]\right), \quad (2.2)$$

where C is defined as the torsional elasticity modulus of the helices. Here, we have assumed that the centres of both molecules are at $z = 0$ and each molecule has length L . The free energy then can be found upon calculating the partition function.

As was discussed previously in [22], with this partition function the problem can be recast in an alternative formulation that mirrors a quantum mechanical problem. Here, we solve the Schrödinger equation

$$-\frac{1}{2} \frac{d^2 \psi_E(\phi)}{d\phi^2} + V(\phi) \psi_E(\phi) = E \psi_E(\phi), \quad (2.3)$$

where

$$V(\phi) = -\frac{\lambda_p^2}{\lambda_0^2} \cos(\phi) + \frac{a_2 \lambda_p^2}{a_1 \lambda_0^2} \cos(2\phi), \quad (2.4)$$

$\lambda_0^2 = C/(2a_1)$ and $\lambda_p = C/(2k_B T)$. In this formulation, the free energy is expressed through the solutions of equation (2.3) as

$$F = -k_B T \ln \sum_E \psi_E^*(\phi_+) \exp\left(-\frac{EL}{\lambda_p}\right) \psi_E(\phi_-) - k_B T \ln \Theta, \quad (2.5)$$

where Θ is a constant which can be neglected when comparing free energies of different states. ϕ_+ and ϕ_- are the values of ϕ at the ends, $z = L/2$ and $z = -L/2$ respectively, of the molecules. Periodic boundary conditions amount to setting $\phi_+ = \phi_-$, and computing the free energy entails summing over ϕ_+ . However, as was pointed out before, both ends should be left to fluctuate freely. Consequently, we should integrate over both ϕ_- and ϕ_+ , allowing ϕ_- to take on any value between 0 and 2π and ϕ_+ to take on any value whatsoever. When the fluctuations are small we may expand $V(\phi)$ to quadratic order in ϕ around its preferred value in the ground state. We shall only consider the case when the preferred value is zero (large interaxial spacings), although this calculation may be easily extended to a non-zero preferred angle. Equation (2.3) may be solved analytically to determine the free energy. Some of the details of the calculation of F are given in appendix A. Here, we shall quote the end result for long molecules

$$F \simeq -k_B T \Theta' + E_0 + \frac{CL}{4\lambda\lambda_p} + \frac{k_B T}{2} \ln\left(\frac{\lambda_p}{\lambda}\right) - \frac{k_B T}{2} \exp\left(-\frac{2L}{\lambda}\right), \quad (2.6)$$

where $E_0 = -a_1 + a_2$ and $\lambda^2 = C/(2(a_1 - 4a_2))$. The last two terms are leading order corrections due to the finite length of the molecules.

Returning to equation (2.2), we now approach the problem directly through path integration, first in the Gaussian or harmonic approximation. In such an approximation, both cosine terms are expanded out to quadratic order in ϕ around the preferred orientation. This

is equivalent to expanding $V(\phi)$ to quadratic order in ϕ in the previous formulation. We have demonstrated this equivalence in [22]. In this approximation the partition function becomes

$$Z = \exp\left(-\frac{E_0}{k_B T}\right) \int \mathcal{D}\phi \exp\left(-\frac{1}{k_B T} \int_{-L/2}^{L/2} dz \left[\frac{C}{4} \left(\frac{d\phi}{dz}\right)^2 + \frac{m}{2} \phi^2 \right]\right), \quad (2.7)$$

where $m = a_1 - 4a_2$. We shall consider the following ansatz for the form of $\phi(z)$:

$$\phi(z) = \phi_p(z) + \frac{\gamma z}{L} + \phi_0, \quad (2.8)$$

where $\phi_p(z)$ is the component of $\phi(z)$ that satisfies periodic boundary conditions, i.e. $\phi_p(-L/2) = \phi_p(L/2)$, and it has a spatial average of zero along the length of the molecules.

Having a period of L , $\phi_p(z)$ may be expressed as

$$\phi_p(z) = \frac{1}{\sqrt{L}} \sum_{n \neq 0} b_n \exp\left(\frac{2\pi i n z}{L}\right). \quad (2.9)$$

The ϕ_0 component of $\phi(z)$ is used for the calculation of rigid body fluctuations of the average relative azimuthal orientation between the two molecules and so does not depend on z . The component of $\phi(z)$ proportional to γ is included in order to account for free fluctuations of the ends by allowing γ to vary, where γ is the difference in the azimuthal angles between the ends of the molecules. We may recast equation (2.7) in the following way, using equations (2.8) and (2.9):

$$\begin{aligned} Z = & \exp\left(-\frac{E_0}{k_B T}\right) \int d\phi_0 \int d\gamma \prod_{n \neq 0} \int db_n \\ & \times \exp\left(-\frac{1}{k_B T} \sum_{n \neq 0} \left[\frac{1}{2G_n} b_n b_{-n} + \frac{\gamma m}{2} J_n b_{-n} + \frac{\gamma m}{2} J_{-n} b_n \right] \right. \\ & \left. - \frac{1}{k_B T} \left[\frac{C}{4L} + \frac{Lm}{24} \right] \gamma^2 + \frac{m}{2k_B T} \phi_0^2 \right), \end{aligned} \quad (2.10)$$

where $G_n = (\frac{C}{2} (\frac{2\pi n}{L})^2 + m)^{-1}$ and $J_n = \frac{1}{\sqrt{L}} \int_{-L/2}^{L/2} dz (\frac{z}{L}) \exp(-\frac{2\pi i n z}{L}) = \frac{i(-1)^n (1 - \delta_{n,0})}{(2\pi n)}$.

The crucial step is to make the variable shift $b_n \rightarrow b_n - m\gamma J_n G_n$ to decouple b_n from γ . In the domain $-L/2 \leq z < L/2$, $\frac{\gamma z}{L}$ may be written as a Fourier series and the effect of the variable shift is to adsorb this into $\phi_p(z)$. At $z = L/2$, however, $\frac{\gamma z}{L}$ cannot be expressed as a Fourier series. At this point there is a difference of γ in the sum of the Fourier series representing $\frac{\gamma z}{L}$ and the actual value of $\frac{\gamma z}{L}$. The torsional energy term, however, contains derivatives of ϕ which are sensitive to this difference. Therefore, when we make this shift we find that the integrand in our partition function still depends on γ . Thus this leads to a difference in the partition function for free boundary conditions as opposed to that assuming periodic boundary conditions⁴.

The partition function thus becomes

$$Z = Z_0 Z_f Z_p \exp\left(-\frac{E_0}{k_B T}\right), \quad (2.11)$$

where $Z_0 = \int_{-\infty}^{\infty} d\phi_0 \exp(-\frac{m}{2k_B T} \phi_0^2)$ corresponds to the component of the partition function that depends only on the average azimuthal orientation of the molecules, $Z_f = \int_{-\infty}^{\infty} d\gamma \exp(-\frac{\gamma^2 \lambda_p}{4\lambda} \coth(\frac{L}{2\lambda}))$ is the part of the partition function that takes into account the

⁴ Note that equation (2.8) is not a unique way of ensuring that $\phi(-L/2) + \gamma = \phi(L/2)$. We could have chosen a different ansatz. Nevertheless, the end result is ansatz independent. Any ansatz that satisfies this criterion will yield the same form for the partition function as long as the correct variable shift to decouple b_n from γ is chosen.

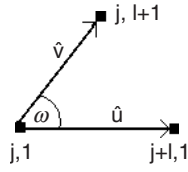


Figure 1. Lattice labelling and relative positions of the lattice vectors \hat{u} and \hat{v} .

free rotations of the ends of the molecules, and $Z_p = \prod_{n \neq 0} \int_{-\infty}^{\infty} db_n \exp(-\frac{1}{2k_B T} \sum_{n \neq 0} \frac{b_n b_{-n}}{G_n})$ is the component that takes into account all z -dependent azimuthal angle orientations in the case where the ends of the molecules share the same orientation.

From equation (2.11) we may compute the free energy (appendix B). We find that

$$F \simeq -k_B T \Theta' + E_0 + \frac{CL}{4\lambda\lambda_p} + \frac{k_B T}{2} \ln\left(\frac{\lambda_p}{\lambda}\right) + \frac{k_B T}{2} \ln\left(1 - \exp\left(-\frac{2L}{\lambda}\right)\right). \quad (2.12)$$

Expanding the log of the last term when L is large, we retrieve equation (2.6), and so we find that this formulation is consistent with the exact one of [22]. We therefore are ready to tackle the many body problem of assemblies.

3. Assemblies of molecules of finite length: the Gaussian approximation

For an assembly, the energy can be written as a sum of the energies of each molecular pair over the entire lattice that defines the assembly as

$$E[\phi] = \int_{-L/2}^{L/2} dz \sum_{j,l} \left[\frac{C}{2} \left(\frac{d\phi_{jl}(z)}{dz} \right)^2 + \sum_{n=0} (-1)^n a_n (R_2) \cos(n(\phi_{jl}(z) - \phi_{j+1l-1}(z))) \right. \\ \left. + (-1)^n a_n (R_1) (\cos(n(\phi_{jl}(z) - \phi_{j-1l}(z))) + \cos(n(\phi_{jl}(z) - \phi_{j,l-1}(z)))) \right]. \quad (3.1)$$

Here, we have introduced two lattice vectors $\vec{u}_i = jR_1\hat{u}$ and $\vec{v}_j = lR_1\hat{v}$, where \hat{u} and \hat{v} are unit vectors that describe the relative positions between molecules situated at the sites of the two dimensional lattice. These two vectors, as well as the convention used in labelling the lattice sites, are shown in figure 1.

In equation (3.1) we have included only the interactions between nearest neighbours and have assumed that all the DNA molecules are of the same length with the centre of each molecule lying at $z = 0$.⁵ Again we may truncate the series at $n = 2$. In calculating the energy of the lattice, we have allowed for two separations, R_1 and R_2 , of the six nearest neighbours of a given molecule, since there may be distortions from the hexagonal lattice [18, 20]. For this distorted or ‘rhombic’ lattice, R_1 corresponds to the distance to the neighbouring molecule at an adjacent corner of the unit cell while R_2 is the distance across the short diagonal of the rhombic cell. We may define a distortion angle ω (shown in figure 1) that characterizes the relationship between the two separations in equation (3.1), $R_2 = R_1\sqrt{2 - 2\cos\omega}$. In the ground state, the amount of distortion is determined by minimization of $E[\phi]$ with respect to the distortion angle ω . The relative strengths of the a coefficients determine the degree of this

⁵ Since our primary concern is to study the effects of azimuthal fluctuations of the molecules, we do not consider their spatial fluctuations about the lattice points. Though coupling between azimuthal fluctuations and spatial fluctuations does occur, this can be neglected within the first approximation.

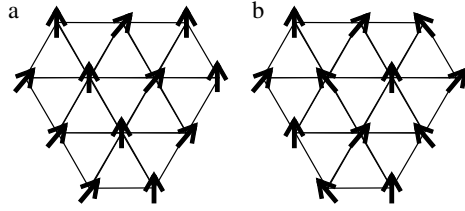


Figure 2. Schematic pictures of the azimuthal orientations of molecules in two of the ground state configurations. The first (a) corresponds to the antiferromagnetic state where the molecules adopt layers in which the molecules are in the same azimuthal alignment. The second (b) corresponds to the Potts state, where the azimuthal orientations of the molecules have one of three values as defined in the text.

distortion, e.g. the a_0 term, which contributes a repulsive component to the overall force, has the effect of reducing the amount of rhombic distortion as on its own it favours a hexagonal state. For certain azimuthal configurations of the molecules at large densities, the distortion angle ω is greater than 60° .

Before considering effects of thermal fluctuations, let us first describe the various ground states that the assembly has. When molecular separations are large, all the relative azimuthal orientations of the molecules are the same. This state may be referred to as the ‘ferromagnetic’ state. For this state the lattice is hexagonal, $R_1 = R_2$. Below a critical value of the separation of nearest neighbours, R_*^1 , the assembly adopts a new state where four of the six nearest neighbours about a specific molecule adopt a different azimuthal orientation to that molecule, as shown in figure 2. This state then may be termed the ‘antiferromagnetic’ state. This configuration of the azimuthal orientations of the molecules favours rhombic distortions, $R_1 \neq R_2$, described in the previous paragraph. The ground state azimuthal configuration for this configuration is characterized by the following equations:

$$(\phi_{jl}(z) - \phi_{j+1l-1}(z)) = 0 \quad (\text{across the short diagonal of the rhombic unit cell}) \quad (3.2a)$$

$$(\phi_{jl}(z) - \phi_{j-1l}(z)) = (\phi_{jl}(z) - \phi_{j1-1}(z)) = \psi \quad (\text{adjacent corners of the unit cell}) \quad (3.2b)$$

where $\cos(\psi) = \frac{a_1(R_1)}{4a_2(R_1)}$. For even denser assemblies, a new critical value of average separation R_*^2 is realized where the most energetically favourable state is the ‘Potts’ state. In this state, the lattice returns to a hexagonal confirmation. As shown in figure 2, the azimuthal orientations of the molecules for this state may have one of three different values: ϕ_0 , $\phi_0 + \psi_p$, and $\phi_0 + 2\psi_p$ where

$$\cos(\psi_p) = \frac{1}{4} \left(1 + \sqrt{1 + \frac{2a_1}{a_2}} \right). \quad (3.3)$$

Upon introducing thermal fluctuations, we shall only consider the ferromagnetic and antiferromagnetic states. (For a discussion of the Potts state, which, again, only occurs at very large densities, at finite temperatures for rigid molecules see [20].) First, for the antiferromagnetic state, the partition function in the Gaussian approximation may be written as

$$Z = \exp\left(-\frac{E_0^{\text{AF}}}{k_B T}\right) \prod_{jl} \int \mathcal{D}\phi'(z) \exp\left(-\frac{E_H^{\text{AF}}[\phi']}{k_B T}\right), \quad (3.4)$$

where

$$E_H^{\text{AF}}[\phi'] = \int_{-L/2}^{L/2} dz \sum_{j,l} \left[\frac{C}{2} \left(\frac{d\phi'_{jl}(z)}{dz} \right)^2 + \frac{m_2}{2} [\phi'_{jl}(z) - \phi'_{j+l-1}(z)]^2 + \frac{m_1}{2} [(\phi'_{jl}(z) - \phi'_{j-1l}(z))^2 + (\phi'_{jl}(z) - \phi'_{jl-1}(z))^2] \right] \quad (3.5)$$

and the ground state energy is $E_0^{\text{AF}} = a_0(R_2) - a_1(R_2) + a_2(R_2) + 2a_0(R_1) - 2a_1(R_1) \cos(\psi) + 2a_2(R_1) \cos(2\psi)$. The azimuthal orientations of the molecules at the lattice points are replaced with the following values:

$$\begin{aligned} \phi_{jl}(z) - \phi_{j-1l}(z) &= \psi + \phi'_{jl}(z) - \phi'_{j-1l}(z), \\ \phi_{jl}(z) - \phi_{jl-1}(z) &= \psi + \phi'_{jl}(z) - \phi'_{jl-1}(z), \\ \phi_{jl}(z) - \phi_{j+l-1}(z) &= \phi'_{jl}(z) - \phi'_{j+l-1}(z). \end{aligned} \quad (3.6)$$

Here, $m_2 = a_1(R_2) - 4a_2(R_2)$ and $m_2 = a_1(R_1) \cos(\psi) - 4a_2(R_1) \cos(2\psi)$. As in the previous section, we introduce the following ansatz:

$$\phi'_{jl}(z) = \phi_{jl}^p(z) + \frac{\gamma_{jl}z}{L}, \quad (3.7)$$

splitting up the azimuthal value along each molecule at each lattice site into a function $\phi_{jl}^p(z)$ that satisfies the periodic boundary conditions, $\phi_{jl}^p(-L/2) = \phi_{jl}^p(L/2)$, linking the ends of the molecules and the correction $\frac{\gamma_{jl}z}{L}$ to account for independent fluctuations of the two ends of each molecule. We may express $\phi_{jl}^p(z)$ in a similar form as equation (2.9) for the previous section (see appendix C). The rigid body part of $\phi_{jl}(z)$ has been included in $\phi_{jl}^p(z)$ and is the spatial average of $\phi_{jl}^p(z)$ along the molecule. The steps in calculating the free energy per molecule in the Gaussian approximation are similar to those given in the previous section (see appendix C) with the end result being

$$\begin{aligned} F &= \frac{k_B T}{2(2\pi)^2} \int_{-\pi}^{\pi} dx \int_{-\pi}^{\pi} dy \ln \left(\frac{\lambda_p}{\lambda_1} \left(\frac{\hat{C}(x, y; \alpha)}{\hat{C}(x, y; 1)} \right)^{1/2} \coth \left(\frac{\hat{C}(x, y; \alpha)^{1/2} L}{2\lambda_1} \right) \right) \\ &\quad + \frac{k_B T}{(2\pi)^2} \int_{-\pi}^{\pi} dx \int_{-\pi}^{\pi} dy \ln \left(\frac{1}{\hat{C}(x, y; 1)} \sinh \left(\frac{L}{2\lambda_1} \hat{C}(x, y; \alpha) \right) \right) \\ &\quad + k_B T \Theta_{\text{asb}}, \end{aligned} \quad (3.8)$$

where $\lambda_1 = \sqrt{\frac{C}{2(a_1(R_1) \cos(\psi) - 4a_2(R_1) \cos(2\psi))}}$, $\lambda_2 = \sqrt{\frac{C}{2(a_1(R_2) - 4a_2(R_2))}}$, $\hat{C}(x, y; \alpha) = (1 - \cos(x)) + (1 - \cos(y)) + \alpha(1 - \cos(x - y))$ and $\alpha = (\lambda_1/\lambda_2)^2$. For the ferromagnetic state we simply set $\psi = 0$ and $R_1 = R_2$.

Additionally, we may compute the correlation functions associated with the thermally induced fluctuations of the azimuthal orientation of the molecules. Calculation of these is particularly useful since they are reflected in the intensity profiles of x-ray diffraction patterns of columnar assemblies [11]. This azimuthal correlation function within the Gaussian approximation is defined as

$$\begin{aligned} \langle \exp(in(\phi'_{jl}(z) - \phi'_{j'l'}(z'))) \rangle_0 &= \exp\left(-\frac{E_0^{\text{AF}}}{k_B T}\right) \frac{1}{Z} \prod_{jl} \int \mathcal{D}\phi'(z) \exp(in(\phi'_{jl}(z) - \phi'_{j'l'}(z'))) \\ &\quad \times \exp\left(-\frac{E_H^{\text{AF}}[\phi']}{k_B T}\right). \end{aligned} \quad (3.9)$$

This may be written as (summarized in appendix D)

$$\begin{aligned} \langle \exp(in(\phi'_{jl}(z) - \phi'_{j'l'}(z'))) \rangle_0 &= \exp(n^2(\langle \phi'_{jl}(z) \phi'_{j'l'}(z') \rangle_0 - \frac{1}{2} \langle \phi'_{jl}(z)^2 \rangle_0 - \frac{1}{2} \langle \phi'_{j'l'}(z')^2 \rangle_0)) \\ &\equiv \exp(n^2 G(j - j', l - l', z, z')). \end{aligned} \quad (3.10)$$

$G(j - j', l - l', z, z')$ may be split up into terms corresponding to three contributions

$$G(s, r, z, z') = G_0(s, r) + G_P(s, r, z - z') + G_{AP}(s, r, z, z'), \quad (3.11)$$

where $s = j - j'$ and $r = l - l'$.

The first contribution takes into account rigid body fluctuations of the azimuthal orientation of the DNA molecules. It has the following form for large separations, i.e. $s, r \gg 1$ (for a general expression see appendix D):

$$G_0(r, s) \approx -\frac{k_B T \lambda_1^2}{\pi L C \sqrt{1 + 2\alpha}} \left(\ln \left(r^2 + s^2 + \frac{2\alpha r s}{(1 + \alpha)} \right) \right) - \Delta_\psi^2, \quad (3.12)$$

where $\Delta_\psi^2 = G_0(1, 0) = G_0(0, 1) = \frac{2k_B T \lambda_1^2}{L C \pi} \arcsin\left(\frac{1}{\sqrt{2(\alpha+1)}}\right)$. The first term in equation (3.12) grows with increasing separation because there is no long range order for such a 2D system. The second contribution of equation (3.9) represents the torsional (z -dependent) azimuthal fluctuations assuming periodic boundary conditions. Again, when the separations are large,

$$\begin{aligned} G_P(j - j', l - l', z - z') &\approx -\Delta_\phi^2 \\ &= -\frac{k_B T}{2C} \frac{1}{(2\pi)^2} \int_{-\pi}^{\pi} dx \int_{-\pi}^{\pi} dy \\ &\quad \times \left(\frac{\lambda_1}{\hat{C}(x, y; \alpha)^{1/2}} \coth\left(\frac{L\hat{C}(x, y; \alpha)^{1/2}}{2\lambda_1}\right) - \frac{2\lambda_1^2}{L\hat{C}(x, y; \alpha)} \right). \end{aligned} \quad (3.13)$$

The last contribution is the correction due to allowing both ends of each molecule to fluctuate independently. This takes the form for large separations of

$$\begin{aligned} G_{AP}^\infty(z, z') &= \frac{k_B T \lambda_1}{4C} \frac{1}{(2\pi)^2} \int_{-\pi}^{\pi} dx \int_{-\pi}^{\pi} dy \frac{1}{\hat{C}(x, y; \alpha)^{1/2}} \\ &\quad \times \exp\left(-\frac{L\hat{C}(x, y; \alpha)^{1/2}}{\lambda_1}\right) \left(1 - \exp\left(-\frac{2L\hat{C}(x, y; \alpha)^{1/2}}{\lambda_1}\right)\right)^{-1} \\ &\quad \times \left[\left(\exp\left(\frac{|z|C(x, y; \alpha)^{1/2}}{\lambda_1}\right) - \exp\left(\frac{-|z|C(x, y; \alpha)^{1/2}}{\lambda_1}\right) \right)^2 \right. \\ &\quad \left. + \left(\exp\left(\frac{|z'|C(x, y; \alpha)^{1/2}}{\lambda_1}\right) - \exp\left(\frac{-|z'|C(x, y; \alpha)^{1/2}}{\lambda_1}\right) \right)^2 \right]. \end{aligned} \quad (3.14)$$

And so the correlation function at large separations can be written as

$$\begin{aligned} \langle \exp(in(\phi'_{jl}(z) - \phi'_{j'l'}(z'))) \rangle_0 &\approx \left((j - j')^2 + (l - l')^2 + \frac{2\alpha(l - l')(j - j')}{(1 + \alpha)} \right)^{-\gamma} \\ &\quad \times \exp(-n^2(\Delta_\phi^2 + \Delta_\psi^2)) \exp(-n^2 G_{AP}^\infty(z, z')), \end{aligned} \quad (3.15)$$

where $\gamma = n^2 k_B T \lambda_1^2 / (\pi L C \sqrt{1 + 2\alpha})$. As the separations increase, the azimuthal correlation is reduced as one might expect. This, again, reflects the fact that in such a 2D system there is no long-range order.

4. Assemblies of molecules of finite length: the self-consistent approximation

Near the point of frustration, i.e. the location of the transition between the distorted 'antiferromagnetic' state and the hexagonal 'ferromagnetic' state, the fluctuations become quite large so that the Gaussian approximation is no longer valid. Thus we must extend the calculation by using a self-consistent approximation, namely, a Hartree approximation.

Unfortunately, we were unable to find a Hartree approximation that takes into account freely fluctuating ends of the molecules, but it is possible to treat this contribution as a small correction to the Hartree approximation for periodic boundary conditions. In such an approximation it is possible to determine how torsionally softening or changing a molecule's length alters the value of $R_*^1(T)$, the separation at which the phase transition occurs. Furthermore, the correlation functions of the previous section also can be calculated within this approximation.

The self-consistent approximation first entails carrying out a series expansion of equation (3.1) in powers of ϕ' where anharmonic terms, terms of $O(\phi^3)$ or greater, are treated as perturbations to the Gaussian approximation. The value of ψ is determined through the requirement that

$$\langle \phi'_{jl}(z) - \phi'_{j-1l}(z) \rangle = \langle \phi'_{jl}(z) - \phi'_{j+1l-1}(z) \rangle = \langle \phi'_{jl}(z) - \phi'_{j+1l-1}(z) \rangle = 0. \quad (4.1)$$

(Details of such a perturbation expansion are given in appendix E.) Terms for the correlation function and the free energy, where periodic boundary conditions are assumed, may be re-summed in a similar fashion to the Hartree approximation calculations of [20, 22]. Following similar steps (given in appendix F), we obtain the Hartree result for the free energy per molecule,

$$\begin{aligned} F_H = & \frac{k_B T}{(2\pi)^2} \int_{-\pi}^{\pi} dx \int_{-\pi}^{\pi} dy \ln \left(\sinh \left(\frac{L \hat{C}(x, y; \alpha_H)^{1/2}}{2\lambda_1^H} \right) \right) \\ & - 2La_1(R_1) \cos \psi_H \exp \left(-\frac{\lambda_1^H}{4\lambda_p} \chi_1 \left(\frac{L}{2\lambda_1^H}, \alpha_H \right) \right) \\ & + 2La_2(R_1) \cos 2\psi_H \exp \left(-\frac{\lambda_1^H}{\lambda_p} \chi_1 \left(\frac{L}{2\lambda_1^H}, \alpha_H \right) \right) \\ & - La_1(R_2) \exp \left(-\frac{\lambda_1^H}{4\lambda_p} \chi_2 \left(\frac{L}{2\lambda_1^H}, \alpha_H \right) \right) \\ & + La_2(R_2) \exp \left(-\frac{\lambda_1^H}{\lambda_p} \chi_2 \left(\frac{L}{2\lambda_1^H}, \alpha_H \right) \right) \\ & - \frac{LC}{8\lambda_1^H \lambda_p} \left(2\chi_1 \left(\frac{L}{2\lambda_1^H}, \alpha_H \right) + \alpha_H \chi_2 \left(\frac{L}{2\lambda_1^H}, \alpha_H \right) \right), \end{aligned} \quad (4.2)$$

where $\alpha_H = (\lambda_1^H / \lambda_2^H)^2$, and λ_1^H and λ_2^H satisfy the following transcendental equations:

$$\begin{aligned} \lambda_1^H &= \sqrt{\frac{C}{2 \left(a_1(R_1) \cos(\psi_H) \exp \left(-\frac{\lambda_1^H}{4\lambda_p} \chi_1 \left(\frac{L}{2\lambda_1^H}, \alpha_H \right) \right) - 4a_2(R_1) \cos(2\psi_H) \exp \left(-\frac{\lambda_1^H}{\lambda_p} \chi_1 \left(\frac{L}{2\lambda_1^H}, \alpha_H \right) \right) \right)}} \\ \lambda_2^H &= \sqrt{\frac{C}{2 \left(a_1(R_2) \exp \left(-\frac{\lambda_1^H}{4\lambda_p} \chi_2 \left(\frac{L}{2\lambda_1^H}, \alpha_H \right) \right) - 4a_2(R_2) \exp \left(-\frac{\lambda_1^H}{\lambda_p} \chi_2 \left(\frac{L}{2\lambda_1^H}, \alpha_H \right) \right) \right)}}. \end{aligned} \quad (4.3)$$

ψ_H satisfies the following relation:

$$\cos(\psi_H) = \frac{a_1(R_1)}{4a_2(R_1)} \exp \left(\frac{3\lambda_1^H}{4\lambda_p} \chi_1 \left(\frac{L}{2\lambda_1^H}, \alpha_H \right) \right). \quad (4.4)$$

The functions $\chi_1(\frac{L}{2\lambda_1^H}, \alpha_H)$ and $\chi_2(\frac{L}{2\lambda_1^H}, \alpha_H)$ are given in appendix E. The free energy is then minimized with respect to ω to determine the degree of distortion of the hexagonal lattice for

the antiferromagnetic state. The ferromagnetic state is simply obtained by setting $\psi = 0$ so that $R_1 = R_2$ and, thus, $\lambda_1^H = \lambda_2^H = \lambda_H$ and $\alpha = 1$.

It is quite interesting to look at the Hartree result for the ferromagnetic state for infinitely long molecules, which is very similar to the result given in [22] for a pair of molecules, since it provides some insight into the nature of the many body effects of the assembly. There are two differences: first of all, λ_p is replaced by $\lambda_p C_{\text{mb}}^{-1}$, where C_{mb} is a constant resulting from the many body effects of the assembly; and secondly, an overall factor of three that multiplies the free energy is included to account for the coordination number of nearest neighbours about a molecule. We calculate that $C_{\text{mb}} \simeq 0.560$ so we find that many body effects suppress thermal fluctuations. This is not surprising considering that the many neighbours in the assembly should increase the effective interaction between molecules. Therefore, thermal fluctuations of the same magnitude in the assembly cost more energy than that for a single pair of molecules.

We may also show that the results above conform to that of the formulation of rigid molecules [20]. Changing variables to J_1^H and J_2^H where $\lambda_1^H = \sqrt{CL/(2J_1^H)}$ and $\lambda_2^H = \sqrt{CL/(2J_2^H)}$, we may rewrite equation (4.3) in terms of J_1^H and J_2^H . Upon taking the limit $L \rightarrow 0$, it is fairly straightforward to recover the Hartree results for the configurational states of [20]. Taking the limit of these equations, i.e. the molecules are treated as completely rigid, also yields this same result. This is fully consistent with the physics we might expect. As we shorten the length of the molecule, the energy cost of torsional fluctuations begins to counter the reduction in free energy due to the entropy gain associated with them. And so with decreasing length, these fluctuations become suppressed and rigid body fluctuations start to dominate.

We first examine how the phase boundary between the ferromagnetic hexagonal state and antiferromagnetic rhombic state changes with the length and flexibility of the molecules assuming periodic boundary conditions. Equating the free energy of the antiferromagnetic state with that of the ferromagnetic state, equations (4.2)–(4.4), we can determine the location of the transition between the two states. The location of this transition in terms of the average interaxial spacing between molecules in the assembly as a function of molecular length is shown in figure 3 for molecules with varying torsional flexibilities. Increasing the flexibility of the molecule results in the transition moving to larger densities (smaller interaxial spacings) as one might expect. With increasing flexibility, there is an increase in thermally induced torsional fluctuations and so the location of the transition as the flexibility is increased moves in the same direction as when the molecule is shortened, where thermally induced rigid-body fluctuations become larger. Also shown, in figure 4, is the level of distortion (value of the rhombic angle ω) from the hexagonal lattice as a function of the average interaxial spacing for the antiferromagnetic state. As seen in the plot, greater flexibility reduces the amount of distortion.

Modifications of the results of the self-consistent Hartree approximation when incorporating corrections for independently rotating ends of the molecules are quite involved and are left to the appendices. When including these corrections, however, we find that the locations of the transition only shift by hundredths of angstroms for all the cases shown in figure 3. And so the formulation assuming periodic boundary conditions, as long as the molecules are long enough, adequately describes the system.

We may also calculate correlation functions within the Hartree approximation for periodic boundary conditions. Here, we may use the results of the previous section, but we now replace λ_1 with λ_1^H and α with $\alpha_H = (\lambda_1^H/\lambda_2^H)^2$. We then may compute Δ_ϕ and Δ_ψ within this approximation. A plot of these quantities is shown in figure 5 for a molecule with a realistic value for its torsional modulus. The correction associated with fluctuations of the free ends of the molecules only results in small changes in the value of Δ_ϕ (the formulation of which is

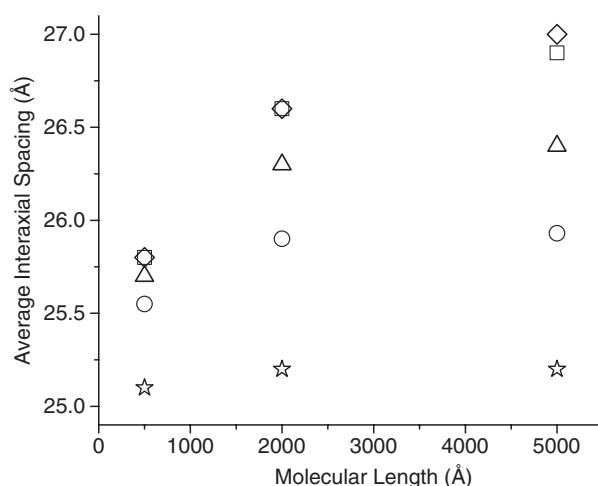


Figure 3. Location of the antiferromagnetic–ferromagnetic transition for molecules of different lengths and torsional flexibilities. At large densities (small interaxial spacings), the antiferromagnetic state is the lowest energy state whereas the ferromagnetic state is the favoured state for more dilute assemblies. Diamonds (◇) correspond to perfectly rigid molecules ($C = \infty$), stars (★) to molecules with a torsional modulus of $C = 3.0 \times 10^{-19}$ erg cm, circles (○) to molecules with $C = 1.0 \times 10^{-18}$ erg cm, triangles (△) to molecules with $C = 3.0 \times 10^{-18}$ erg cm, and squares (□) to molecules with $C = 3.0 \times 10^{-17}$ erg cm. Results are shown for molecules with 70% charge compensation and a 70/30 major/minor groove charge distribution in a solution with an inverse Debye screening length of about 7 Å.

again left to the appendices). On this plot, we also show the variation of the relative azimuthal angle due to rigid body fluctuations, Δ_ψ , for a molecule of the same length. These results are consistent with fits of x-ray diffraction data of hydrated DNA assemblies [11].

Lastly, we show in appendix H the high temperature expansion for the azimuthally disordered or Kosterlitz–Thouless vortex phase, mentioned in the introduction, that includes torsional fluctuations. Granted, in the case of real DNA it is very unlikely that this situation is realized [20]. At larger separations where thermal fluctuations dominate intermolecular azimuthal interactions the DNA assembly is likely to lose columnar ordering before such a transition in the azimuthal configuration of the columnar assembly occurs. Because of this reservation, this work has not been included in the main text. However, in other helical biomolecule assemblies where azimuthal interactions might be weaker but spatial interactions are strong, a Kosterlitz–Thouless-like transition could possibly occur within a smectic layer with short range two-dimensional ordering.

5. Discussion and conclusions

We have developed a method for calculating the contribution to the free energy due to azimuthal fluctuations for torsionally flexible molecules of finite length. Using this method we can determine the influence of azimuthal flexibility of molecules within a DNA columnar assembly on the position of the phase transition between the antiferromagnetic state where the hexagonal lattice is distorted and the ferromagnetic state for various molecular lengths. For molecules with torsional moduli of $C = 3 \times 10^{-19}$ erg cm, the approximate value deduced from experiments [28], torsional flexibility reduces the separation at which this occurs compared to that found for the case of rigid molecules. We see that the effects of torsional fluctuations are more pronounced for assemblies of long molecules, whereas the results for short molecules

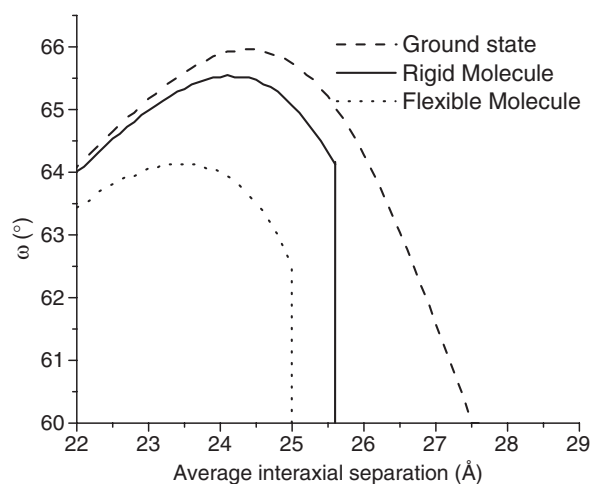


Figure 4. The level of distortion (ω) from the hexagonal lattice for the antiferromagnetic state as a function of the average interaxial separation of the molecules in the columnar assemblies. The distortion is shown for the ground state configuration (no spin fluctuations), for a rigid molecule of length 500 Å with spin fluctuations, and for a flexible molecule ($C = 3.0 \times 10^{-19}$ erg cm) with torsional fluctuations of the same length.

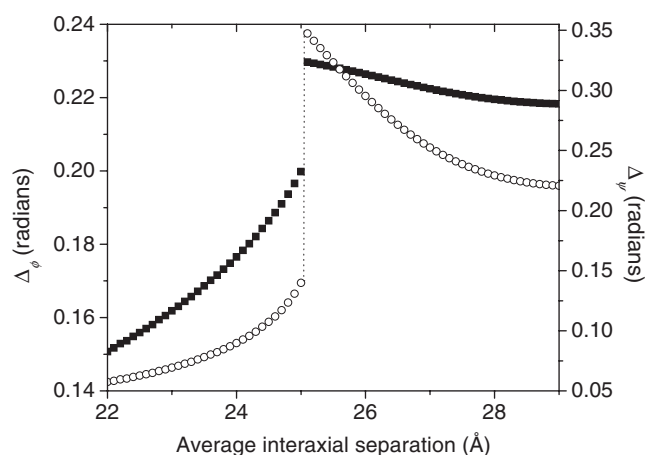


Figure 5. The contributions of torsional fluctuations Δ_ϕ (filled squares) and rigid body fluctuations Δ_ψ (open circles) to the correlation function of the relative azimuthal angles between molecules in an assembly as a function of the average molecular separation. Again, the break at 25.1 Å corresponds to the transition from the antiferromagnetic state (at smaller molecular separations) to the ferromagnetic state. Values are shown for an assembly of molecules that are 500 Å long and have torsional moduli of 3.0×10^{-19} erg cm.

are little different from those rigid body calculations of [20], thereby showing that shortening the molecule is nearly equivalent to making the molecule less flexible.

We found that torsional fluctuations considerably reduce the degree of lattice distortion, for long molecules in the antiferromagnetic state, as compared to that found for calculations for rigid molecules of the same length. Since flexibility allows for readjustment of the azimuthal coordinate along the length of the molecules in the lattice, less distortion is required to minimize the free energy of the assembly due to the antiferromagnetic coupling of the pair potential.

Hence, as compared to ground state [18] or finite-temperature rigid body calculations [20], x-ray diffraction patterns must have even better resolution to pick out this distortion [3].

We were also able to calculate the asymptotic form of the correlation function $\langle \exp(in(\phi_{jl}(z) - \phi_{j'l'}(z'))) \rangle$ including both rigid body and torsional fluctuations. This term is found in the formulation of the intensity of x-ray diffraction patterns of assemblies [11] and is therefore a direct means by which one can determine the extent of these fluctuations. Our results for the parameters chosen agree quite well with the fits made to x-ray diffraction data of hydrated DNA assemblies. Conversely, comparing these fits to the correlation function formulation may reveal the strength of the azimuthal interaction, which in turn may say something about the charge distribution on the DNA molecules in the assembly.

Although we have discovered a number of effects associated with allowing for torsional flexibility in columnar DNA assemblies, this analysis, however, is limited by the form of the DNA–DNA interaction [16] we have employed. The effects of nonlocal polarizability of the water in the narrow interstitial regions between the DNA could alter the results [24–26]. Also, the potential assumes a given charge distribution of readsorbed counter-ions that changes very little with density. Once these effects have been incorporated into the pair potential the same analysis as developed here may be used. But even upon considering these effects, the qualitative aspects of this analysis should remain unchanged.

One may also need to consider the effect of sequence dependent distortions from the ideal double helical structure seen in real DNA [28–32] in the analysis of the assemblies. This may well be included in calculations for assemblies of non-homologous DNA by employing ensemble averaging [31]. Such averaging is easiest in an assembly made up of with several different DNA sequences. Again, as in [22], these effects may be incorporated into a combined persistence length that incorporates both distortions arising from thermal fluctuations and from different base pair sequences of neighbouring molecules. For assemblies containing DNA sequences with only a few different texts (and thus different distortions from an ideal helix) the interaction is much more difficult to treat and has yet been considered. Nevertheless, in the case of homologous DNA assemblies, distortions from an ideal helix make little difference as the electrostatic interaction depends only on the relative azimuthal orientations between the molecules.

Finally, we should point out that this is by no means a complete statistical mechanical picture of a columnar assembly. For example, we have not included lattice vibrations, fluctuations in the z -position of the centre of each molecule, bending fluctuations, or fluctuations due to other geometrical distortions of each molecule. However, fluctuations in the azimuthal degrees of freedom are probably the most important feature for determining the structure of the mesophases of columnar assemblies as seen in the fits of x-ray diffraction patterns [11]. Furthermore, coupling of the azimuthal degrees of freedom to other geometrical distortions, which are likely to be small, may be incorporated into our model.

Acknowledgments

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Appendix A. Details of the ‘quantum mechanical’ calculation of the free energy at finite length

We start with equation (2.5) of the text, namely

$$F = -k_B T \ln \sum_{E,+,-} \langle \phi_+ | E \rangle \exp\left(-\frac{EL}{\lambda_p}\right) \langle E | \phi_- \rangle - k_B T \ln \Theta. \quad (\text{A.1})$$

We will now, using equation (D.1), derive expressions for finite size correction terms for the Gaussian approximation. But first we will need to derive some general results.

Now each eigenstate of equation (2.3) is characterized by two numbers; the band number $b \geq 0$, an integer, and the wavenumber in the band $-1/2 < k < 1/2$, a continuous variable. Each eigenstate should then be written as

$$\psi_{b,k}(\phi) = \langle \phi | E_{b,k} \rangle = \lim_{N \rightarrow \infty} \frac{1}{\sqrt{N_P}} \sum_n G_{n,b,k} \exp(i(n+k)\phi), \quad (\text{A.2})$$

where the $G_{n,b,k}$ satisfy

$$\left[\frac{(n+k)^2}{2} - E_{b,k} \right] G_{n,b,k} - \frac{\lambda_p^2}{2\lambda_0^2} [G_{n-1,b,k} + G_{n+1,b,k}] + \frac{a_2\lambda_p^2}{2a_1\lambda_0^2} [G_{n-2,b,k} + G_{n+2,b,k}] = 0. \quad (\text{A.3})$$

Here, N_P is the number of periods the potential has in ϕ -space and is proportional to the ‘system size’: the range of values which ϕ is allowed to take. As ϕ will fluctuate between $-\infty$ and ∞ , except at ϕ_+ , we take N_P to be infinite. It is easy, then, to show that the following is true:

$$\int_0^{2\pi} \psi_{b,k}(\phi) d\phi = \lim_{N_P \rightarrow \infty} \frac{2\pi}{\sqrt{N_P}} \delta_{k,0} G_{0,b,0}. \quad (\text{A.4})$$

Using equation (D.4) we rewrite F as

$$F = -k_B T \ln \sum_b |G_{0,b,0}|^2 \exp\left(-\frac{E_b L}{\lambda_p}\right) - k_B T \ln \Theta. \quad (\text{A.5})$$

In the Gaussian approximation we assume that $\psi_{b,0}$ can be written as a linear supposition of simple harmonic oscillator eigenstates

$$\psi_{b,0} = \lim_{N_P \rightarrow \infty} \frac{c_b}{\sqrt{N_P}} \sum_{j=-N_P/2}^{N_P/2} H_b(\sqrt{\omega}(\phi - 2\pi j)) \exp\left(\frac{-\omega(\phi - 2\pi j)^2}{2}\right), \quad (\text{A.6})$$

where the $H_b(x)$ are the Hermite polynomials and the c_b are the normalization constants for each state. In the Gaussian approximation

$$\begin{aligned} \omega^2 &= \left(\frac{\lambda_p^2}{\lambda_0^2}\right) \cos \phi_0 - \left(\frac{4a_2\lambda_p^2}{a_1\lambda_0^2}\right) \cos 2\phi_0 \quad \text{and} \\ E_b &= \left(\frac{1}{2} + b\right)\omega - \left(\frac{\lambda_p^2}{\lambda_0^2}\right) \cos(\phi_0) + \left(\frac{a_2\lambda_p^2}{a_1\lambda_0^2}\right) \cos(2\phi_0). \end{aligned} \quad (\text{A.7})$$

Assuming negligible overlap between the wavefunctions in the Superposition, we find on retaining the first two terms in the sum in equation (D.5) and expanding out the logarithm and writing $\omega = \lambda_p/\lambda$ that

$$F = E_0 + \frac{CL}{4\lambda_p\lambda} - \frac{k_B T}{2} \exp\left(-\frac{(E_2 - E_0)L}{\lambda_p}\right) + \frac{k_B T}{2} \ln\left(\frac{\lambda}{\lambda_p}\right) - k_B T \ln \Theta. \quad (\text{A.8})$$

We should point out that this result differs from (D9) of [22], as the previous version contains a couple of mistakes that have been corrected. Substituting for E_0 and E_2 we thus so obtain equation (2.6) of the text.

Appendix B. Calculation of the free energy for the DNA pair by Gaussian integration

We may readily perform the Gaussian integrations in equation (2.10) of the text

$$Z = Z_0 Z_f Z_p \exp\left(-\frac{E_0}{k_B T}\right), \quad (\text{B.1})$$

where now

$$\begin{aligned} Z_0 &= \left(\frac{2\pi k_B T}{m}\right)^{1/2}, \\ Z_f &= \left(\frac{4\pi\lambda}{\lambda_p} \tanh\left(\frac{L}{2\lambda}\right)\right)^{1/2}, \\ Z_p &= \prod_{n \neq 0} (2\pi k_B T G_n)^{1/2}. \end{aligned} \quad (\text{B.2})$$

Using the definition of free energy $F = -k_B T \ln Z$ we are then able to write the free energy as

$$F = \frac{k_B T}{2} \sum_n \ln\left(\frac{C}{2} \left(\frac{2\pi n}{L}\right)^2 + m\right) + \frac{k_B T}{2} \ln\left(\frac{\lambda_p}{2\lambda} \coth\left(\frac{L}{2\lambda}\right)\right) + k_B T \Theta, \quad (\text{B.3})$$

where we have adsorbed terms that do not depend on λ and are not important to our analysis into Θ . The first term may be evaluated by means of a trick

$$\frac{\partial}{\partial m} \sum_n \ln\left(\frac{C}{2} \left(\frac{2\pi n}{L}\right)^2 + m\right) = \sum_n \left(\frac{C}{2} \left(\frac{2\pi n}{L}\right)^2 + m\right)^{-1} = \frac{L\lambda}{C} \coth\left(\frac{L}{2\lambda}\right). \quad (\text{B.4})$$

We then by integrate up (B.3) and so arrive at

$$F = k_B T \ln\left(\sinh\left(\frac{L}{2\lambda}\right)\right) + \frac{k_B T}{2} \ln\left(\frac{\lambda_p}{2\lambda} \coth\left(\frac{L}{2\lambda}\right)\right) + k_B T \Theta, \quad (\text{B.5})$$

where extra constants, such as constants of integration, have been adsorbed into Θ . On rearrangement we arrive at (2.11) in the text.

Appendix C. Calculation of the free energy for Gaussian fluctuations in the assembly

We start our analysis by substituting (3.7) into (3.5) of the text and so obtain the following expression for $E_H^{\text{AF}}[\phi']$:

$$\begin{aligned} E_H^{\text{AF}}[\phi'] &= \sum_{jl} \int_{-L/2}^{L/2} dz \left[\frac{C}{2} \left(\frac{d\phi_{jl}^p}{dz}\right)^2 + \frac{C\gamma_{jl}^2}{2L^2} \right. \\ &\quad \left. + \frac{m_1}{2} \left[\left(\phi_{jl}^p - \phi_{j-1l}^p + \frac{z\gamma_{jl}}{L} - \frac{z\gamma_{j-1l}}{L}\right)^2 + \left(\phi_{jl}^p - \phi_{jl-1}^p + \frac{z\gamma_{jl}}{L} - \frac{z\gamma_{jl-1}}{L}\right)^2 \right] \right. \\ &\quad \left. + \frac{m_2}{2} \left(\phi_{jl}^p - \phi_{j+1l-1}^p + \frac{z\gamma_{jl}}{L} - \frac{z\gamma_{j+1l-1}}{L}\right)^2 \right]. \end{aligned} \quad (\text{C.1})$$

We then introduce the following lattice Fourier transforms:

$$\phi_{jl}^p(z) = \frac{1}{\sqrt{A}} \sum_{k_u k_v} \phi^p(\vec{k}, z) e^{i(jk_u + lk_v)r_0} \quad \text{and} \quad \gamma_{jl} = \frac{1}{\sqrt{A}} \sum_{k_u k_v} \gamma(\vec{k}) e^{i(jk_u + lk_v)r_0}, \quad (\text{C.2})$$

where A is total area of the lattice and r_0 is the lattice spacing. We have chosen reciprocal lattice vectors corresponding to the rhombic Bravais lattice defined by \hat{u} and \hat{v} ; see figure 1 of

the text. Then k_u and k_v take on values which lie within the first Brillouin zone for a rhombic lattice (e.g. $-\pi/r_0 < k_u < \pi/r_0$). We are then able to write in the limit $A \rightarrow \infty$

$$E_H^{\text{AF}}[\phi] = \frac{1}{(2\pi)^2} \int_{-\pi}^{\pi} dx \int_{-\pi}^{\pi} dy \int_{-L/2}^{L/2} dz \left[\frac{C}{2} \left(\frac{\partial \phi^P(x, y, z)}{\partial z} \frac{\partial \phi^P(-x, -y, z)}{\partial z} \right) + \frac{C\gamma(x, y)\gamma(-x, -y)}{2L^2} + m_1 \hat{C}(x, y; \alpha) \right. \\ \left. \times \left[\left(\phi^P(x, y, z) + \frac{z\gamma(x, y)}{L} \right) \left(\phi^P(-x, -y, z) + \frac{z\gamma(-x, -y)}{L} \right) \right] \right], \quad (\text{C.3})$$

where $x = r_0 k_u$ and $y = r_0 k_v$. We then may express $\phi^P(x, y, z)$ through Fourier series

$$\phi^P(x, y, z) = \frac{1}{\sqrt{L}} \sum_{n=0} b_n(x, y) \exp\left(\frac{2\pi i n z}{L}\right), \quad (\text{C.4})$$

and so re-express (C.3)

$$E_H^{\text{AF}}[\phi] = \frac{1}{(2\pi)^2} \int_{-\pi}^{\pi} dx \int_{-\pi}^{\pi} dy \left(\sum_n \left[\frac{b_n(x, y)b_{-n}(-x, -y)}{2G_n(x, y)} + m \hat{C}(x, y; \alpha)\gamma(x, y)J_n b_{-n}(-x, -y) + m \hat{C}(x, y; \alpha)\gamma(-x, -y)J_{-n} b_n(x, y) \right] + \left(\frac{C}{L^2} + \frac{Lm}{6} \hat{C}(x, y; \alpha) \right) \frac{\gamma(x, y)\gamma(-x, -y)}{2L^2} \right), \quad (\text{C.5})$$

where $G_n(x, y) = (C(\frac{2\pi n}{L})^2 + 2m\hat{C}(x, y; \alpha))^{-1}$, $J_n = \frac{i(-1)^n \sqrt{L}}{2\pi n}(1 - \delta_{n,0})$, $\hat{C}(x, y; \alpha) = (1 - \cos(x)) + (1 - \cos(y)) + \alpha(1 - \cos(x - y))$ and $\alpha = m_2/m_1$. On making the variable shift $b_n(x, y) \rightarrow b_n(x, y) - m_1\gamma(x, y)\hat{C}(x, y; \alpha)J_n G_n(x, y)$ we may write this as

$$E_H^{\text{AF}}[\phi] = \frac{1}{(2\pi)^2} \int_{-\pi}^{\pi} dx \int_{-\pi}^{\pi} dy \left(\sum_n \left[\frac{b_n(x, y)b_{-n}(-x, -y)}{2G_n(x, y)} + 2m^2 \hat{C}(x, y; \alpha)^2 \gamma(x, y)\gamma(-x, -y)J_{-n} G_n(x, y)J_n \right] + \left(\frac{C}{L} + \frac{Lm}{6} \hat{C}(x, y; \alpha) \right) \frac{\gamma(x, y)\gamma(-x, -y)}{2L^2} \right). \quad (\text{C.6})$$

We find that on further manipulation we may write

$$Z = Z_f Z_p \exp\left(-\frac{E_0^{\text{AF}}}{k_B T}\right), \quad (\text{C.7})$$

where

$$Z_f = \int \mathcal{D}\gamma(x, y) \exp\left(-\frac{1}{(2\pi)^2} \int_{-\pi}^{\pi} dx \int_{-\pi}^{\pi} dy \frac{\gamma(x, y)\gamma(-x, -y)}{2S(x, y)}\right), \\ Z_p = \prod_n \int \mathcal{D}b_n(x, y) \exp\left(-\frac{1}{(2\pi)^2} \sum_n \int_{-\pi}^{\pi} dx \int_{-\pi}^{\pi} dy \frac{b_n(x, y)b_{-n}(-x, -y)}{2G_n(x, y)k_B T}\right),$$

and $S(x, y) = \frac{\lambda}{\lambda_p} \frac{1}{\hat{C}(x, y; \alpha)^{1/2}} \tanh\left(\frac{L}{2\lambda} \hat{C}(x, y; \alpha)^{1/2}\right)$. We may evaluate the path integrals giving

$$Z_f = \lim_{\substack{N_x \rightarrow \infty \\ N_y \rightarrow \infty}} \prod_{n_x, n_y} \left(2\pi S\left(\frac{n_x}{2\pi N_x}, \frac{n_y}{2\pi N_y}\right) \right)^{1/2} \\ Z_p = \prod_n \lim_{\substack{N_x \rightarrow \infty \\ N_y \rightarrow \infty}} \prod_{n_x, n_y} \left(2\pi k_B T G_n\left(\frac{n_x}{2\pi N_x}, \frac{n_y}{2\pi N_y}\right) \right)^{1/2}. \quad (\text{C.8})$$

The product $N = N_x N_y$ is the number of molecules in the assembly which we have taken to be infinite as $A \rightarrow \infty$. From (C.8) we find the following result for the free energy per molecule:

$$F = -\frac{k_B T}{2(2\pi)^2} \int_{-\pi}^{\pi} dx \int_{-\pi}^{\pi} dy \ln(S(x, y)) + \frac{k_B T}{2(2\pi)^2} \sum_n \int_{-\pi}^{\pi} dx \int_{-\pi}^{\pi} dy \ln\left(C\left(\frac{2\pi n}{L}\right)^2 + 2m_1 \hat{C}(x, y; \alpha)\right) + k_B T \Theta_{\text{asb}}, \quad (\text{C.9})$$

where unimportant terms that do not depend on m_1 or α have been adsorbed into Θ_{asb} . Using the trick illustrated by equation (B.3), it is possible to write

$$F = \frac{k_B T}{2(2\pi)^2} \int_{-\pi}^{\pi} dx \int_{-\pi}^{\pi} dy \ln\left(\frac{\lambda_p}{\lambda} \left(\frac{\hat{C}(x, y; \alpha)}{\hat{C}(x, y; 1)}\right)^{1/2} \coth\left(\frac{\hat{C}(x, y; \alpha)^{1/2} L}{2\lambda}\right)\right) + \frac{k_B T}{(2\pi)^2} \int_{-\pi}^{\pi} dx \int_{-\pi}^{\pi} dy \ln\left(\frac{1}{\hat{C}(x, y; 1)} \sinh\left(\frac{L}{2\lambda} \hat{C}(x, y; \alpha)\right)\right) + k_B T \Theta_{\text{asb}}, \quad (\text{C.10})$$

where additional constants have been adsorbed into Θ_{asb} .

Appendix D. Correlation functions for Gaussian fluctuations in the assembly

It is first useful to consider the following correlation function:

$$G(j - j', l - l', z, z') = \langle \phi'_{jl}(z) \phi'_{j'l'}(z') \rangle_0 - \frac{1}{2} \langle \phi'_{jl}(z)^2 \rangle_0 - \frac{1}{2} \langle \phi'_{j'l'}(z')^2 \rangle_0, \quad (\text{D.1})$$

where in general for any quantity $A[\phi]$

$$\langle A[\phi] \rangle_0 = \exp\left(-\frac{E_0^{\text{AF}}}{k_B T}\right) \frac{1}{Z} \prod_{jl} \int \mathcal{D}\phi_{jl}(z) A[\phi] \exp\left(-\frac{E_H^{\text{AF}}[\phi]}{k_B T}\right), \quad (\text{D.2})$$

using the ansatz (3.7) we may write (D.1) as

$$G(j - j', l - l', z, z') = \langle \phi_{jl}^p(z) \phi_{j'l'}^p(z') \rangle_0 - \frac{1}{2} \langle \phi_{jl}^p(z)^2 \rangle_0 - \frac{1}{2} \langle \phi_{j'l'}^p(z')^2 \rangle_0 + \frac{z}{L} [\langle \gamma_{jl} \phi_{j'l'}^p(z') \rangle_0 - \langle \gamma_{j'l} \phi_{jl}^p(z) \rangle_0] + \frac{z'}{L} [\langle \phi_{jl}^p(z) \gamma_{j'l'} \rangle_0 - \langle \phi_{j'l'}^p(z') \gamma_{j'l} \rangle_0] - \frac{z^2}{2L^2} \langle \gamma_{jl}^2 \rangle_0 - \frac{z'^2}{2L^2} \langle \gamma_{j'l'}^2 \rangle_0 + \frac{zz'}{L^2} \langle \gamma_{jl} \gamma_{j'l'} \rangle_0. \quad (\text{D.3})$$

This may be rewritten as

$$G(j - j', l - l', z, z') = \frac{1}{(2\pi)^2 L} \sum_{n, n'} \int_{-\pi}^{\pi} dx \int_{-\pi}^{\pi} dy \left([\langle b_n(x, y) b_{n'}(-x, -y) \rangle_0 + J_n \langle \gamma(x, y) b_{n'}(-x, -y) \rangle_0 + J_{n'} \langle \gamma(-x, -y) b_n(x, y) \rangle_0 + J_n J_{n'} \langle \gamma(-x, -y) \gamma(x, y) \rangle_0] \times \left(\exp\left(i(j - j')x + i(l - l')y + \frac{2i\pi(nz + n'z')}{L}\right) - \frac{1}{2} \exp\left(\frac{2i\pi(n + n')z}{L}\right) - \frac{1}{2} \exp\left(\frac{2i\pi(n + n')z'}{L}\right) \right) \right). \quad (\text{D.4})$$

We then make the variable shift $b_n(x, y) \rightarrow b_n(x, y) - m_1 \gamma(x, y) \hat{C}(x, y; \alpha) J_n G_n(x, y)$ and obtain the following:

$$G(j - j', l - l', z, z') = \tilde{G}_P(j - j', l - l', z - z') + G_{AP}(j - j', l - l', z, z'), \quad (\text{D.5})$$

where

$$\tilde{G}_P(j, l, z) = \frac{k_B T}{(2\pi)^2 L} \sum_n \int_{-\pi}^{\pi} dx \int_{-\pi}^{\pi} dy G_n(x, y) \left(\exp\left(i(jx + ly) + \frac{2i\pi n z}{L}\right) - 1 \right), \quad (\text{D.6})$$

and

$$\begin{aligned} G_{AP}(j, l, z, z') &= \frac{1}{(2\pi)^2 L} \sum_{n, n'} \int_{-\pi}^{\pi} dx \int_{-\pi}^{\pi} dy \left(S(x, y) \right. \\ &\quad \times C^2 \left(\frac{(2\pi)^2 n n'}{L^2} \right) (-1)^{n+n'} \left(C \left(\frac{2\pi n}{L} \right)^2 + 2m \hat{C}(x, y; \alpha) \right)^{-1} \\ &\quad \times \left(C \left(\frac{2\pi n'}{L} \right)^2 + 2m \hat{C}(x, y; \alpha) \right)^{-1} \\ &\quad \times \left(\exp\left(i(jx + ly) + \frac{2i\pi(nz + n'z')}{L}\right) - \frac{1}{2} \exp\left(\frac{2i\pi(n+n')z'}{L}\right) \right. \\ &\quad \left. - \frac{1}{2} \exp\left(\frac{2i\pi(n+n')z}{L}\right) \right) \Bigg). \end{aligned} \quad (\text{D.7})$$

In these expressions we are able to perform the sum and we also separate out the rigid body contribution by writing $\tilde{G}_P(j, l, z) = G_P(j, l, z) + G_0(j, l)$, where $G_0(j, l)$ is the part of $G(j, l, z, z')$ that arises purely from rigid body fluctuations. We obtain the following results:

$$\begin{aligned} G_0(j, l) &= \frac{k_B T}{(2\pi)^2 2Lm_1} \int_{-\pi}^{\pi} dx \int_{-\pi}^{\pi} dy \frac{1}{\hat{C}(x, y; \alpha)} (\exp(i(jx + ly)) - 1), \\ G_P(j, l, z) &= \frac{k_B T}{2C} \frac{1}{(2\pi)^2} \int_{-\pi}^{\pi} dx \int_{-\pi}^{\pi} dy \left[\left\{ \frac{\lambda_1}{\hat{C}(x, y; \alpha)^{1/2}} \left(\exp\left(-\frac{|z|\hat{C}(x, y; \alpha)^{1/2}}{\lambda_1}\right) \right. \right. \right. \\ &\quad \left. \left. + \exp\left(\frac{(|z| - L)\hat{C}(x, y; \alpha)^{1/2}}{\lambda_1}\right) \right) \left(1 - \exp\left(-\frac{L\hat{C}(x, y; \alpha)^{1/2}}{\lambda_1}\right) \right)^{-1} \right. \\ &\quad \left. - \frac{2\lambda_1^2}{L\hat{C}(x, y; \alpha)} \right\} \exp(i(jx + ly)) \\ &\quad \left. - \left(\frac{\lambda_1}{\hat{C}(x, y; \alpha)^{1/2}} \coth\left(\frac{L\hat{C}(x, y; \alpha)^{1/2}}{2\lambda_1}\right) - \frac{2\lambda_1^2}{L\hat{C}(x, y; \alpha)} \right) \right], \\ G_{AP}(j, l, z, z') &= \frac{k_B T \lambda_1}{2C} \frac{1}{(2\pi)^2} \int_{-\pi}^{\pi} dx \int_{-\pi}^{\pi} dy \frac{1}{\hat{C}(x, y; \alpha)^{1/2}} \\ &\quad \times \exp\left(-\frac{L\hat{C}(x, y; \alpha)^{1/2}}{\lambda_1}\right) \left(1 - \exp\left(-\frac{2L\hat{C}(x, y; \alpha)^{1/2}}{\lambda_1}\right) \right)^{-1} \\ &\quad \times \left[\text{sgn}(z) \text{sgn}(z') \left(\exp\left(\frac{|z|\hat{C}(x, y; \alpha)^{1/2}}{\lambda_1}\right) \right. \right. \\ &\quad \left. - \exp\left(-\frac{|z|\hat{C}(x, y; \alpha)^{1/2}}{\lambda_1}\right) \right) \left(\exp\left(\frac{|z'|\hat{C}(x, y; \alpha)^{1/2}}{\lambda_1}\right) \right. \right. \\ &\quad \left. - \exp\left(-\frac{|z'|\hat{C}(x, y; \alpha)^{1/2}}{\lambda_1}\right) \right) \exp(i(jx + ly)) \\ &\quad \left. - \frac{1}{2} \left[\left(\exp\left(\frac{|z|\hat{C}(x, y; \alpha)^{1/2}}{\lambda_1}\right) - \exp\left(-\frac{|z|\hat{C}(x, y; \alpha)^{1/2}}{\lambda_1}\right) \right)^2 \right. \right. \\ &\quad \left. \left. + \left(\exp\left(\frac{|z'|\hat{C}(x, y; \alpha)^{1/2}}{\lambda_1}\right) - \exp\left(-\frac{|z'|\hat{C}(x, y; \alpha)^{1/2}}{\lambda_1}\right) \right)^2 \right] \right]. \end{aligned} \quad (\text{D.8})$$

Now from these expressions let us find their behaviour when $l, j \gg 1$. For both $G_{AP}(j, l, z, z')$ and $G_P(j, l, z)$ this is simple. As j and l increase, the terms in the integrands of $G_{AP}(j, l, z, z')$ and $G_P(j, l, z)$ that depend on j and l oscillate more rapidly, so that their contribution gets smaller and smaller. So when $l, j \gg 1$ we may neglect terms that depend on j and l in both integrands, so arriving at (3.13) and (3.14) of the text. The term $G_0(j, l)$ is trickier as neglecting terms that depend on j and l leads to a logarithmic divergence. It is, however, possible to do one of the integrations in (D.8) (by contour integration around a unit circle), which leads to the following result (for $j > 0$):

$$G_0(j, l) = \frac{k_B T}{2(2\pi)Lm_1} \int_{-\pi}^{\pi} dy (\exp(ily + j \ln(z^-(y))) + \exp(-ily - j \ln(z^+(y))) - 2) \times \frac{1}{(z^-(y) - z^+(y))} \frac{1}{(1 + \alpha \exp(-iy))}, \quad (\text{D.9})$$

where

$$z^{\pm}(y) = \frac{(2 + \alpha - \cos(y)) \pm 2|\sin(y/2)|\sqrt{2 + 2\alpha - \cos^2(y/2)}}{(1 + \alpha \exp(-iy))}. \quad (\text{D.10})$$

Now when $l, j \gg 1$ the integral is dominated by small values of y . We may expand out the integrand for small y , and so obtain

$$I(j, l) = G_0(j, l) - G_0(1, 0) \simeq \frac{2k_B T}{(2\pi)\sqrt{1 + 2\alpha}Lm_1} \int_0^{\infty} dy \left(\cos\left(\frac{\alpha y}{1 + \alpha}\right) \exp\left(-\frac{y\sqrt{1 + 2\alpha}}{1 + \alpha}\right) - \cos(ry) \exp\left(-\frac{yj\sqrt{1 + 2\alpha}}{1 + \alpha}\right) \right) \frac{1}{y}, \quad (\text{D.11})$$

where $r = l + \alpha j / (\alpha + 1)$.

Here, it is convenient to subtract off $G_0(1, 0)$ as we shall see. We may evaluate (D.11) by differentiating (D.11), which enables us to perform the resulting integrals, and so we obtain the following differential equations:

$$\left(\frac{\partial I}{\partial j}\right)_r = \frac{2k_B T}{(2\pi)Lm_1(1 + \alpha)} \frac{\frac{\sqrt{1 + 2\alpha}}{(1 + \alpha)} j}{\frac{1 + 2\alpha}{(1 + \alpha)^2} j^2 + r^2}, \quad (\text{D.12})$$

$$\frac{\partial I}{\partial r} = \frac{2k_B T}{(2\pi)Lm_1\sqrt{1 + 2\alpha}} \frac{r}{\frac{1 + 2\alpha}{(1 + \alpha)^2} j^2 + r^2}.$$

with the boundary condition that $I(1, 0) = 0$. By solving (D.12), subject to the boundary condition, substituting for r , we find the following asymptotic form:

$$I = \frac{k_B T}{(2\pi)Lm_1\sqrt{1 + 2\alpha}} \ln\left(j^2 + l^2 + \frac{2\alpha jl}{(1 + \alpha)}\right), \quad (\text{D.13})$$

and so we are able to obtain (3.12) of the text.

We find that we are able to show that on applying (3.7), (D.2) and (C.6) and making the shift $b_n(x, y) \rightarrow b_n(x, y) - m_1 \gamma(x, y) \hat{C}(x, y; \alpha) J_n G_n(x, y)$ we may write

$$\langle \exp(in(\phi'_{jl}(z) - \phi'_{j'l}(z'))) \rangle_0 = \frac{1}{Z} \exp\left(-\frac{E_0^{\text{AF}}}{k_B T}\right) \prod_n \int \mathcal{D}b_n(x, y) \int \mathcal{D}\gamma(x, y) \times \exp\left(\sum_n \int_{-\pi}^{\pi} dx \int_{-\pi}^{\pi} dy \frac{in}{\sqrt{L}(2\pi)^2} (b_n(x, y) + \gamma(x, y) \hat{J}_n(x, y))\right)$$

$$\begin{aligned} & \times \exp\left(-\frac{1}{(2\pi)^2} \int_{-\pi}^{\pi} dx \int_{-\pi}^{\pi} dy \frac{\gamma(x, y)\gamma(-x, -y)}{2S(x, y)}\right. \\ & \left. - \frac{1}{(2\pi)^2} \sum_n \int_{-\pi}^{\pi} dx \int_{-\pi}^{\pi} dy \frac{b_n(x, y)b_{-n}(-x, -y)}{2G_n(x, y)k_B T}\right), \end{aligned} \quad (\text{D.14})$$

where $\hat{J}_n(x, y) = J_n(1 - 2m\hat{C}(x, y; \alpha)G_n(x, y))$. Now on completing the square and using (C.7) we may show (3.10).

Appendix E. Perturbation theory

The interaction energy may be expanded out to beyond quadratic order in ϕ' according to the prescription given by equations (3.6) and (4.1).

$$Z = \exp\left(-\frac{E_0^{\text{AF}}}{k_B T}\right) \prod_{jl} \int \mathcal{D}\phi'(z) \exp\left(-\frac{E_H^{\text{AF}}[\phi'] + E_L^{\text{AF}}[\phi'] + E_{AH}^{\text{AF}}[\phi']}{k_B T}\right). \quad (\text{E.1})$$

The first two terms, E_0^{AF} and $E_H^{\text{AF}}[\phi]$, are given in the text. The next term, $E_L^{\text{AF}}[\phi]$, comes from linear terms, which no longer vanish as (3.2) is no longer satisfied. This term takes the form

$$\begin{aligned} E_L^{\text{AF}}[\phi'] &= \sum_{jl} \int_{-L/2}^{L/2} dz (a_1 \sin(\psi) - 2a_2 \sin(2\psi)) ((\phi'_{jl}(z) - \phi'_{j-l}(z)) \\ & \quad + (\phi'_{jl}(z) - \phi'_{j-l-1}(z))). \end{aligned} \quad (\text{E.2})$$

The last term may be split into two pieces, $E_{AH}^{\text{AF}}[\phi'] = E_{AH}^{(1)}[\phi'] + E_{AH}^{(2)}[\phi']$, where we have

$$\begin{aligned} E_{AH}^{(1)}[\phi'] &= L \sum_{jl} \sum_{n=2}^{\infty} \int_{-L/2}^{L/2} dz \frac{1}{(2n)!} \times \{(\tilde{a}_1(-1)^{n-1} + \tilde{a}_2(-4)^n)(\phi'_{j,l}(z) - \phi'_{j+1,l-1}(z))^{2n} \\ & \quad + (a_1(-1)^{n-1} \cos(\psi) + \cos(2\psi)a_2(-4)^n)((\phi'_{j,l}(z) - \phi'_{j-1,l}(z))^{2n} \\ & \quad + (\phi'_{j,l}(z) - \phi'_{j,l-1}(z))^{2n})\}, \end{aligned} \quad (\text{E.3})$$

$$\begin{aligned} E_{AH}^{(2)}[\phi'] &= L \sum_{jl} \sum_{n=2}^{\infty} \int_{-L/2}^{L/2} dz \frac{1}{(2n-1)!} (a_1 \sin \psi (-1)^{n-1} + a_2 \sin 2\psi (-4)^n / 2) \\ & \quad \times ((\phi'_{j,l}(z) - \phi'_{j-1,l}(z))^{2n-1} + (\phi'_{j,l}(z) - \phi'_{j-1,l+1}(z))^{2n-1}). \end{aligned}$$

Here, and throughout the appendices, we adopt the convention $a_n = a_n(R_1)$ and $\tilde{a}_n = a_n(R_2)$. For the moment let us truncate these series at $n = 2$ terms. We then use the ansatz (3.7) and perform the lattice Fourier transforms given by (C.2) as well (C.4). We may then write

$$\begin{aligned} E_L^{\text{AF}}[\phi'] &= (a_1 \sin(\psi) - 2a_2 \sin(2\psi)) \sqrt{L} \lim_{\substack{x \rightarrow 0 \\ y \rightarrow 0}} [(2 - \exp(ix) - \exp(iy))b_0(x, y)], \\ E_{AH}^{(1)}[\phi'] &= -\frac{1}{4!L(2\pi)^6} \sum_{n,n',n''} \int_{-\pi}^{\pi} dx \int_{-\pi}^{\pi} dx' \int_{\pi}^{\pi} dx'' \int_{-\pi}^{\pi} dy \\ & \quad \times \int_{-\pi}^{\pi} dy' \int_{\pi}^{\pi} dy'' (g_1 F_1^{(4)}(x, x', x'', y, y', y'') \\ & \quad + g_2 F_2^{(4)}(x, x', x'', y, y', y'')) \{b_n(x, y)b_{n'}(x', y')b_{n''}(x'', y'') \\ & \quad \times b_{-n-n'-n''}(-x-x'-x'', -y-y'-y'') \\ & \quad + 4b_n(x, y)b_{n'}(x', y')b_{n''}(x'', y'')\gamma(-x-x'-x'', -y-y'-y'') \} \end{aligned}$$

$$\begin{aligned}
& \times \hat{J}_{-n-n'-n''}(-x-x'-x'', -y-y'-y'') \\
& + 6b_n(x, y)b_{n'}(x', y')\gamma(x'', y'')\gamma(-x-x'-x'', -y-y'-y'')\hat{J}_{n''}(x'', y'') \\
& \times \hat{J}_{-n-n'-n''}(-x-x'-x'', -y-y'-y'') \\
& + 4b_n(x, y)\gamma(x', y')\gamma(x'', y'')\gamma(-x-x'-x'', -y-y'-y'') \\
& \times \hat{J}_{n'}(x', y')\hat{J}_{n''}(x'', y'')\hat{J}_{-n-n'-n''}(-x-x'-x'', -y-y'-y'') \\
& + \gamma(x, y)\gamma(x', y')\gamma(x'', y'')\gamma(-x-x'-x'', -y-y'-y'') \\
& \times \hat{J}_n(x, y)\hat{J}_{n'}(x', y')\hat{J}_{n''}(x'', y'')\hat{J}_{-n-n'-n''}(-x-x'-x'', -y-y'-y'')\}, \\
E_{AH}^{(2)}[\phi'] = & -\frac{1}{3!\sqrt{L}(2\pi)^4} \sum_{n, n'} \int_{-\pi}^{\pi} dx \int_{-\pi}^{\pi} dx' \int_{-\pi}^{\pi} dy \int_{-\pi}^{\pi} dy' g^{(3)} F^{(3)}(x, x', y, y') \\
& \times \{b_n(x, y)b_{n'}(x', y')b_{-n-n'}(-x-x', -y-y') + 3\gamma(x, y) \\
& \times \hat{J}_n(x, y)b_{n'}(x', y')b_{-n-n'}(-x-x', -y-y') \\
& + 3\gamma(x, y)\gamma(x', y')\hat{J}_n(x, y)\hat{J}_{n'}(x', y')b_{-n-n'}(-x-x', -y-y') \\
& + \gamma(x, y)\gamma(x', y')\gamma(-x-x', -y-y') \\
& \times \hat{J}_n(x, y)\hat{J}_{n'}(x', y')\hat{J}_{-n-n'}(-x-x', -y-y')\}, \tag{E.4}
\end{aligned}$$

where

$$\begin{aligned}
F^{(3)}(x, x', y, y') &= (1 - \exp(-ix))(1 - \exp(-ix'))(1 - \exp(i(x+x'))) \\
& + (1 - \exp(-iy'))(1 - \exp(-iy''))(1 - \exp(i(y+y''))), \\
F_1^{(4)}(x, x', x'', y, y', y'') &= (1 - \exp(-ix))(1 - \exp(-ix'))(1 - \exp(-ix'')) \\
& \times (1 - \exp(i(x+x'+x''))) \\
& + (1 - \exp(-iy))(1 - \exp(-iy'))(1 - \exp(-iy''))(1 - \exp(i(y+y'+y''))), \\
F_2^{(4)}(x, x', x'', y, y', y'') &= (1 - \exp(-i(x-y)))(1 - \exp(-i(x'-y'))) \\
& \times (1 - \exp(-i(x''-y'')))(1 - \exp(i(x-y+x'-y'+x''-y''))), \tag{E.5}
\end{aligned}$$

$g^{(3)} = a_1 \sin \psi - 8a_2 \sin 2\psi$, $g_1^{(4)} = a_1 \cos \psi - 16a_2 \cos 2\psi$ and $g_2^{(4)} = \tilde{a}_1 - 16\tilde{a}_2$. Let us calculate the leading order correction to the Gaussian result for

$$\begin{aligned}
G_n^F(x, y) &= \exp\left(-\frac{E_0^{\text{AF}}}{k_B T}\right) \frac{1}{Z} \prod_n \int \mathcal{D}b_n(x, y) \int \mathcal{D}\gamma(x, y) b_n(x, y) b_{-n}(-x, -y) \\
& \times \exp\left(-\frac{E_H^{\text{AF}}[\phi] + E_L^{\text{AF}}[\phi] + E_{AH}^{\text{AF}}[\phi]}{k_B T}\right), \tag{E.6}
\end{aligned}$$

when we neglect $E_{AH}^{\text{AF}}[\phi]$ and set $E_L^{\text{AF}}[\phi] = 0$, in the Gaussian approximation, we find that $G_n^F(x, y) = k_B T G_n(x, y)$. We derive the leading order correction by expanding out $E_{AH}^{(1)}[\phi]$

$$\begin{aligned}
G_n^F(x, y) &= k_B T G_n(x, y) \\
& + \exp\left(-\frac{E_0^{\text{AF}}}{k_B T}\right) \frac{1}{Z} \prod_n \int \mathcal{D}b_n(x, y) \int \mathcal{D}\gamma(x, y) b_n(x, y) b_{-n}(-x, -y) \\
& \times \frac{E_{AH}^{(1)}[\phi]}{k_B T} \exp\left(-\frac{E_H^{\text{AF}}[\phi]}{k_B T}\right). \tag{E.7}
\end{aligned}$$

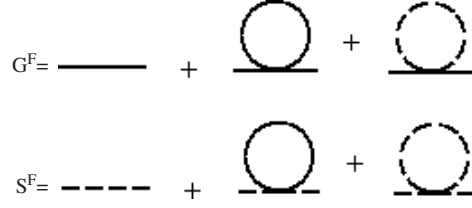


Figure E.1. Diagrammatic representations that contain the leading order corrections to the Gaussian results for the full correlation functions $G_n^F(x, y)$ and $S^F(x, y)$ defined in the text. For $G_n^F(x, y)$ the first graph on the left represents the Gaussian result, the middle graph the correction from Δ_p , and the last graph the correction from Δ_f . Similarly, for $S^F(x, y)$ the first graph on the left represents the Gaussian result, the middle graph the correction from Σ_p and the last graph the correction from Σ_f .

$E_{AH}^{(2)}[\phi]$ and $E_L^{AF}[\phi]$ do not contribute directly to the correction, but do contribute to ψ . Using standard procedures⁶, we may perform the path integrations and so obtain the following result:

$$G_n^F(x, y) = k_B T G_n(x, y) + (k_B T)^2 G_n(x, y)^2 (\Delta_p(x, y) + \Delta_f(x, y)) \quad (\text{E.8})$$

where

$$\begin{aligned} \Delta_p = & \frac{1}{2(2\pi)^2 L} \sum_n \int_{-\pi}^{\pi} dx' \int_{-\pi}^{\pi} dy' G_n(x', y') (g_1^{(4)} F_1^{(4)}(x, -x, x', y, -y, y') \\ & + g_2^{(4)} F_2^{(4)}(x, -x, x', y, -y, y')) \end{aligned} \quad (\text{E.9})$$

and

$$\begin{aligned} \Delta_f = & \frac{1}{2(2\pi)^2 L (k_B T)} \sum_n \int_{-\pi}^{\pi} dx' \int_{-\pi}^{\pi} dy' S(x', y') (g_1^{(4)} F_1^{(4)}(x, -x, x', y, -y, y') \\ & + g_2^{(4)} F_2^{(4)}(x, -x, x', y, -y, y')) \hat{J}_{-n'}(-x', -y') \hat{J}_{n'}(x', y'). \end{aligned} \quad (\text{E.10})$$

The first term represents the correction that comes purely from periodic boundary conditions and second term is the contribution from allowing both ends of the molecule to fluctuate independently of each other. Both these corrections may be represented diagrammatically in figure E.1.

We may perform the sums, which then gives us

$$\begin{aligned} \Delta_p = & \frac{\lambda_1}{2C} \left[g_1^{(4)} \chi_1 \left(\frac{L}{2\lambda_1^H}, \alpha_H \right) [(2 - 2 \cos(x)) + (2 - 2 \cos(y))] \right. \\ & \left. + g_2^{(4)} \chi_2 \left(\frac{L}{2\lambda_1^H}, \alpha_H \right) (2 - 2 \cos(x - y)) \right] \\ \Delta_f = & \frac{\lambda_1}{(2\pi)^2 C} \int_{-\pi}^{\pi} dx' \int_{-\pi}^{\pi} dy' \{ g_1^{(4)} [(2 - 2 \cos(x)) + (2 - 2 \cos(y))] (1 - \cos(x')) \\ & + g_2^{(4)} [(2 - 2 \cos(x - y)) (1 - \cos(x' - y'))] \} \left(\frac{\lambda_1}{2L} \frac{1}{\hat{C}(x', y'; \alpha)} \right. \\ & \left. - \frac{1}{4\hat{C}(x', y'; \alpha)^{1/2}} \left(\sinh \left(\frac{L\hat{C}(x', y'; \alpha)^{1/2}}{2\lambda_1} \right) \cosh \left(\frac{L\hat{C}(x', y'; \alpha)^{1/2}}{2\lambda_1} \right) \right)^{-1} \right). \end{aligned} \quad (\text{E.11})$$

⁶ The reader is referred to any text in field theoretical methods.

The functions $\chi_1(\frac{L}{2\lambda_1^H}, \alpha_H)$ and $\chi_2(\frac{L}{2\lambda_1^H}, \alpha_H)$ are given by

$$\begin{aligned}\chi_1\left(\frac{L}{2\lambda_1^H}, \alpha_H\right) &= \frac{1}{(2\pi)^2} \int_{-\pi}^{\pi} dx \int_{-\pi}^{\pi} dy \coth\left(\frac{L}{2\lambda_1^H} \hat{C}(x, y; \alpha)^{1/2}\right) \frac{(1 - \cos x)}{\hat{C}(x, y; \alpha)^{1/2}}, \\ \chi_2\left(\frac{L}{2\lambda_1^H}, \alpha_H\right) &= \frac{1}{(2\pi)^2} \int_{-\pi}^{\pi} dx \int_{-\pi}^{\pi} dy \coth\left(\frac{L}{2\lambda_1^H} \hat{C}(x, y; \alpha)^{1/2}\right) \frac{(1 - \cos(x - y))}{\hat{C}(x, y; \alpha)^{1/2}}.\end{aligned}\quad (\text{E.12})$$

We may also calculate the leading order correction to the Gaussian result for

$$\begin{aligned}S^F(x, y) &= \exp\left(-\frac{E_0^{\text{AF}}}{k_B T}\right) \frac{1}{Z} \prod_n \int \mathcal{D}b_n(x, y) \int \mathcal{D}\gamma(x, y) \gamma(x, y) \gamma(-x, -y) \\ &\quad \times \exp\left(-\frac{E_H^{\text{AF}}[\phi] + E_L^{\text{AF}}[\phi] + E_{AH}^{\text{AF}}[\phi]}{k_B T}\right).\end{aligned}\quad (\text{E.13})$$

We find that

$$S^F(x, y) = S(x, y) + S(x, y)^2 (\Sigma_p(x, y) + \Sigma_f(x, y)), \quad (\text{E.14})$$

where

$$\begin{aligned}\Sigma_p &= \frac{1}{2(2\pi)^2 L} \sum_{n, n'} \int_{-\pi}^{\pi} dx' \int_{-\pi}^{\pi} dy' G_n(x', y') (g_1^{(4)} F_1(x, -x, x', y, -y, y') \\ &\quad + g_2^{(4)} F_2(x, -x, x', y, -y, y')) \hat{J}_{n'}(x, y) \hat{J}_{-n'}(x, y), \\ \Sigma_f &= \frac{1}{2(2\pi)^2 (k_B T) L} \sum_{n, n'} \int_{-\pi}^{\pi} dx' \int_{-\pi}^{\pi} dy' S(x', y') (g_1^{(4)} F_1(x, -x, x', y, -y, y') \\ &\quad + g_2^{(4)} F_2(x, -x, x', y, -y, y')) \hat{J}_n(x', y') \hat{J}_{n'}(x', y') \hat{J}_{n''}(x, y) \hat{J}_{-n-n''}(x, y).\end{aligned}\quad (\text{E.15})$$

In figure E.1, we show how the corrections are represented diagrammatically. On evaluation of all sums we find

$$\begin{aligned}\Sigma_f &= \frac{\lambda_1^2}{2(2\pi)^2 C} \int_{-\pi}^{\pi} dx' \int_{-\pi}^{\pi} dy' (g_1^{(4)} ((2 - 2 \cos(x)) + (2 - 2 \cos(y))) (1 - \cos(x')) \\ &\quad + g_2^{(4)} (2 - 2 \cos(x - y)) (1 - \cos(x' - y'))) H\left(x, y, x', y'; \frac{\lambda_1}{L}, \alpha\right), \\ \Sigma_p &= \left(\frac{\lambda_1^2}{8C}\right) \left[\frac{1}{\hat{C}(x, y; \alpha)^{1/2}} \coth\left(\frac{L}{2\lambda_1} \hat{C}(x, y; \alpha)^{1/2}\right) \right. \\ &\quad \left. - \frac{L}{2\lambda_1} \left(\sinh\left(\frac{L}{2\lambda_1} \hat{C}(x, y; \alpha)^{1/2}\right) \right)^{-2} \right] \\ &\quad \times \frac{1}{(2\pi)^2} \int_{-\pi}^{\pi} dx' \int_{-\pi}^{\pi} dy' (g_1^{(4)} ((2 - 2 \cos(x)) \\ &\quad + (2 - 2 \cos(y))) (1 - \cos(x')) \\ &\quad + g_2^{(4)} (2 - 2 \cos(x - y)) (1 - \cos(x' - y'))) \\ &\quad \times \frac{1}{\hat{C}(x', y'; \alpha)^{1/2}} \coth\left(\frac{L \hat{C}(x', y'; \alpha)^{1/2}}{2\lambda_1}\right),\end{aligned}\quad (\text{E.16})$$

where

$$\begin{aligned}H\left(x, y, x', y'; \frac{\lambda_1}{L}, \alpha\right) &= \frac{1}{\hat{C}(x', y'; \alpha)^{1/2}} \left[\frac{1}{4} \coth\left(\frac{L \hat{C}(x, y; \alpha)^{1/2}}{2\lambda_1}\right) \right. \\ &\quad \left. \times \left[\frac{1}{\hat{C}(x', y'; \alpha) - \hat{C}(x, y; \alpha)} \left(\hat{C}(x', y'; \alpha)^{1/2} \coth\left(\frac{L \hat{C}(x, y; \alpha)^{1/2}}{\lambda_1}\right) \right) \right] \right]\end{aligned}$$

$$\begin{aligned}
& - \hat{C}(x, y; \alpha)^{1/2} \coth\left(\frac{L\hat{C}(x', y'; \alpha)^{1/2}}{\lambda_1}\right) \Big] \\
& + \frac{L}{8\lambda_1} \left(\sinh\left(\frac{L\hat{C}(x, y; \alpha)^{1/2}}{2\lambda_1}\right) \right)^{-2} \left[\frac{1}{2} \left(\sinh\left(\frac{L\hat{C}(x', y'; \alpha)^{1/2}}{2\lambda_1}\right) \right) \right. \\
& \times \cosh\left(\frac{L\hat{C}(x', y'; \alpha)^{1/2}}{2\lambda_1}\right) \Big]^{-1} - \frac{\lambda_1}{L\hat{C}(x, y; \alpha)^{1/2}} \Big] \\
& - \frac{1}{C(x, y; \alpha)^{1/2} 8} \coth\left(\frac{L\hat{C}(x, y; \alpha)^{1/2}}{2\lambda_1}\right) \left(\sinh\left(\frac{L\hat{C}(x', y'; \alpha)^{1/2}}{2\lambda_1}\right) \right) \\
& \times \cosh\left(\frac{L\hat{C}(x', y'; \alpha)^{1/2}}{2\lambda_1}\right) \Big]^{-1} \Big]. \tag{E.17}
\end{aligned}$$

Now let us determine ψ . We do this through the requirement that

$$\begin{aligned}
0 &= \frac{1}{N} \sum_{jl} \langle \phi_{jl}(z) - \phi_{jl-1}(z) \rangle = \frac{1}{(2\pi)^2 \sqrt{L}} \sum_n \exp\left(\frac{i\pi n z}{L}\right) \\
& \times \left(\lim_{\substack{x \rightarrow 0 \\ y \rightarrow 0}} \{(1 - \exp(-iy)) \langle b_n(x, y) \rangle\} \right. \\
& \left. + \lim_{\substack{x \rightarrow 0 \\ y \rightarrow 0}} \{(1 - \exp(-iy)) J_n(\gamma(x, y))\} \right). \tag{E.18}
\end{aligned}$$

Again, in the Gaussian approximation we may neglect $E_{AH}^{\text{AF}}[\phi]$. Equation (E.18) is then satisfied by requiring that

$$0 = \Gamma_1 = - \lim_{\substack{x \rightarrow 0 \\ y \rightarrow 0}} \{(2 - 2 \cos y) G_0(x, y)\} (a_1 \sin \psi_0 - 2a_2 \sin 2\psi_0). \tag{E.19}$$

This implies that ψ_0 or $\psi_0 = \arccos(a_1/(4a_2))$, where ψ_0 is ψ for the Gaussian approximation, for Γ_1 to vanish.

When we go beyond the Gaussian approximation to leading order in perturbation theory we find that Γ_1 becomes

$$\begin{aligned}
\Gamma_1^F &= - \lim_{\substack{x \rightarrow 0 \\ y \rightarrow 0}} \{(2 - 2 \cos y) G_0(x, y)\} (a_1 \sin \psi - 2a_2 \sin 2\psi) \\
& - \lim_{\substack{x \rightarrow 0 \\ y \rightarrow 0}} \{(2 - 2 \cos y) G_0(x, y)\} (a_1 \sin \psi - 8a_2 \sin 2\psi) (\Gamma'_p + \Gamma'_f), \tag{E.20}
\end{aligned}$$

where

$$\begin{aligned}
\Gamma'_p &= \frac{k_B T}{2(2\pi)^2 L} \sum_n \int_{-\pi}^{\pi} dx' \int_{-\pi}^{\pi} dy' (2 - 2 \cos y') G_n(x', y'), \\
\Gamma'_f &= \frac{1}{2(2\pi)^2 L} \sum_n \int_{-\pi}^{\pi} dx' \int_{-\pi}^{\pi} dy' S(x', y') (2 - 2 \cos(y')) \hat{J}_n(x', y') \hat{J}_{-n}(-x', -y'). \tag{E.21}
\end{aligned}$$

Again, the first term, Γ'_p , arises purely from periodic boundary conditions and Γ'_f is the contribution from allowing the ends to fluctuate independently of each other. Both these terms may be represented diagrammatically in figure E.2.

We may compute the leading order correction to ψ setting $\Gamma_1 = 0$ by writing $\psi = \psi_0 + \psi'$ and expanding out for small ψ' . We may also perform the summations in both Γ'_p and Γ'_f . We find that

$$\psi' = - \frac{(a_1 \sin \psi_0 - 8a_2 \sin 2\psi_0)}{(a_1 \cos \psi_0 - 4a_2 \cos 2\psi_0)} (\Gamma'_p + \Gamma'_f), \tag{E.22}$$

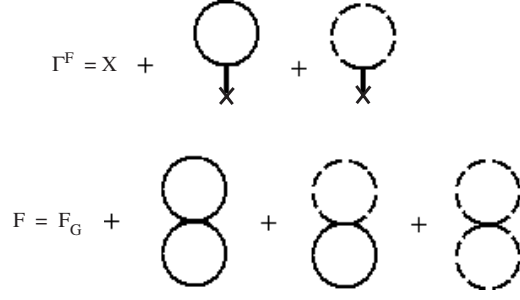


Figure E.2. Diagrammatic representations that contain the leading order corrections to the Gaussian results for $\Gamma_1^f(x, y)$ and the free energy F defined in the text. For $\Gamma_1^f(x, y)$ the first graph on the left represents the Gaussian result, the middle graph the correction from Δ_p , and the last graph the correction from Δ_f . For F the first graph on the left represents the Gaussian result. The next graph along is G_1 , that arises purely from periodic boundary conditions. Third from the left is G_2 and the last is G_3 . These terms are corrections due to free boundary conditions.

where now

$$\begin{aligned} \Gamma'_p &= \frac{\lambda_1}{4\lambda_p} \chi_1 \left(\frac{L}{2\lambda_1^H}, \alpha_H \right), \\ \Gamma'_f &= \frac{\lambda_1^2}{(2\pi)^2 4\lambda_p L} \int_{-\pi}^{\pi} dx' \int_{-\pi}^{\pi} dy' (1 - \cos(y')) \left[\frac{1}{\hat{C}(x', y'; \alpha)} - \frac{L}{2\lambda_1} \frac{1}{\hat{C}(x', y'; \alpha)^{1/2}} \right. \\ &\quad \left. \times \left(\sinh \left(\frac{L\hat{C}(x', y'; \alpha)^{1/2}}{2\lambda_1} \right) \cosh \left(\frac{L\hat{C}(x', y'; \alpha)^{1/2}}{2\lambda_1} \right) \right)^{-1} \right]. \end{aligned} \quad (\text{E.23})$$

We may also look at corrections to the free energy. We may write $F = F_G - k_B T \Delta F$ where F_G is F evaluated in the Gaussian approximation (cf (C.10)) and ΔF is the correction. We find for ΔF

$$\begin{aligned} \Delta F &= G_1 + G_2 + G_3, \\ G_1 &= \frac{1}{8} \frac{k_B T}{L(2\pi)^4} \sum_{n, n'} \int_{-\pi}^{\pi} dx \int_{-\pi}^{\pi} dy \int_{-\pi}^{\pi} dx' \int_{-\pi}^{\pi} dy' G_n(x, y) G_{n'}(x', y') \\ &\quad \times (g_1^{(4)} F_1^{(4)}(x, -x, x', y, -y, y') + g_2^{(4)} F_2^{(4)}(x, -x, x', y, -y, y')), \\ G_2 &= \frac{1}{4} \frac{1}{L(2\pi)^4} \sum_{n, n'} \int_{-\pi}^{\pi} dx \int_{-\pi}^{\pi} dy \int_{-\pi}^{\pi} dx' \\ &\quad \times \int_{-\pi}^{\pi} dy' S(x, y) G_{n'}(x', y') \hat{J}_n(x, y) \hat{J}_{-n}(x, y) \\ &\quad \times (g_1^{(4)} F_1^{(4)}(x, -x, x', y, -y, y') + g_2^{(4)} F_2^{(4)}(x, -x, x', y, -y, y')), \\ G_3 &= \frac{1}{8} \frac{1}{k_B T L(2\pi)^4} \sum_{n, n', n''} \int_{-\pi}^{\pi} dx \int_{-\pi}^{\pi} dy \int_{-\pi}^{\pi} dx' \\ &\quad \times \int_{-\pi}^{\pi} dy' S(x, y) S(x', y') \hat{J}_n(x, y) \hat{J}_{n'}(x, y) \hat{J}_{n''}(x', y') \\ &\quad \times \hat{J}_{-n-n'-n''}(x', y') (g_1^{(4)} F_1^{(4)}(x, -x, x', y, -y, y') \\ &\quad + g_2^{(4)} F_2^{(4)}(x, -x, x', y, -y, y')). \end{aligned} \quad (\text{E.24})$$

These corrections are represented graphically in figure E.2. The sums may, again, be evaluated, yielding the following expressions:

$$\begin{aligned}
G_1 &= \frac{L}{8} \frac{k_B T}{(2\pi)^4} \left(\frac{\lambda_1}{C}\right)^2 \left[2g_1^{(4)} \chi_1 \left(\frac{L}{2\lambda_1^H}, \alpha_H\right)^2 + g_2^{(4)} \chi_2 \left(\frac{L}{2\lambda_1^H}, \alpha_H\right)^2 \right], \\
G_2 &= \frac{L}{2} \frac{k_B T}{(2\pi)^4} \left(\frac{\lambda_1}{C}\right)^2 \int_{-\pi}^{\pi} dx \int_{-\pi}^{\pi} dy \int_{-\pi}^{\pi} dx' \int_{-\pi}^{\pi} dy' (2g_1^{(4)} (1 - \cos x)(1 - \cos x') \\
&\quad + g_2^{(4)} (1 - \cos(x - y))(1 - \cos(x' - y'))) \\
&\quad \times \frac{1}{\hat{C}(x, y; \alpha)^{1/2}} \coth\left(\frac{L\hat{C}(x, y; \alpha)^{1/2}}{2\lambda_1}\right) \\
&\quad \times \left[\frac{\lambda_1}{2L} \frac{1}{\hat{C}(x', y'; \alpha)} - \frac{1}{4} \frac{1}{\hat{C}(x', y'; \alpha)^{1/2}} \right. \\
&\quad \left. \times \left(\sinh\left(\frac{LC(x', y'; \alpha)^{1/2}}{2\lambda_1}\right) \cosh\left(\frac{LC(x', y'; \alpha)^{1/2}}{2\lambda_1}\right) \right)^{-1} \right], \\
G_3 &= \frac{1}{4} \frac{\lambda_1^2}{C(2\pi)^4} \int_{-\pi}^{\pi} dx \int_{-\pi}^{\pi} dy \int_{-\pi}^{\pi} dx' \int_{-\pi}^{\pi} dy' [2g_1^{(4)} (1 - \cos x)(1 - \cos x') \\
&\quad + g_2^{(4)} (1 - \cos(x - y))(1 - \cos(x' - y'))] S(x, y) H\left(x, y, x', y'; \frac{L}{\lambda_1}, \alpha\right).
\end{aligned} \tag{E.25}$$

In $G_n^F(x, y)$, $S^F(x, y)$ and F there are additional corrections that come from inserting ψ into $G_n(x, y)$ and $S(x, y)$ and F_G ; then expanding these terms out to leading order in ψ' . For the purposes of illustration we will show

$$\begin{aligned}
G_n^F(x, y) &= k_B T G_n(x, y) + (k_B T)^2 [\Delta_f^H + [(2 - 2 \cos(x)) \\
&\quad + (2 - 2 \cos(y))] \psi' (a_1 \sin \psi_0 - 8a_2 \sin 2\psi_0) / (k_B T)] G_n(x, y)^2.
\end{aligned} \tag{E.26}$$

Appendix F. Derivation of self-consistent approximation for periodic boundary conditions

Now, for the moment, let us concentrate on periodic boundary conditions and set $\Gamma(x, y) = 0$. We may represent each term in the perturbation theory diagrammatically. The Feynman rules, the correspondence between a graph and its algebraic expression, are now given. On expanding out $E[\phi(k)]$ we need three types of diagrams (or vertices) to represent each ϕ^n -term in this expansion, for $n > 0$. The Feynman rules are similar to those given in appendix A of [20], but with a few modifications⁷. They are as follows. Each graph will contain N_F vertices, all of which will be connected to each other by lines. We assign a label $i = 1 \dots N_V$ to each vertex. For each vertex i , representing ϕ^n , we must write down for a type 1 or 2 vertex

$$\begin{aligned}
&(a_1 (-1)^{n/2-1} \cos(\psi) + a_2 (-4)^{n/2} \cos(2\psi)) \delta_{-k_1^i, k_{2n}^i + k_{2n-1}^i + \dots + k_2^i} / n! \quad \text{when } n \text{ is even} \\
&\left(a_1 (-1)^{(n+1)/2-1} \sin(\psi) + a_2 \frac{(-4)^{(n+1)/2}}{2} \sin(2\psi) \right) \delta_{-k_1^i, k_{2n}^i + k_{2n-1}^i + \dots + k_2^i} / n! \quad \text{when } n \text{ is odd}
\end{aligned} \tag{F.1}$$

and either one of the ‘form’ factors

$$\prod_{m=1}^n (1 - e^{-ix_m^i}), \quad \prod_{m=1}^n (1 - e^{-iy_m^i}), \tag{F.2}$$

⁷ There was a mistake in the Feynman rules stated in [20], namely each vertex represents ϕ^{2n} not ϕ^n . However, the correct expression for the Hartree result was obtained in appendix A of [20].

depending on whether the vertex is type 1 or 2, respectively. For a type 3 vertex, n is allowed only to be even, and we write down

$$(\tilde{a}_1(-1)^{n/2-1} + \tilde{a}_2(-4)^{n/2})\delta_{-k_1^i, k_{2n}^i + k_{2n-1}^i + \dots + k_2^i} / n!, \quad (\text{F.3})$$

multiplied by the form factor

$$\prod_{m=1}^n (1 - e^{-i(x_m^i - y_m^i)}). \quad (\text{F.4})$$

Each full Feynman graph will also consist of N_E external lines (connected to only one vertex) each associated with a wave vector $\vec{q}_j = (x_j/r_0, y_j/r_0, 2\pi n_j/L)$ ($j = 1, \dots, N_E$). For each of these external lines we write down $G_{n_i}(x_i, y_i)$ and set $\vec{k}_m^i = \vec{q}_j$ for one of the $\vec{k}_m^i = (x_m^i/r_0, y_m^i/r_0, 2\pi n_m^i/L)$ in the vertex to which the line is connected. There will also be N_I internal lines, each associated with a wavevector \vec{p}_k ($k = 1, \dots, N_I$), where each end is connected to two vertices, i and i' . For each of these internal lines we write down $G(\vec{p}_k)$ and set $\vec{k}_m^i = \vec{k}_m^{i'} = \vec{p}_j$ for one of the \vec{k}_m^i in each of the two vertices. Then all the wavevectors for the internal lines are summed over. Last of all, there is also a symmetry factor that multiplies this, which accounts for how many ways a term (graph) in the expansion may be generated. If we restrict the wavevectors to the form $\vec{q}_j = (x_j/r_0, y_j/r_0)$ we get back the results for the rigid body case [20].

To obtain the Hartree approximation we first consider the same set of graphs as for appendix A of [20] as contributions to the full correlation function. The sum of these graphs we denote by $G_{1n}(x, y)$. These form a series which we may easily sum

$$\begin{aligned} \frac{k_B T G_{1n}^{-1}(x, y)}{C} &= \left(\frac{2\pi n}{L}\right)^2 + \left(\lambda_{1,1}\left(\frac{L}{\lambda_1}, \alpha, \frac{\lambda_1}{\lambda_p}\right)\right)^{-2} ((1 - \cos x) + (1 - \cos y)) \\ &+ \left(\lambda_{2,1}\left(\frac{L}{\lambda_1}, \alpha, \frac{\lambda_1}{\lambda_p}\right)\right)^{-2} (1 - \cos(x - y)), \end{aligned} \quad (\text{F.5})$$

where

$$\begin{aligned} \lambda_{1,1}\left(\frac{L}{\lambda_1}, \alpha, \frac{\lambda_1}{\lambda_p}\right) &= \sqrt{\frac{C}{2\left(a_1 \cos(\psi) \exp\left(-\frac{\lambda_1 \chi_1(L/(2\lambda_1), \alpha)}{4\lambda_p}\right) - 4a_2 \cos(2\psi) \exp\left(-\frac{\lambda_1 \chi_1(L/(2\lambda_1), \alpha)}{\lambda_p}\right)\right)}}} \\ \lambda_{2,1}\left(\frac{L}{\lambda_1}, \alpha, \frac{\lambda_1}{\lambda_p}\right) &= \sqrt{\frac{C}{2\left(\tilde{a}_1 \exp\left(-\frac{\lambda_1 \chi_2(L/(2\lambda_1), \alpha)}{4\lambda_p}\right) - 4\tilde{a}_2 \exp\left(-\frac{\lambda_1 \chi_2(L/(2\lambda_1), \alpha)}{\lambda_p}\right)\right)}}}, \end{aligned} \quad (\text{F.6})$$

In the same procedure as discussed in appendix A of [20], we may replace G_n in each loop (of our diagrammatic series) with G_{1n} . Now, G_{1n} will be replaced on the lhs of (F.5) with a new correlation function G_{2n} . On the rhs of (F.5) we replace $\lambda_{1,1}$ with $\lambda_{1,2}$ and $\lambda_{2,1}$ with $\lambda_{2,2}$. Expressions for $\lambda_{1,2}$ and $\lambda_{2,2}$ are similar to (F.6), but with λ replaced by $\lambda_{1,1}$ and α replaced by $\alpha_1 = (\lambda_{1,1}/\lambda_{2,1})^2$. We then keep iterating this process until we have $\lambda_1^H = \lambda_{1,\infty} = \lambda_{1,\infty-1}$, $\lambda_2^H = \lambda_{2,\infty} = \lambda_{2,\infty-1}$ and $\alpha_H = (\lambda_1^H/\lambda_2^H)^2$, so obtain equation (4.3) of the text. Through the same reasoning as was discussed in appendix B of [20], we find that $\psi = \psi_H$ where

$$\cos \psi_H = \frac{a_1}{4a_2} \exp\left(\frac{3\lambda_1 \chi_1(L/(2\lambda_1), \alpha)}{4\lambda_p}\right). \quad (\text{F.7})$$

To calculate the free energy we consider the same set of graphs as those considered for free energy in [20]. To get the free energy in the Hartree approximation we then renormalize

the sum of these graphs, by taking care in replacing λ_1 with λ_1^H , λ_2 with λ_2^H , and α with α_H ; and so arrive at equation (4.2) of the text.

Appendix G. Correction to self-consistent approximation for periodic boundary conditions from freely fluctuating ends

To calculate the corrections arising from free fluctuating ends we must utilize the results of both the previous two appendices. We perform a renormalization where we replace $\lambda_1, \lambda_2, \alpha$ and ψ_0 with $\lambda_1^H, \lambda_2^H, \alpha_H$ and ψ_H in the results of appendix E. The renormalization process relies on counter-terms, which take care of terms already included in $\lambda_1^H, \lambda_2^H, \alpha_H$ and ψ_H , to prevent over-counting. In the interests of brevity we will not discuss this process of renormalization; instead, we refer those not acquainted with such processes to a standard text in field theoretical methods.

The first quantity to consider is ψ' , which on renormalization becomes

$$\psi'_H = -\frac{(a_1 \sin \psi_H - 8a_2 \sin 2\psi_H)}{(a_1 \cos \psi_H - 4a_2 \cos 2\psi_H)}(\Gamma'_f{}^H), \quad (\text{G.1})$$

where

$$\Gamma'_f{}^H = \frac{(\lambda_1^H)^2}{4(2\pi)^2 \lambda_p L} \int_{-\pi}^{\pi} dx' \int_{-\pi}^{\pi} dy' (1 - \cos(y')) \left[\frac{1}{\hat{C}(x', y'; \alpha_H)} - \frac{L}{2\lambda_1} \frac{1}{\hat{C}(x', y'; \alpha_H)^{1/2}} \right. \\ \left. \left(\sinh\left(\frac{L\hat{C}(x', y'; \alpha_H)^{1/2}}{2\lambda_1^H}\right) \cosh\left(\frac{L\hat{C}(x', y'; \alpha_H)^{1/2}}{2\lambda_1^H}\right) \right)^{-1} \right]. \quad (\text{G.2})$$

It is important to notice that there is no $\Gamma'_p{}^H$; this is because such a term is already accounted for in ψ_H . On renormalization, a counter-term removes this term.

Let us next consider $G_n^F(x, y)$; to obtain the correction from free boundary conditions we perform a renormalization of (E.8), where we obtain

$$G_n^{F,R}(x, y) = k_B T G_n^H(x, y) + (k_B T)^2 G_n^H(x, y)^2 (\Delta_f^H + [(2 - 2 \cos(x) + (2 - 2 \cos(y)) \\ \times \psi'_H (a_1 \sin \psi_H - 8a_2 \sin 2\psi_H) / (k_B T)), \quad (\text{G.3})$$

where

$$\Delta_f^H = [(2 - 2 \cos(x)) + (2 - 2 \cos(y))] \Delta_f^{1,H} + (2 - 2 \cos(x - y)) \Delta_f^{2,H}, \\ \Delta_f^{1,H} = \frac{\lambda_1^H g_1^{(4)}}{(2\pi)^2 C} \int_{-L/2}^{L/2} dx' \int_{-L/2}^{L/2} dy' (1 - \cos x') \left(\frac{\lambda_1^H}{2L} \frac{1}{\hat{C}(x', y'; \alpha_H)} - \frac{1}{4\hat{C}(x', y'; \alpha_H)^{1/2}} \right. \\ \left. \times \left(\sinh\left(\frac{L\hat{C}(x', y'; \alpha_H)^{1/2}}{2\lambda_1^H}\right) \cosh\left(\frac{L\hat{C}(x', y'; \alpha_H)^{1/2}}{2\lambda_1^H}\right) \right)^{-1} \right), \\ \Delta_f^{2,H} = \frac{\lambda_1^H g_2^{(4)}}{(2\pi)^2 C} \int_{-\pi}^{\pi} dx' \int_{-\pi}^{\pi} dy' (1 - \cos(x' - y')) \left(\frac{\lambda_1^H}{2L} \frac{1}{\hat{C}(x', y'; \alpha_H)} \right. \\ \left. - \frac{1}{4\hat{C}(x', y'; \alpha_H)^{1/2}} \left(\sinh\left(\frac{L\hat{C}(x', y'; \alpha_H)^{1/2}}{2\lambda_1^H}\right) \right. \right. \\ \left. \left. \times \cosh\left(\frac{L\hat{C}(x', y'; \alpha_H)^{1/2}}{2\lambda_1^H}\right) \right)^{-1} \right), \quad (\text{G.4})$$

and

$$\frac{k_B T G_n^H(x, y)^{-1}}{C} = \left(\frac{2\pi n}{L} \right)^2 + (\lambda_1^H)^{-2} ((1 - \cos x) + (1 - \cos y)) \\ + (\lambda_2^H)^{-2} (1 - \cos(x - y)). \quad (\text{G.5})$$

There is no Δ_p^H ; this is because such a term is already accounted for in $G_n^H(x, y)$, so is removed on renormalization. We may go further and make the approximation that

$$\begin{aligned} G_n^{F,R}(x, y) &\simeq k_B T G_n^H(x, y) + (k_B T)^2 G_n^H(x, y)^2 (\Delta_f^H + [(2 - 2 \cos(x) \\ &\quad + (2 - 2 \cos(y)) \psi'_H (a_1 \sin \psi_H - 8a_2 \sin 2\psi_H) / (k_B T)) \\ &\quad + (k_B T)^3 G_n^H(x, y)^3 (\Delta_f^H + [(2 - 2 \cos(x) + (2 - 2 \cos(y))] \\ &\quad \times \psi'_H (a_1 \sin \psi_H - 8a_2 \sin 2\psi_H) / (k_B T))^2 + \dots \\ &\simeq k_B T G_n^H(x, y) + (k_B T)^2 (\Delta_f^H + [(2 - 2 \cos(x) \\ &\quad + (2 - 2 \cos(y)) \psi'_H (a_1 \sin \psi_H - 8a_2 \sin 2\psi_H) / (k_B T)) \\ &\quad \times G_n^H(x, y) G_n^{F,R}(x, y). \end{aligned} \quad (\text{G.6})$$

From (G.6) we may write

$$\begin{aligned} \frac{k_B T G_n^{F,R}(x, y)^{-1}}{C} &= \left(\frac{2\pi n}{L} \right)^2 \\ &\quad + (\lambda_1^F)^{-2} ((1 - \cos x) + (1 - \cos y)) + (\lambda_2^F)^{-2} (1 - \cos(x - y)), \end{aligned} \quad (\text{G.7})$$

where

$$\begin{aligned} (\lambda_1^F)^{-2} &= (\lambda_1^H)^{-2} - 2C^{-1} (k_B T \Delta_f^{1,H} + \psi'_H (a_1 \sin \psi_H - 8a_2 \sin 2\psi_H)) \\ (\lambda_2^F)^{-2} &= (\lambda_2^H)^{-2} - 2C^{-1} k_B T \Delta_f^{2,H}. \end{aligned} \quad (\text{G.8})$$

Now, we renormalize $S^F(x, y)$

$$\begin{aligned} S^{F,R}(x, y) &= S^H(x, y) + S^H(x, y)^2 \left(\Sigma_f^H - \frac{(a_1 \sin \psi_H - 8a_2 \sin 2\psi_H) \psi'_H \lambda_1^H}{2k_B T} \right. \\ &\quad \times [(1 - \cos x) + (1 - \cos y)] \\ &\quad \times \left(\frac{L}{2\lambda_1^R} \left(\sinh \left(\frac{L \hat{C}(x, y; \alpha)^{1/2}}{2\lambda_1^R} \right) \right)^{-2} \right. \\ &\quad \left. \left. - \frac{1}{\hat{C}(x, y; \alpha)} \coth \left(\frac{L \hat{C}(x, y; \alpha)^{1/2}}{2\lambda_1^R} \right) \right) \right), \\ \Sigma_f^H &= \frac{(\lambda_1^H)^2}{2(2\pi)^2 C} \int_{-\pi}^{\pi} dx' \int_{-\pi}^{\pi} dy' (g_1^{(4)} ((2 - 2 \cos(x)) + (2 - 2 \cos(y)) (1 - \cos(x')) \\ &\quad + g_2^{(4)} (2 - 2 \cos(x - y)) (1 - \cos(x' - y')))) H \left(x, y, x', y'; \frac{\lambda_1^H}{L}, \alpha_H \right). \end{aligned} \quad (\text{G.9})$$

There is no Σ_p^H because such a term is already accounted for in $S^F(x, y)$.

We may also renormalize the free energy. The free energy then becomes $F_T = F_H + F_F + \Delta F$, where

$$\begin{aligned} F_F &= \frac{k_B T}{2(2\pi)^2} \int_{-\pi}^{\pi} dx \int_{-\pi}^{\pi} dy \ln \left(\frac{\lambda_p}{\lambda_1^H} \left(\frac{\hat{C}(x, y; \alpha_H)}{\hat{C}(x, y; 1)} \right)^{1/2} \coth \left(\frac{\hat{C}(x, y; \alpha_H)^{1/2} L}{2\lambda_1^H} \right) \right), \\ \Delta F &= -L (\psi'_H)^2 m_1 - k_B T G_3^H, \end{aligned} \quad (\text{G.10})$$

and

$$\begin{aligned} G_3^H &= \frac{1}{4} \frac{(\lambda_1^H)^2}{C(2\pi)^4} \int_{-\pi}^{\pi} dx \int_{-\pi}^{\pi} dy \int_{-\pi}^{\pi} dx' \int_{-\pi}^{\pi} dy' [2g_1^{(4)} (1 - \cos x) (1 - \cos x') \\ &\quad + g_2^{(4)} (1 - \cos(x - y)) (1 - \cos(x' - y'))] \\ &\quad \times S(x, y) H \left(x, y, x', y'; \frac{L}{\lambda_1^H}, \alpha_H \right). \end{aligned} \quad (\text{G.11})$$

We may also calculate correlation functions within this approximation scheme. Here, we may use the results of the previous section, but we now make the following replacements: λ_1 is replaced by λ_1^F , α is replaced by $\alpha_F = (\lambda_1^F/\lambda_2^F)^2$ and $S(x, y)$ is replaced by $S^{F,R}(x, y)$.

Appendix H. High temperature expansion

We start the analysis of this appendix by dividing (3.1) into three terms

$$E[\phi] = E_{\text{int}}^0 + E'_{\text{int}}[\phi] + E_T[\phi], \quad (\text{H.1})$$

where

$$\begin{aligned} E_{\text{int}}^0 &= 3a_0(R_1), \\ E'_{\text{int}}[\phi] &= \int_{-L/2}^{L/2} dz \sum_{j,l} \sum_{m=1}^{\infty} [(-1)^m a_m(R_1) (\cos(m(\phi_{jl}(z) - \phi_{j+1l-1}(z))) \\ &\quad + \cos(m(\phi_{jl}(z) - \phi_{j-1l}(z))) + \cos(m(\phi_{jl}(z) - \phi_{j-1l}(z))))], \\ E_T[\phi] &= \int_{-L/2}^{L/2} dz \sum_{j,l} \frac{C}{2} \left(\frac{d\phi_{jl}(z)}{dz} \right)^2. \end{aligned} \quad (\text{H.2})$$

First, let us look at the high temperature expansion of the free energy. We start by expanding out the partition function in the following way:

$$Z = \exp\left(-\frac{E_{\text{int}}^0}{k_B T}\right) \prod_{jl} \int \mathcal{D}\phi_{jl}(z) \left(1 - \frac{E'_{\text{int}}[\phi]}{k_B T} + \frac{1}{2} \left(\frac{E'_{\text{int}}[\phi]}{k_B T}\right)^2 + \dots\right) \exp\left(-\frac{E_T[\phi]}{k_B T}\right). \quad (\text{H.3})$$

From this expansion the lowest order terms in Z that depend on the coefficients a_n are

$$\begin{aligned} Z_1^m &= \frac{a_m^2}{2(k_B T)^2} \exp\left(-\frac{E_{\text{int}}^0}{k_B T}\right) \prod_{j,l} \int \mathcal{D}\phi_{jl}^p(z) \int d\gamma_{jl} \int d\phi_{jl}^0 \sum_{j',l'} \sum_{j'',l''} \int_{-L/2}^{L/2} dz \int_{-L/2}^{L/2} dz' \\ &\quad \times \left[\cos\left(m\left(\tilde{\phi}_{j'l'}^p(z) - \tilde{\phi}_{j'-1l'}^p(z) + \frac{z}{L}(\gamma_{j'l'} - \gamma_{j'-1l'}) + \phi_{j'l'}^0 - \phi_{j'-1l'}^0\right)\right) \right. \\ &\quad + \cos\left(m\left(\tilde{\phi}_{j'l'}^p(z) - \tilde{\phi}_{j'l'-1}^p(z) + \frac{z}{L}(\gamma_{j'l'} - \gamma_{j'l'-1}) + \phi_{j'l'}^0 - \phi_{j'l'-1}^0\right)\right) \\ &\quad + \cos\left(m\left(\tilde{\phi}_{j'l'}^p(z) - \tilde{\phi}_{j'+1l'-1}^p(z) + \frac{z}{L}(\gamma_{j'l'} - \gamma_{j'+1l'-1}) + \phi_{j'l'}^0 - \phi_{j'+1l'-1}^0\right)\right) \left. \right] \\ &\quad \times \left[\cos\left(m\left(\tilde{\phi}_{j''l''}^p(z') - \tilde{\phi}_{j''-1l''}^p(z') + \frac{z'}{L}(\gamma_{j''l''} - \gamma_{j''-1l''}) + \phi_{j''l''}^0 - \phi_{j''-1l''}^0\right)\right) \right. \\ &\quad + \cos\left(m\left(\tilde{\phi}_{j''l''}^p(z') - \tilde{\phi}_{j''l''-1}^p(z') + \frac{z'}{L}(\gamma_{j''l''} - \gamma_{j''l''-1}) + \phi_{j''l''}^0 - \phi_{j''l''-1}^0\right)\right) \\ &\quad + \cos\left(m\left(\tilde{\phi}_{j''l''}^p(z') - \tilde{\phi}_{j''+1l''-1}^p(z') \right. \right. \\ &\quad \left. \left. + \frac{z'}{L}(\gamma_{j''l''} - \gamma_{j''+1l''-1}) + \phi_{j''l''}^0 - \phi_{j''+1l''-1}^0\right)\right) \left. \right] \exp\left(-\frac{E_T[\phi]}{k_B T}\right), \end{aligned} \quad (\text{H.4})$$

where we have employed (3.7) of the text, but now separating out the rigid body mode ϕ_{jl}^0 so that $\phi_{jl}^p(z) = \tilde{\phi}_{jl}^p(z) + \phi_{jl}^0$, and the spatial average of $\tilde{\phi}_{jl}^p(z)$ along the length of the molecule is zero. We find that only a few of these terms survive integration over the rigid body modes.

$$Z_1^m = \frac{a_m^2 (2\pi)^N}{4(k_B T)^2} \exp\left(-\frac{E_{\text{int}}^0}{k_B T}\right) \prod_{j,l} \int \mathcal{D}\phi_{jl}^p(z) \int d\gamma_{jl} \sum_{j',l'} \int_{-L/2}^{L/2} dz$$

$$\begin{aligned}
& \times \int_{-L/2}^{L/2} dz' \exp\left(-\frac{E_T[\phi]}{k_B T}\right) \\
& \times [\cos(m(\tilde{\phi}_{j'l'}^p(z) - \tilde{\phi}_{j'l'}^p(z') - \tilde{\phi}_{j'-1l'}^p(z) + \tilde{\phi}_{j'-1l'}^p(z') \\
& + (z - z')(\gamma_{j'l'} - \gamma_{j'-1l'})/L)) \\
& + \cos(m(\tilde{\phi}_{j'l'}^p(z) - \tilde{\phi}_{j'l'}^p(z') - \tilde{\phi}_{j'l'-1}^p(z) + \tilde{\phi}_{j'l'-1}^p(z') \\
& + (z - z')(\gamma_{j'l'} - \gamma_{j'l'-1})/L)) \\
& + \cos(m(\tilde{\phi}_{j'l'}^p(z) - \tilde{\phi}_{j'l'}^p(z') - \tilde{\phi}_{j'+1l'-1}^p(z) \\
& + \tilde{\phi}_{j'+1l'-1}^p(z') + (z - z')(\gamma_{j'l'} - \gamma_{j'+1l'-1})/L))]. \tag{H.5}
\end{aligned}$$

Now we may rewrite $E_T[\phi]$ as $E_T = E_T^f + E_T^p$ where

$$E_T^f = \sum_{j,l} \frac{C}{2L} \gamma_{jl}^2 \quad \text{and} \quad E_T^p = \sum_{j,l} \frac{C}{2} \left(\frac{d\tilde{\phi}_{jl}^p}{dz}\right)^2. \tag{H.6}$$

We find that we may then write the following expansion of Z :

$$\begin{aligned}
\ln Z & \simeq \ln Z_0 + \sum_m Z_1^m / Z_0 + \dots, \\
\frac{Z_1^m}{Z_0} & = \frac{a_n^2}{4(k_B T)^2} \sum_{j,l'} \int_{-L/2}^{L/2} dz \int_{-L/2}^{L/2} dz' \exp\left(-\frac{E_T[\phi]}{k_B T}\right) \\
& \times [\langle \cos(m(\tilde{\phi}_{j'l'}^p(z) - \tilde{\phi}_{j'l'}^p(z') - \tilde{\phi}_{j'-1l'}^p(z) + \tilde{\phi}_{j'-1l'}^p(z'))) \rangle_{E_T^p} \\
& \times \langle \cos(m((z - z')(\gamma_{j'l'} - \gamma_{j'-1l'})/L)) \rangle_{E_T^f} \\
& + \langle \cos(m(\tilde{\phi}_{j'l'}^p(z) - \tilde{\phi}_{j'l'}^p(z') - \tilde{\phi}_{j'l'-1}^p(z) \\
& + \tilde{\phi}_{j'l'-1}^p(z'))) \rangle_{E_T^p} \langle \cos(m((z - z')(\gamma_{j'l'} - \gamma_{j'l'-1})/L)) \rangle_{E_T^f} \\
& + \langle \cos(m(\tilde{\phi}_{j'l'}^p(z) - \tilde{\phi}_{j'l'}^p(z') - \tilde{\phi}_{j'+1l'-1}^p(z) \\
& + \tilde{\phi}_{j'+1l'-1}^p(z'))) \rangle_{E_T^p} \langle \cos(m((z - z')(\gamma_{j'l'} - \gamma_{j'+1l'-1})/L)) \rangle_{E_T^f}] \tag{H.7}
\end{aligned}$$

where

$$\begin{aligned}
& \langle \cos(m(\tilde{\phi}_{j'l'}^p(z) - \tilde{\phi}_{j'l'}^p(z') - \tilde{\phi}_{j'-1l'}^p(z) + \tilde{\phi}_{j'-1l'}^p(z'))) \rangle_{E_T^p} \\
& = \left[\prod_{j,l} \int \mathcal{D}\phi_{jl}^p(z) \cos(m(\tilde{\phi}_{j'l'}^p(z) - \tilde{\phi}_{j'l'}^p(z') - \tilde{\phi}_{j'-1l'}^p(z) + \tilde{\phi}_{j'-1l'}^p(z'))) \right. \\
& \quad \times \exp\left(-\frac{E_T^p[\phi]}{k_B T}\right) \left. \right] \left[\prod_{j,l} \int \mathcal{D}\phi_{jl}^p(z) \exp\left(-\frac{E_T^p[\phi]}{k_B T}\right) \right]^{-1}, \tag{H.8} \\
& \left\langle \cos\left(m\left(\frac{(z - z')}{L}(\gamma_{j'l'} - \gamma_{j'-1l'})\right)\right) \right\rangle_{E_T^p} \\
& = \frac{\prod_{j,l} \int d\gamma_{jl} \cos\left(m\left(\frac{(z - z')}{L}(\gamma_{j'l'} - \gamma_{j'-1l'})\right)\right) \exp\left(-\frac{E_T^f[\phi]}{k_B T}\right)}{\prod_{j,l} \int d\gamma_{jl} \exp\left(-\frac{E_T^f[\phi]}{k_B T}\right)}.
\end{aligned}$$

The term $\langle \cos(m((z - z')(\gamma_{j'l'} - \gamma_{j'-1l'})/L)) \rangle_{E_T^p}$ is easy to evaluate and we find

$$\begin{aligned}
& \left\langle \cos\left(m\left(\frac{(z - z')}{L}(\gamma_{j'l'} - \gamma_{j'-1l'})\right)\right) \right\rangle_{E_T^p} = \left\langle \cos\left(m\left(\frac{(z - z')}{L}(\gamma_{j'l'} - \gamma_{j'l'-1})\right)\right) \right\rangle_{E_T^p} \\
& = \left\langle \cos\left(m\left(\frac{(z - z')}{L}(\gamma_{j'l'} - \gamma_{j'+1l'-1})\right)\right) \right\rangle_{E_T^p} = \exp\left(-\frac{m^2(z - z')^2}{2\lambda_p L}\right). \tag{H.9}
\end{aligned}$$

The term $\langle \cos(m(\tilde{\phi}_{j'l'}^p(z) - \tilde{\phi}_{j'l'}^p(z') - \tilde{\phi}_{j'-1l'}^p(z) + \tilde{\phi}_{j'-1l'}^p(z'))) \rangle_{E_T^p}$ is slightly more involved, where to evaluate this term we express $\tilde{\phi}_{j'l'}^p(z)$ in terms of its Fourier series $\tilde{\phi}_{j'l'}^p(z) = \sum_{n \neq 0} b_{jl}^n \exp(\frac{2i\pi n z}{L})$; we then find that

$$\begin{aligned} & \langle \cos(m(\tilde{\phi}_{j'l'}^p(z) - \tilde{\phi}_{j'l'}^p(z') - \tilde{\phi}_{j'-1l'}^p(z) + \tilde{\phi}_{j'-1l'}^p(z'))) \rangle_{E_T^p} \\ &= \langle \cos(m(\tilde{\phi}_{j'l'}^p(z) - \tilde{\phi}_{j'l'}^p(z') - \tilde{\phi}_{j'l'-1}^p(z) + \tilde{\phi}_{j'l'-1}^p(z'))) \rangle_{E_T^p} \\ &= \langle \cos(m(\tilde{\phi}_{j'l'}^p(z) - \tilde{\phi}_{j'l'}^p(z') - \tilde{\phi}_{j'+1l'-1}^p(z) + \tilde{\phi}_{j'+1l'-1}^p(z'))) \rangle_{E_T^p} \\ &= \exp\left(-\sum_n \frac{2Lm^2}{\lambda_p(2\pi n)^2} \left(1 - \cos\left(\frac{2\pi n(z-z')}{L}\right)\right)\right). \end{aligned} \quad (\text{H.10})$$

The sum may be evaluated, leaving us with

$$\begin{aligned} & \langle \cos(m(\tilde{\phi}_{j'l'}^p(z) - \tilde{\phi}_{j'l'}^p(z') - \tilde{\phi}_{j'+1l'-1}^p(z) + \tilde{\phi}_{j'+1l'-1}^p(z'))) \rangle_{E_T^p} \\ &= \exp\left(-\frac{m^2|z-z'|}{2\lambda_p}\right) \exp\left(\frac{m^2|z-z'|^2}{2\lambda_p L}\right). \end{aligned} \quad (\text{H.11})$$

Putting this all together we find

$$\frac{Z_1^m}{Z_0} = \frac{3a_m^2 N}{4(k_B T)^2} \int_{-L/2}^{L/2} dz \int_{-L/2}^{L/2} dz' \exp\left(-\frac{|z-z'|}{2\lambda_p}\right) = \frac{3a_m^2 L^2 N}{4(k_B T)^2} f_2\left(\frac{m^2 L}{\lambda_p}\right), \quad (\text{H.12})$$

where

$$f_2(x) = \frac{[8x + 8 \exp(-x/2) - 8]}{x^2}. \quad (\text{H.13})$$

If we truncate the sum in (H.1) over the a_m , according to [16] for a DNA molecule, at $m = 2$, then we may also calculate the next to leading order correction to the free energy per molecule,

$$\begin{aligned} F = F_0 - & \frac{3(a_1^2 L^2 f_2(L/\lambda_p) + a_2^2 L^2 f_2(4L/\lambda_p))}{4(k_B T)} - \frac{(a_1^3 L^3 f_{3,1}(L/\lambda_p) - a_2^3 L^3 f_{3,1}(4L/\lambda_p))}{2(k_B T)^2} \\ & + \frac{3a_2 a_1^2 L^3 f_{3,2}(L/\lambda_p)}{8(k_B T)^2} + \dots, \end{aligned} \quad (\text{H.14})$$

where F_0 is a term independent of a_1 and a_2 , and

$$\begin{aligned} f_{3,1}(x) &= \frac{24[\exp(-x/2)(4+x) + (-4+x)]}{x^3}, \\ f_{3,2}(x) &= \frac{[\exp(-x/2)(128+24x) + 36x - 126 - 2 \exp(-2x)]}{3x^3}. \end{aligned} \quad (\text{H.15})$$

We may look at limiting cases. When the molecules are either very short or rigid, so that $L \ll \lambda_p$, then we find that we may write

$$F = F_0 - \frac{3L^2(a_1^2 + a_2^2)}{4(k_B T)} - \frac{(a_1^3 L^3 - a_2^3 L^3)}{2(k_B T)^2} + \frac{3a_2 a_1^2 L^3}{8(k_B T)^2} + \dots \quad (\text{H.16})$$

This yields the following specific heat:

$$\frac{C_v}{k_B} = \frac{3}{2} \left(\frac{(La_1)^2 + (La_2)^2}{k_B T} \right) + 3 \left(\frac{(La_1)^3 - (La_2)^3}{(k_B T)^2} \right) - \frac{9a_2 a_1^2 L^3}{4(k_B T)^2} + \dots \quad (\text{H.17})$$

Here we have an additional term when compared with [20]; this term was overlooked previously. We may also look at the limit where molecules are very long or soft. Here we find

$$F = F_0 - \frac{3(4a_1^2 L \lambda_p + a_2^2 L \lambda_p)}{2(k_B T)} - \frac{(48a_1^3 L \lambda_p^2 - 3a_2^3 L \lambda_p^2)}{4(k_B T)^2} + \frac{9a_2 a_1^2 L \lambda_p^2}{2(k_B T)^2} + \dots \quad (\text{H.18})$$

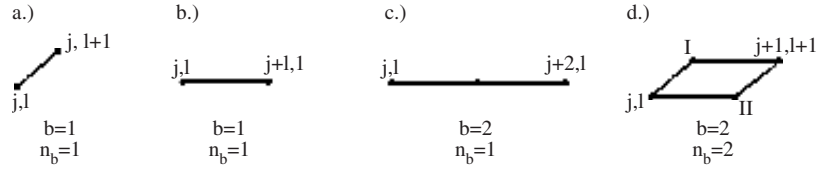


Figure H.1. The paths with the shortest number of links for the correlation functions: (a) $\langle \exp(in(\phi_{jl}(z) - \phi_{j,l+1}(z'))) \rangle$; (b) $\langle \exp(in(\phi_{jl}(z) - \phi_{j+1,l}(z'))) \rangle$; (c) $\langle \exp(in(\phi_{jl}(z) - \phi_{j+2,l}(z'))) \rangle$ and (d) $\langle \exp(in(\phi_{jl}(z) - \phi_{j+1,l+1}(z'))) \rangle$. Now, (a) and (b) contain only one link, while (c) and (d) two. (d) is the only one shown here to have two different paths, path I and II.

When comparing the two limits we see that as we move from short rigid molecules to long flexible molecules our high temperature expansion changes from power series expansions in $La_1/(k_B T)$ and $La_2/(k_B T)$ to power series expansions in $\lambda_p a_1/(k_B T)$ and $\lambda_p a_2/(k_B T)$. So for $L \gg \lambda_p$, the high temperature expansion is valid when we have $\lambda_p a_1/(k_B T) \ll 1$ and $\lambda_p a_2/(k_B T) \ll 1$, not necessarily $La_1/(k_B T) \ll 1$ and $La_2/(k_B T) \ll 1$. It is also interesting to look at the correlation function

$$\langle \exp(in(\phi_{jl}(z) - \phi_{j'l'}(z'))) \rangle = \frac{1}{Z} \prod_{jl} \int \mathcal{D}\phi(z) \exp(in(\phi_{jl}(z) - \phi_{j'l'}(z'))) \exp\left(-\frac{E[\phi]}{k_B T}\right) \quad (\text{H.19})$$

evaluated for nearest and next nearest neighbours. To generate the high temperature expansion we make the following expansion:

$$\begin{aligned} & \langle \exp(in(\phi_{jl}(z) - \phi_{j'l'}(z'))) \rangle \\ &= \left(\prod_{jl} \int \mathcal{D}\phi(z) \left(1 - \frac{E'_{\text{int}}[\phi]}{k_B T} + \frac{1}{2} \left(\frac{E'_{\text{int}}[\phi]}{k_B T} \right)^2 + \dots \right) \exp\left(-\frac{E_T[\phi]}{k_B T}\right) \right)^{-1} \\ & \times \left(\prod_{j'l'} \int \mathcal{D}\phi(z) \left(1 - \frac{E'_{\text{int}}[\phi]}{k_B T} + \left(\frac{1}{2} \frac{E'_{\text{int}}[\phi]}{k_B T} \right)^2 + \dots \right) \right. \\ & \times \left. \exp(in(\phi_{jl}(z) - \phi_{j'l'}(z'))) \exp\left(-\frac{E_T[\phi]}{k_B T}\right) \right). \end{aligned} \quad (\text{H.20})$$

In general, the leading order term in the correlation function—that describes how azimuthal correlations are lost—is of the form

$$\langle \exp(in(\phi_{jl}(z) - \phi_{j'l'}(z'))) \rangle \simeq n_b \left(\frac{a_n}{2k_B T} \right)^b \tilde{f}_b \left(\frac{z}{L}, \frac{z'}{L}; \frac{n^2 L}{\lambda_p} \right). \quad (\text{H.21})$$

Here, b is the smallest number of links or bonds between sites (i, j) and (i', j') , a link being defined as a translation of $\pm R_1 \hat{\mathbf{u}}$, $\pm R_1 \hat{\mathbf{v}}$ or $\pm R_1 (\hat{\mathbf{v}} - \hat{\mathbf{u}})$ between two sites on the 2D lattice. The factor n_b is the number of paths using the smallest number of links that go between the two sites (i, j) and (i', j') . This is illustrated for the examples for which we give explicit results in figure H.1. Also, the scaling function should always have the property that for torsionally rigid molecules $\tilde{f}_b = 1$.

First let us calculate the correlation function where $b = 1$. This is the correlation function between nearest neighbours. We find to leading order in the high temperature expansion

$$\begin{aligned} & \langle \exp(in(\phi_{jl}(z) - \phi_{j-1,l}(z'))) \rangle = \langle \exp(in(\phi_{jl}(z) - \phi_{j+1,l-1}(z'))) \rangle \\ &= \langle \exp(in(\phi_{jl}(z) - \phi_{j+1,l-1}(z'))) \rangle = \frac{a_n (-1)^n}{2k_B T} \tilde{f}_1 \left(\frac{z}{L}, \frac{z'}{L}; \frac{n^2 L}{\lambda_p} \right), \end{aligned} \quad (\text{H.22})$$

where

$$f_1(x, x'; y) = \frac{1}{y} \left(4 \exp\left(-\frac{y|x-x'|}{4}\right) + y|x-x'| \exp\left(-\frac{y|x-x'|}{4}\right) - 2 \exp\left(-\frac{y}{4}\right) \left(\exp\left(\frac{y(x+x')}{4}\right) + \exp\left(-\frac{y(x+x')}{4}\right) \right) \right). \quad (\text{H.23})$$

When $\lambda_p \gg L$ we do, indeed, find that $f_1(x, x'; y) \simeq 1$.

We may also compute correlations where $b = 2$. This is between next to nearest neighbours and next to next to nearest order correlations. We find to leading order

$$\begin{aligned} 2\langle \exp(\text{in}(\phi_{jl}(z) - \phi_{j-2l}(z'))) \rangle &= 2\langle \exp(\text{in}(\phi_{jl}(z) - \phi_{j-2}(z'))) \rangle \\ &= 2\langle \exp(\text{in}(\phi_{jl}(z) - \phi_{j+2l-2}(z'))) \rangle = \langle \exp(\text{in}(\phi_{jl}(z) - \phi_{j-1l-1}(z'))) \rangle \\ &= \langle \exp(\text{in}(\phi_{jl}(z) - \phi_{j-2l+1}(z'))) \rangle = \langle \exp(\text{in}(\phi_{jl}(z) - \phi_{j-1l+2}(z'))) \rangle \\ &= \frac{a_n(-1)^n}{2k_B T} \tilde{f}_2\left(\frac{z}{L}, \frac{z'}{L}; \frac{n^2 L}{\lambda_p}\right), \end{aligned} \quad (\text{H.24})$$

where

$$\begin{aligned} \tilde{f}_2(x, x'; y) &= \frac{4\tilde{f}(x, x'; y)}{y} + \frac{8}{y^2} \exp\left(-\frac{y|x-x'|}{4}\right) \\ &\quad - 2\left(\frac{1}{y} + 4\frac{1}{y^2}\right) \exp\left(-\frac{y}{4}\right) \left[\exp\left(\frac{y(x+x')}{4}\right) + \exp\left(-\frac{y(x+x')}{4}\right) \right] \\ &\quad + \frac{2(x+x')}{y} \exp\left(-\frac{y}{4}\right) \left[\exp\left(\frac{y(x+x')}{4}\right) - \exp\left(-\frac{y(x+x')}{4}\right) \right] \\ &\quad + \left(\frac{2|x-x'|}{y} + \frac{(x-x')^2}{2}\right) \exp\left(-\frac{y|x-x'|}{4}\right) \\ &\quad + \frac{4}{y^2} \exp\left(-\frac{y}{2}\right) \left[\exp\left(\frac{y(x-x')}{4}\right) + \exp\left(-\frac{y(x-x')}{4}\right) \right]. \end{aligned} \quad (\text{H.25})$$

Again, when $\lambda_p \gg L$, we find that $f_2(x, x'; y) \simeq 1$.

We may also look at self-correlations ($b = 0$), due to torsional fluctuations, for a single DNA molecule

$$\langle \exp(\text{in}(\phi_{jl}(z) - \phi_{jl}(z'))) \rangle = \exp\left(\frac{-n^2|z-z'|}{4\lambda_p}\right). \quad (\text{H.26})$$

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