Two-dimensional polymer configuration via mean-field theory

1997 J. Phys. A: Math. Gen. 30 467

(http://iopscience.iop.org/0305-4470/30/2/013)

J. Phys. A: Math. Gen. **30** (1997) 467–483. Printed in the UK PII: S0305-4470(97)74833-9

Two-dimensional polymer configuration via mean-field theory

Gerald G Pereira†

Department of Mathematics, The University of Melbourne, Parkville 3052, Victoria, Australia and

Department of Computational Science, National University of Singapore, Lower Kent Ridge Road, Singapore 119260

Received 24 May 1996

Abstract. We consider determining the configurational properties of a neutral polymer in two dimensions (2D) via self-consistent mean-field methods. By suitably scaling the problem we recover the Flory result for polymers under the excluded volume interaction, i.e. $R_N \sim N^{3/4}$, where R_N is the mean scaling length of a polymer which consists of $(N+1)$ monomers. If we let x denote the scaled distance from one end of the polymer to a point in space we find that there exists a point y^*, where the scaled polymer density $f_N(x)$, decays rapidly to zero. Physically the existence of such a point is expected since the polymer has a finite length. For $y^*-x > \mathrm{O}(N^{-1/3})$ we find $f_N(x) \sim \frac{1}{2x[f_N(x)-f_N(y^*)]^{1/2}}$ while for $x-y^* > \mathrm{O}(N^{-1/3})$ we obtain $f_N(x) \sim \mathrm{o}(1)$. We discuss the consequence of these results on the validity of the asymptotic methods used.

1. Introduction

The configurational properties of long-chain polymers has been studied extensively by a variety of theoretical methods for many years. The simplest model of a polymer chain is that of the random flight chain. This model, however, is only applicable to polymer systems in the vicinity of the θ temperature [1]. Away from the θ temperature volume exclusion effects, which prevent any two monomers from occupying the same volume in space, dominate the configurational properties of the polymer. Determining the principal quantities of interest, such as the mean end-to-end length of the polymer, denoted by R_N, or the polymer density at a point $\boldsymbol{r}$ in space, denoted by $n_{N+1}(\boldsymbol{r})$, become mathematically difficult to obtain due to these long-range correlations [2]. (Note that in this work we consider the polymer to consist of $(N+1)$ monomers in total.)

Self-consistent mean-field theory, as first introduced by Edwards [3], and later clarified by Freed and co-workers [2] provides the necessary framework for a quantitative analysis of these systems. However, Edwards' mathematical analysis of the excluded volume problem was criticized because he obtained a Gaussian function for the probability distribution function for the nth monomer in an infinitely long chain, whereas it is known to be skew-Gaussian [4, 5]. The cause of this problem can be attributed to factors which Edwards has neglected when calculating the probability distribution function for the nth monomer, and have subsequently been shown [6] to be non-negligible. Therefore a re-analysis of mean-field theory for polymer chains is warranted. Furthermore, recently there has appeared a

† E-mail address: geraldp@galaxy.cz3.nus.sg

0305-4470/97/020467+17$19.50

new perturbative method by Shannon *et al* [7], based on Edwards' mean-field results, to obtain corrections to scaling exponents for polymers in 2D.

Consequently, we feel it is important to analyse the problem in 2D. In section 2 we present a mathematical formalism for the problem, while in section 3 we apply this formalism to the excluded volume problem. We attempt to find a solution that is valid globally, as opposed to other studies [2, 3]. In section 4 we discuss the results.

2. Formal theory

Let us consider a polymer chain made up of $(N+1)$ monomers. The configurational partition function for this polymer chain, with the zeroth monomer at $\boldsymbol{R}'$ and the Nth monomer at $\boldsymbol{R}$, is then $G_{N+1}(\boldsymbol{R}', \boldsymbol{R})$ where

$$G_{N+1}(\boldsymbol{R}', \boldsymbol{R}) = \int \mathrm{d}\boldsymbol{r}_1 \cdots \int \mathrm{d}\boldsymbol{r}_{N-1}\, \mathrm{e}^{-\beta W(\boldsymbol{r}_N)} \prod_{j=1}^{N} \tau(\boldsymbol{r}_j - \boldsymbol{r}_{j-1}) \tag{1}$$

for $N = 2, 3, 4, \ldots$. We note that the zeroth and Nth monomers have not been weighted since they have been constrained to be at $\boldsymbol{R}'$ and at $\boldsymbol{R}$, respectively. The function $\tau(\boldsymbol{r})$ accounts for bond connectivity, which we assume has the usual Gaussian bond law form

$$\tau(\boldsymbol{r}) = (3/2\pi b^2) \exp(-3r^2/2b^2) \tag{2}$$

where b is the effective bond length. The function $W(\boldsymbol{r}_N)$ plays the role of the mean force potential and can be written in terms of a pairwise decomposable field [8] Φ, as

$$W(\boldsymbol{r}_N) = \sum_{i=1}^{N-1} \Phi(\boldsymbol{r}_i)\,. \tag{3}$$

We impose the initial condition

$$G_2(\boldsymbol{R}', \boldsymbol{R}) = \tau(\boldsymbol{R} - \boldsymbol{R}') \tag{4}$$

indicating for two monomers, only connectivity need be considered. Using equations (1) and (4) we obtain the recurrence relation

$$G_{N+1}(\boldsymbol{R}', \boldsymbol{R}) = \int \mathrm{d}\boldsymbol{r}\, G_N(\boldsymbol{R}', \boldsymbol{r}) \mathrm{e}^{-\beta\Phi(\boldsymbol{r})} \tau(\boldsymbol{R} - \boldsymbol{r})\,. \tag{5}$$

We now define the polymer generating function for chains from $\boldsymbol{R}'$ to $\boldsymbol{R}$ as

$$G(s|\boldsymbol{R}', \boldsymbol{R}) = \sum_{N=1}^{\infty} s^N G_{N+1}(\boldsymbol{R}', \boldsymbol{R}) \tag{6}$$

so that on substituting equation (5) into (6) and manipulating the result [6] we obtain the integral equation

$$G(s|\boldsymbol{R}', \boldsymbol{R}) = G^f(s||\boldsymbol{R}' - \boldsymbol{R}|) - \int \mathrm{d}\boldsymbol{r}\, F(\boldsymbol{r}) G(s|\boldsymbol{R}', \boldsymbol{r}) G^f(s||\boldsymbol{R} - \boldsymbol{r}|) \tag{7}$$

where $F(\boldsymbol{r}) = 1 - \mathrm{e}^{-\beta\Phi(\boldsymbol{r})}$ and $G^f(s||\boldsymbol{R}' - \boldsymbol{R}|)$ is known as the free-space polymer generating function. Using the central limit theorem [9] for Gaussian functions, the free-space polymer generating function can then be written as

$$G^f(s|r) = \frac{3}{2\pi b^2} \sum_{n=0}^{\infty} \frac{\exp(-3r^2/2b^2 n)}{n} s^n\,. \tag{8}$$

Since we are interested in the region of large r, that is $r \sim N^{1/2}b$, terms for small n in the above sum are negligible compared to terms of $O(N)$. In this case the sum may be converted to an integral yielding the approximate expression

$$G^f(s|r) \sim \left(\frac{3}{\pi b^2}\right) K_0(\kappa r) \tag{9}$$

where $\kappa = [(6/b^2)\log(1/s)]^{1/2}$. The function $K_0(z)$ is the modified Bessel function of zeroth order [10] and has the following properties which we shall use:

$$K_0(z) \sim \begin{cases} \log(1/z) & \text{as} \quad z \to 0 \\ \left(\dfrac{\pi}{2z}\right)^{1/2} \exp(-z) & \text{as} \quad z \to \infty\,. \end{cases} \tag{10}$$

The advantage of working with this approximation is that it satisfies the differential equation

$$(\nabla^2 - \kappa^2)G^f(s|r) = \frac{-6}{b^2}\delta(\boldsymbol{r}) \tag{11}$$

where ∇^2 is the two-dimensional circular Laplacian operator and $\delta(\boldsymbol{r})$ is the two-dimensional circular δ-function. Equation (9) is an inaccurate approximation to the exact free-space generating function for $r \leqslant b$. However, equation (11) represents a good approximation in the region of interest to us, i.e. $r \gg b$.

In this study we shall concentrate our efforts on determining the total monomer density at a point $\boldsymbol{r}$ in space. Consequently, we define $n_{N+1}(\boldsymbol{r}; \boldsymbol{R}', \boldsymbol{R})$ as the mean density of monomers at the point $\boldsymbol{r}$ in an ensemble of chains with $(N+1)$ monomers and with corresponding partition function $G_{N+1}(\boldsymbol{R}', \boldsymbol{R})$. This function satisfies the normalization condition

$$\int n_{N+1}(\boldsymbol{r}; \boldsymbol{R}', \boldsymbol{R})\,\mathrm{d}\boldsymbol{r} = N - 1 \tag{12}$$

since the first and last monomers are kept fixed. In terms of the configurational partition functions we may then write

$$n_{N+1}(\boldsymbol{r}; \boldsymbol{R}', \boldsymbol{R}) = \frac{\sum_{i=1}^{N-1} G_{i+1}(\boldsymbol{R}', \boldsymbol{r}) G_{N-i+1}(\boldsymbol{r}, \boldsymbol{R}) \mathrm{e}^{-\beta\Phi(r)}}{G_{N+1}(\boldsymbol{R}', \boldsymbol{R})} \tag{13}$$

for $N = 2, 3, \ldots$. Defining the monomer density generating function as

$$D(s|\boldsymbol{r}, \boldsymbol{R}', \boldsymbol{R}) = \sum_{N=2}^{\infty} s^N n_{N+1}(\boldsymbol{r}; \boldsymbol{R}', \boldsymbol{R}) G_{N+1}(\boldsymbol{R}', \boldsymbol{R}) \tag{14}$$

and substituting (13) into (14) yields, after some algebra,

$$D(s|\boldsymbol{r}, \boldsymbol{R}', \boldsymbol{R}) = G(s|\boldsymbol{R}', \boldsymbol{r}) G(s|\boldsymbol{r}, \boldsymbol{R}) \mathrm{e}^{-\beta\Phi(r)}\,. \tag{15}$$

The mean density is therefore essentially the coefficient of s^N in $D(s|\boldsymbol{r}, \boldsymbol{R}', \boldsymbol{R})$. To obtain $G(s|\boldsymbol{R}', \boldsymbol{r})$, etc, we convert the integral equation (7) into a differential equation. This is done by applying the operator $(\nabla_R^2 - \kappa^2)$, with the aid of (11), to yield

$$[\nabla_R^2 - q^2(\boldsymbol{R})]G(s|\boldsymbol{R}', \boldsymbol{R}) = \frac{-6}{b^2}\delta(\boldsymbol{R} - \boldsymbol{R}') \tag{16}$$

where

$$q(\boldsymbol{R}) = \left[\frac{6}{b^2}F(\boldsymbol{R}) + \kappa^2\right]^{1/2} \tag{17}$$

and $G(s|\boldsymbol{R}', \boldsymbol{R})$ is the Green's function solution of (16).

It is well known that individual polymer chains are elongated in shape. The density and mean field must model this property. When this is done it is found [6] that the first term we must solve for, after making an appropriate series expansion, has circular symmetry. Thus any treatment must necessarily solve for this lowest-order term first, which is our objective in this paper. Solving for higher-order terms will be pursued in future work. Now consider the zeroth monomer to be at the origin. Circular symmetry about the origin then implies $\Phi(\boldsymbol{r}) = \Phi(r)$ and

$$n_{N+1}(\boldsymbol{r}) = n_{N+1}(r) = \int n_{N+1}(\boldsymbol{r}; 0, \boldsymbol{R}) \mathrm{e}^{-\beta\Phi(R)}\, \mathrm{d}\boldsymbol{R} \tag{18}$$

where we weight the end monomer, since it is now allowed to be anywhere in space. The normalization condition, equation (12), now equals N. In the case of a circularly symmetric field, the density generating function becomes

$$D(s|r) = G(s|0, r)\mathcal{G}(s|r)\mathrm{e}^{-\beta\Phi(r)} \tag{19}$$

where

$$\mathcal{G}(s|r) = \int G(s|\boldsymbol{r}, \boldsymbol{R})\mathrm{e}^{-\beta\Phi(R)}\, \mathrm{d}\boldsymbol{R}\,. \tag{20}$$

The function $G(s|0, r)$ satisfies

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{1}{r}\frac{\mathrm{d}}{\mathrm{d}r} - \kappa^2 - F(r)\right] G(s|r) = \frac{-6}{b^2}\delta(r)\,. \tag{21}$$

The function $G(s|\boldsymbol{r}, \boldsymbol{R})$ does not have circular symmetry, so we write it as

$$G(s|\boldsymbol{r}, \boldsymbol{R}) = \frac{3}{\pi b^2}\sum_{n=0}^{\infty} G_n(s|r, R)\cos(n\theta) \tag{22}$$

where θ is the angle between the end-to-end vector of the polymer and the vector $\boldsymbol{r}$. (The vector $\boldsymbol{r}$ joins the zeroth monomer at the origin to the ith monomer at $\boldsymbol{r}$.) The G_n's can then be shown to satisfy

$$\left[\frac{\partial^2}{\partial R^2} + \frac{1}{R}\frac{\partial}{\partial R} - \frac{n^2}{R^2} - \kappa^2 - F(R)\right] G_n(r, R) = 0 \qquad \text{for} \quad r \neq R \tag{23}$$

with boundary conditions

$$\left.\frac{\partial G_n(r, R)}{\partial R}\right|_{R=r_+} - \left.\frac{\partial G_n(r, R)}{\partial R}\right|_{R=r_-} = \frac{-2}{r} \tag{24}$$

and

$$G_n(r, R)|_{R=r_+} = G_n(r, R)|_{R=r_-} \tag{25}$$

at $r = R$. On completing the integral in (20) we find only the $n = 0$ term is required from (22) and so $\mathcal{G}(s|r)$ is just

$$\mathcal{G}(s|r) = \frac{6}{b^2}\int_0^{\infty} \mathrm{e}^{-\beta\Phi(R)} G_0(s|r, R) R\, \mathrm{d}R\,. \tag{26}$$

Finally, the monomer density is given by

$$n_{N+1}(r) = \frac{[D(s|r)]_N}{\mathcal{G}_{N+1}(0)} \tag{27}$$

where $[\,]_N$ denotes the coefficient of s^N of the quantity in the square braces and $\mathcal{G}_{N+1}(0)$ is the coefficient of s^N in $\mathcal{G}(s|0)$ where

$$\mathcal{G}(s|0) = \int G(s|0, \boldsymbol{R}) \mathrm{e}^{-\beta\Phi(R)}\, \mathrm{d}\boldsymbol{R}\,. \tag{28}$$

The coefficients of s^N that are required in (27) can be obtained by using Taylor's theorem for complex variables [11, 12, 6].

3. Excluded volume problem

We now apply our formalism to the excluded volume problem in 2D. In the mean-field treatment of the excluded volume problem [3] we write

$$F(r) = v n_{N+1}(r) \tag{29}$$

where v is the excluded volume parameter and is positive for repulsive interactions.

3.1. Scaling

Since we are concerned in the properties of long-chain polymers, that is in the $N \to \infty$ limit, we initially scale the mean density using the strong scaling hypothesis [13–15]

$$n_{N+1}(r) = \frac{N}{2\pi R_N^2} f_N(x) \tag{30}$$

where $f_N(x)$ is an O(1) function of its argument, $x = r/R_N$, and R_N is the typical scaling length for the excluded volume problem. The scaled density $f_N(x)$ then satisfies

$$\int_0^\infty x f_N(x)\, \mathrm{d}x = 1\,. \tag{31}$$

To scale the differential equations for $G(s|0, r)$ and $G(s|\boldsymbol{r}, \boldsymbol{R})$ we write

$$\log(1/s) = N v z / 2\pi R_N^2 \tag{32}$$

so that (21) becomes

$$\frac{\mathrm{d}^2 G}{\mathrm{d}x^2} + \frac{1}{x}\frac{\mathrm{d}G}{\mathrm{d}x} - \lambda_N^2 [f_N(x) + z] G = \frac{-6R_N^2}{b^2}\delta(x) \tag{33}$$

where we identify

$$\lambda_N^2 = \frac{3Nv}{\pi b^2}\,. \tag{34}$$

One may similarly scale the differential equation for G_0, equation (23). (We write $y = R/R_N$.) When this is done and the scaled density is constructed appropriately we find

$$f_N(x) = \frac{\gamma_N}{2\pi \mathrm{i}} \mathcal{N}^{-1} \frac{6R_N^2}{Nb^2} \int_{C-\mathrm{i}\omega_N}^{C+\mathrm{i}\omega_N} \mathrm{d}z\, \exp\left(\frac{N^2 v z}{2\pi R_N^2}\right) G(z|x) \mathrm{e}^{-\beta\Phi(x)} \times \int_0^\infty \mathrm{e}^{-\beta\Phi(y)} G_0(z|x, y)\, y\, \mathrm{d}y \tag{35}$$

the normalization constant $\mathcal{N}$, is

$$\mathcal{N} = \frac{\gamma_N}{2\pi \mathrm{i}} \int_{C-\mathrm{i}\omega_N}^{C+\mathrm{i}\omega_N} \mathrm{d}z\, \exp\left(\frac{N^2 v z}{2\pi R_N^2}\right) \int_0^\infty \mathrm{e}^{-\beta\Phi(y)} G(z|y)\, y\, \mathrm{d}y \tag{36}$$

where

$$\gamma_N = \frac{Nv}{2\pi R_N^2} \tag{37}$$

$$\omega_N = \frac{2\pi^2 R_N^2}{Nv} \tag{38}$$

and C is to the right of all singularities of the integrands. It now remains to determine the N dependence of the variables we have defined above. To do this we must solve the differential equations for $G(z|x)$ and $G_0(z|x, y)$.

To solve (33) we note that the δ-function on the right-hand side implies that as $x \to 0$ we require $G(z|x) \sim \log x$. With this in mind we now solve the equation for non-zero x. We write

$$G(z|x) = G(x) = \frac{3}{\pi b^2}\frac{g(x)}{x^{1/2}} \tag{39}$$

and substituting into (33) we find

$$\frac{\mathrm{d}^2 g}{\mathrm{d}x^2} - \lambda_N^2\left[f_N(x) + z - \frac{1}{(2\lambda_N x)^2}\right]g = 0 \qquad x > 0\,. \tag{40}$$

We assume λ_N is a large parameter (which we shall see is valid for $N \to \infty$). Then for x sufficiently large the $1/(2\lambda_N x)^2$ term in (40) is negligible, and hence the WKB solutions are

$$g(x) = \frac{\exp(\pm\lambda_N \int_0^x q(x')\,\mathrm{d}x')}{q^{1/2}(x)}\,. \tag{41}$$

Now for x small we shall show that $f_N(x) \sim (2x)^{-2/3}$ so that for $x < \mathrm{O}(\lambda^{-3/2})$ the WKB methods breakdown [16, 17, 6]. In the region where $x < \mathrm{O}(\lambda^{-3/2})$ equation (40) may be re-written approximately as

$$\frac{\mathrm{d}^2 g}{\mathrm{d}x^2} - \frac{\lambda_N^2 g}{(2x)^{2/3}} + \frac{g}{4x^2} = 0 \tag{42}$$

and has linearly independent solutions

$$g(x) = p^{3/4}K_0(p) \qquad \text{and} \qquad p^{3/4}I_0(p) \tag{43}$$

where $p = \frac{3}{2}\lambda 2^{-1/3}x^{2/3}$. The particular solutions are those that satisfy the boundary conditions as $p \to 0$ and for p large. For p large the solutions, equation (43), must match the WKB solutions. When this is done, we find our particular solutions are

$$G^{(1)}(x) = \frac{3}{\pi b^2}\frac{3}{2}K_0(p) \to \frac{3}{\pi b^2}\left(\frac{3\pi}{4\lambda}\right)^{1/2}\frac{\exp(-\lambda_N \int_0^x q(x')\,\mathrm{d}x')}{x^{1/2}q^{1/2}(x)} \tag{44}$$

and

$$G^{(2)}(x) = \frac{3}{\pi b^2}\frac{3}{2}\left[K_0(p) + \frac{\pi}{2}I_0(p)\right] \to \frac{3}{\pi b^2}\left(\frac{3\pi}{4\lambda}\right)^{1/2}\frac{\exp(\lambda_N \int_0^x q(x')\,\mathrm{d}x')}{2x^{1/2}q^{1/2}(x)}\,. \tag{45}$$

Both these solutions are proportional to $\log(x)$ as $x \to 0$, as required. Finally, since we require the solution to be bounded as $x \to \infty$ we only select $G^{(1)}(x)$.

Now to complete our scaling analysis we consider the normalization constant $\mathcal{N}$ given by (36). (Note, the ensuing argument also applies to (35) for the scaled density.) If $G(y)$ is given by (44) we can write

$$\mathcal{N} = \frac{\gamma_N}{2\pi\mathrm{i}}\int_{C-\mathrm{i}\omega_N}^{C+\mathrm{i}\omega_N}\mathrm{d}z\,\exp\left(\frac{N^2 v z}{2\pi R_N^2}\right)\int_0^\infty\left(\frac{3\pi}{4\lambda}\right)^{1/2}\frac{\exp(-\lambda_N \int_0^y q(x')\,\mathrm{d}x')}{q^{1/2}(y)}\mathrm{e}^{-\beta\Phi(y)}y^{1/2}\,\mathrm{d}y\,. \tag{46}$$

Recall that we are dealing with the $N \to \infty$ limit and so the above integral will be dominated by the terms $\exp\left(N^2 v z/2\pi R_N^2\right)$ and $\exp\left(-\lambda_N \int_0^y q(x')\,\mathrm{d}x'\right)$. If we are to have any interaction between these two exponential terms we require

$$\frac{N^2 v}{2\pi R_N^2} = \lambda_N = \left(\frac{3Nv}{\pi b^2}\right)^{1/2} \tag{47}$$

which defines the typical scaling length R_N as

$$R_N = \left(\frac{vb^2}{12\pi}\right)^{1/4} N^{3/4}. \tag{48}$$

Continuing, we find $\lambda_N \sim N^{1/2}$, $\omega_N \sim N^{1/2}$ and $\gamma_N \sim N^{-1/2}$. Since λ_N is a large parameter (for $N \to \infty$) we are justified in making a WKB solution of (40). Equation (48), which defines the typical scaling length of the polymer, may be identified as the Flory result [1] for excluded volume polymers in 2D.

It can be shown that the Boltzmann weighting factor in (46) is, to leading order, just one. Thus the normalization constant $\mathcal{N}$, defined by (36), after being appropriately scaled in the $N \to \infty$ limit yields, to leading order,

$$\mathcal{N} = \frac{\gamma_N}{2\pi \mathrm{i}}\left(\frac{3\pi}{4\lambda}\right)^{1/2} \int_{c-\mathrm{i}\infty}^{c+\mathrm{i}\infty} \mathrm{d}z \int_0^\infty \frac{1}{q^{1/2}(y)} \mathrm{e}^{\lambda_N[z - \int_0^y q(x')\,\mathrm{d}x']} y^{1/2}\,\mathrm{d}y \tag{49}$$

and c is to the right of all singularities of the integrand.

3.2. Turning point solutions

To complete the z-contour integral in (49) we shall wrap the contour around the negative real axis. However, before we do this we must be aware of two problems. Firstly, when analytically continuing the integrand of (49) into the negative z-plane we will encounter the Stokes phenomenon [16, 17]. Secondly, along the negative real axis the integrand has a branch cut, with a branch point at the zero of $q^2(x)$. This point is, in fact, a turning point of (40), so that a WKB solution is invalid in the neighbourhood of this point [16].

To address these problems we re-solve (40) along the upper and lower branches of the branch cut by writing $z = \mathrm{e}^{\pm \mathrm{i}\pi} f(x_s)$. The point $y = x_s$ is the turning point. In the neighbourhood of the turning point we solve (40) exactly and match the solution into the WKB solutions, which are valid well away from x_s. In doing this we obtain a solution which is uniformly valid along the entire negative real axis. We have also circumvented any problems associated with analytically continuing the integrand of (49) into the negative z-plane.

When this is done we obtain the solution

$$g_\pm(y) \sim \left(\frac{3\pi}{4\lambda}\right)^{1/2} \mathrm{e}^{-\lambda w_1(x_s)} \pi^{1/2} [\mathrm{bi}(x_s, y) \mp \mathrm{i}\,\mathrm{ai}(x_s, y)] \tag{50}$$

where

$$\mathrm{ai}(x_s, y) = \begin{cases} \left(\frac{3}{2}\lambda w_3\right)^{1/6} \dfrac{\mathrm{Ai}\left[\left(\frac{3}{2}\lambda w_3\right)^{2/3}\right]}{[f(y) - f(x_s)]^{1/4}} & y \leqslant x_s \\ \left(\frac{3}{2}\lambda w_2\right)^{1/6} \dfrac{\mathrm{Ai}\left[-\left(\frac{3}{2}\lambda w_2\right)^{2/3}\right]}{[f(x_s) - f(y)]^{1/4}} & y \geqslant x_s \end{cases} \tag{51}$$

and

$$\mathrm{bi}(x_s, y) = \begin{cases} \left(\frac{3}{2}\lambda w_3\right)^{1/6} \dfrac{\mathrm{Bi}\left[\left(\frac{3}{2}\lambda w_3\right)^{2/3}\right]}{[f(y) - f(x_s)]^{1/4}} & y \leqslant x_s \\ \left(\frac{3}{2}\lambda w_2\right)^{1/6} \dfrac{\mathrm{Bi}\left[-\left(\frac{3}{2}\lambda w_2\right)^{2/3}\right]}{[f(x_s) - f(y)]^{1/4}} & y \geqslant x_s\,. \end{cases} \tag{52}$$

The functions w_1, w_2 and w_3 are defined as

$$w_1(x_s) = \int_0^{x_s} [f(x) - f(x_s)]^{1/2}\,\mathrm{d}x \tag{53}$$

$$w_2(x_s, y) = \int_{x_s}^{y} [f(x_s) - f(x)]^{1/2}\,\mathrm{d}x \tag{54}$$

and

$$w_3(y, x_s) = \int_{y}^{x_s} [f(x) - f(x_s)]^{1/2}\,\mathrm{d}x\,. \tag{55}$$

The solutions are now written in terms of Airy functions [18], which have an exponential form for large positive values and a trigonometric form for large negative values. The normalization constant, valid for all real $q^2(x)$, becomes

$$\mathcal{N} = \frac{\gamma_N}{\pi^{1/2}}\left(\frac{3\pi}{4\lambda}\right)^{1/2} \int_0^{\infty} \mathrm{d}(f(x_s))\,\mathrm{e}^{-\lambda[f(x_s + w_1(x_s)]} \times \left\{\int_0^{x_s} \mathrm{ai}(x_s, y) y^{1/2}\,\mathrm{d}y + \int_{x_s}^{\infty} \mathrm{ai}(x_s, y) y^{1/2}\,\mathrm{d}y\right\}. \tag{56}$$

The scaled density is now given by

$$f_N(x) = \frac{D_N(x)}{\mathcal{N}} \tag{57}$$

where $D_N(x)$ is

$$D_N(x) = \frac{\lambda}{2\pi\mathrm{i}}\gamma_N \int_{c-\mathrm{i}\infty}^{c+\mathrm{i}\infty} \mathrm{d}z\,\mathrm{e}^{\lambda z} \int_0^{\infty} \frac{g(x)}{x^{1/2}} G_0(x, y) y\,\mathrm{d}y\,. \tag{58}$$

The two functions $g(x)$ and $G_0(x, y)$ are required to construct $D_N(x)$. The function $g(x)$ has been determined above, while $G_0(x, y)$ is the Green's function solution of the scaled version of (23)–(25), suitably solved along the negative real axis. The solution of (23) is tedious to obtain and, furthermore, the function $D_N(x)$ which is subsequently formed is particularly cumbersome. For clarity of presentation we have therefore relegated a discussion of the solution for $G_0(x, y)$ and the construction of $D_N(x)$ to the appendix. In summary we find

$$f_N(x) \sim \frac{I_1(x) + I_2(x)}{\mathcal{N}} \tag{59}$$

where $I_1(x)$ and $I_2(x)$ are given by (A9) and (A10) and $\mathcal{N}$ is given by (56). The important point to note about the I_i integrals is that their structure is quite similar to $\mathcal{N}$, except for a factor $\mathrm{ai}(x_s, x)\,\mathrm{bi}(x_s, x)$ or $\mathrm{ai}^2(x_s, x)$. Note that there is a factor $\left(3\pi/4\lambda\right)^{1/2}\gamma_N$ common to all integrals on the right-hand side of equation (59). This factor will cancel when calculating $f_N(x)$ so we shall dispense with writing it from now on.

3.3. Integral analysis

The analysis of the integrals $\mathcal{N}$, $I_1(x)$ and $I_2(x)$ is governed by their large λ dependence. As such they may be evaluated using asymptotic techniques [17] to determine their leading-order behaviour. Consider the $f_N(x_s)$ integration, which is common to all the integrals. These integrals are dominated by the behaviour of the exponential term $\exp(-\lambda[f(x_s)+w_1(x_s)])$. Since $f(x_s)+w_1(x_s)$ is positive for all $x_s > 0$, integrals involving this term are dominated by the values of x_s which minimize $f(x_s) + w_1(x_s)$. Thus let us define $A(x)$ to be

$$A(x) = f(x) + w_1(x) = f(x) + \int_0^x [f(x') - f(x)]^{1/2}\,\mathrm{d}x' . \tag{60}$$

Since $f_N(x)$ represents the scaled density, we assume that it is a monotonically decreasing function of x. Differentiating $A(x)$ we find

$$\frac{\mathrm{d}}{\mathrm{d}x}A(x) = f'(x)B(x) \tag{61}$$

where

$$B(x) = 1 - \tfrac{1}{2}\int_0^x [f(x') - f(x)]^{-1/2}\,\mathrm{d}x' . \tag{62}$$

Consider the function $B(x)$. Clearly $B(0) = 1$ and as the integrand in (62) is positive for $x > 0$, $B(x) < 1$ for $x > 0$. For $x \to \infty$ the integral in (62) can be shown to become divergent. Thus $B(x) \to -\infty$ as $x \to \infty$. Thus there must exist at least one value of x for which $B(x)$ is zero. We therefore define y^* as the point where $B(x)$ has its first zero. Since $f_N'(x)$ is negative, by assumption, y^* must correspond to a minimum of $A(x)$. Once we have derived the leading-order functional form for $f_N(x)$ we shall show that the above definitions are consistent with $f_N(x)$. The above discussion implies that the $f_N(x_s)$ integrals are dominated by $f_N(x_s) \sim f_N(y^*)$.

We now define a change of variables which enables easier handling of the integrals. We define

$$\epsilon = f(y) - f(y^*) \qquad \eta' = f(x') - f(y^*) \qquad s = f(x_s) - f(y^*) . \tag{63}$$

With this change of variables the normalization constant becomes

$$\mathcal{N} = \frac{\mathrm{e}^{-\lambda f(y^*)}}{\pi^{1/2}} \int_{-f(y^*)}^{\infty} \mathrm{d}s\, \mathrm{e}^{-\lambda \mathcal{F}(s)} \left\{ \int_{\infty}^{s} \frac{\mathrm{d}\epsilon\, y^{1/2}(\epsilon)}{f'(y(\epsilon))} \left(\tfrac{3}{2}\lambda\Gamma\right)^{1/6} \frac{\mathrm{Ai}\left[\left(\tfrac{3}{2}\lambda\Gamma\right)^{2/3}\right]}{(\epsilon - s)^{1/4}} \right.$$
$$\left. + \int_{s}^{-f(y^*)} \frac{\mathrm{d}\epsilon\, y^{1/2}(\epsilon)}{f'(y(\epsilon))} \left(\tfrac{3}{2}\lambda G\right)^{1/6} \frac{\mathrm{Ai}\left[-\left(\tfrac{3}{2}\lambda G\right)^{2/3}\right]}{(s - \epsilon)^{1/4}} \right\} \tag{64}$$

where

$$\mathcal{F}(s) = s + \int_s^{\infty} \frac{\mathrm{d}\eta'}{(-f'(x(\eta')))} (\eta' - s)^{1/2}$$
$$\Gamma(s, \epsilon) = \int_s^{\epsilon} \frac{\mathrm{d}\eta'}{(-f'(x(\eta')))} (\eta' - s)^{1/2} \tag{65}$$
$$G(\epsilon, s) = \int_{\epsilon}^{s} \frac{\mathrm{d}\eta'}{(-f'(x(\eta')))} (s - \eta')^{1/2}$$

and we note that $\mathcal{F}(s)$ has its minimum at $s = 0$, since $A(x_s)$ has a minimum at y^*.

For convenience we define

$$I_g = \int_{\infty}^{s} \frac{\mathrm{d}\epsilon\, y^{1/2}(\epsilon)}{f'(y(\epsilon))} \left(\tfrac{3}{2}\lambda\Gamma\right)^{1/6} \frac{\mathrm{Ai}\left[\left(\tfrac{3}{2}\lambda\Gamma\right)^{2/3}\right]}{(\epsilon - s)^{1/4}} \tag{66}$$

and

$$I_{gg} = \int_{s}^{-f(y^*)} \frac{\mathrm{d}\epsilon\, y^{1/2}(\epsilon)}{f'(y(\epsilon))} \left(\tfrac{3}{2}\lambda G\right)^{1/6} \frac{\mathrm{Ai}\left[-\left(\tfrac{3}{2}\lambda G\right)^{2/3}\right]}{(s - \epsilon)^{1/4}} \tag{67}$$

corresponding to the integrals in the curly brackets of (64). Now consider the ϵ-integrals, I_g and I_{gg}. I_g is dominated by the region $\Gamma < \mathrm{O}(\lambda^{-1})$ while I_{gg} is dominated by $G < \mathrm{O}(\lambda^{-1})$ [16, 17, 6]. These regions correspond to $y \sim x_s$, so that when these integrals are evaluated we find, to leading order,

$$\mathcal{N} \sim \frac{(y^*)^{1/2}\mathrm{e}^{-\lambda f(y^*)}}{\pi^{1/2}[\lambda(-f'(y^*))]^{1/2}} \int_{-f(y^*)}^{\infty} \mathrm{d}s\, \mathrm{e}^{-\lambda\mathcal{F}(s)}. \tag{68}$$

The remaining s-integral is dominated by the region $s \sim 0$, which corresponds to $x_s \sim y^*$. We shall leave the s-integral undone for the moment. (Note, to obtain (68) we have evaluated all non-exponential s-dependent terms at $s = 0$.)

Now we consider the integrals $I_1(x)$ and $I_2(x)$. Due to the close similarity in structure between these integrals and the normalization constant we may make the change of variables defined by (63). We also need to define $\eta = f(x) - f(y^*)$.

In the appendix (equations (A11) and (A12)) we show the result of this change of variable on the two integrals. The central point of our asymptotic analysis is that the function $\mathcal{F}(s)$ has a minimum at $s = 0$, so that all s-integrals are dominated by this region. As long as the terminals of the s-integral contain the neighbourhood of the origin they will be the dominant integrals. With this in mind, it is evident that our problem now reduces to evaluating $I_1(x)$ and $I_2(x)$ in three different zones.

Zone I. This zone corresponds to η positive. For $3\lambda\xi/2 > \mathrm{O}(1)$ the Airy functions may be written down in their large argument (exponential) form. The criterion for validity of this form can be shown to correspond to $\eta > \mathrm{O}(\lambda^{-2/3})$ or $y^* - x > \mathrm{O}(\lambda^{-2/3})$. Using a similar analysis to that already shown for evaluating $\mathcal{N}$ we find the leading-order contribution to the integrals is

$$I_1(x) + I_2(x) \sim \frac{\mathrm{e}^{-\lambda f(y^*)}}{\pi^{1/2}x} \int_{-f(y^*)}^{\eta} \mathrm{d}s\, \mathrm{e}^{-\lambda\mathcal{F}(s)} \frac{1}{2(\eta - s)^{1/2}} \left\{I_g + I_{gg}\right\}. \tag{69}$$

The x dependence of the integrals in (69) is contained in the factor $1/2x(\eta - s)^{1/2}$ and the upper terminal, η, of the s-integral. Except for this x dependence one may identify (69) as exactly the same integral that constitutes the normalization constant, equation (64). This structure is indeed important in solving the problem and shall be used repeatedly. The term in the curly brackets may be evaluated as before. Noting once again, that since the minimum of $\mathcal{F}(s)$ occurs at $s = 0$, the s-integral is dominated by $s \sim 0$. For $\eta > \mathrm{O}(\lambda^{-2/3})$ the peak of the s-integral is contained within the range of the terminals and so for purposes of evaluating the s-integral, we may replace the upper terminal η by infinity. Doing this we obtain

$$I_1(x) + I_2(x) \sim \frac{(y^*)^{1/2}\mathrm{e}^{-\lambda f(y^*)}}{2x\eta^{1/2}\pi^{1/2}[\lambda(-f'(y^*))]^{1/2}} \int_{-f(y^*)}^{\infty} \mathrm{d}s\, \mathrm{e}^{-\lambda\mathcal{F}(s)}. \tag{70}$$

Due to the structure of the problem there is no need to complete the remaining integral. When forming $f_N(x)$, as in (59), the leading-order contributions to the s-integrals will cancel in the numerator and denominator, leaving

$$f_N(x) \sim \frac{1}{2x\eta^{1/2}} \qquad \eta > 0\,. \tag{71}$$

For $\eta > \mathrm{O}(\lambda^{-2/3})$ and positive, $f_N(x)$ is an O(1) function as expected.

Zone II. The next zone we consider is in the neighbourhood of the point $\eta = 0$. In this zone we are not entitled to write down the large argument form of the Airy functions. We find that the leading-order contributions to the integrals $I_1(x)$ and $I_2(x)$, for η small, are

$$\begin{aligned} I_1(x) + I_2(x) \sim \frac{\pi^{1/2}\mathrm{e}^{-\lambda f(y^*)}}{x}\Bigg(&\int_{-f(y^*)}^{\eta} \mathrm{d}s\, \mathrm{e}^{-\lambda\mathcal{F}(s)} 2\left(\tfrac{3}{2}\lambda\xi\right)^{1/3} \frac{\mathrm{Ai}\left[\left(\frac{3}{2}\lambda\xi\right)^{2/3}\right]\mathrm{Bi}\left[\left(\frac{3}{2}\lambda\xi\right)^{2/3}\right]}{(\eta - s)^{1/2}} \\ &+ \int_{\eta}^{\infty} \mathrm{d}s\, \mathrm{e}^{-\lambda\mathcal{F}(s)} 2\left(\tfrac{3}{2}\lambda\zeta\right)^{1/3} \frac{\mathrm{Ai}\left[-\left(\frac{3}{2}\lambda\zeta\right)^{2/3}\right]\mathrm{Bi}\left[-\left(\frac{3}{2}\lambda\zeta\right)^{2/3}\right]}{(s - \eta)^{1/2}} \Bigg)\left\{2I_g + I_{gg}\right\} \end{aligned} \tag{72}$$

where

$$\begin{aligned} \xi(s,\eta) &= \int_s^{\eta} \frac{\mathrm{d}\eta'}{(-f'(x(\eta')))}(\eta' - s)^{1/2} \\ \zeta(\eta,s) &= \int_{\eta}^{s} \frac{\mathrm{d}\eta'}{(-f'(x(\eta')))}(s - \eta')^{1/2}\,. \end{aligned} \tag{73}$$

Except for the factor of 2, the term $(2I_g + I_{gg})$ may be identified as the same integrals in the curly brackets of (64). Let us evaluate $f_N(x)$ at the point y^*. To evaluate the necessary integrals we may use the same procedure as before. Setting $\eta = 0$ in (73) yields

$$\xi \sim \frac{2(-s)^{3/2}}{3(-f'(x_s))} > 0 \quad s < 0 \qquad \text{and} \qquad \zeta \sim \frac{2s^{3/2}}{3(-f'(x_s))} > 0 \quad s > 0\,. \tag{74}$$

The resulting s-integral will be dominated by the exponential term $\mathrm{e}^{-\lambda\mathcal{F}(s)}$ so that all s-dependent terms may be simply evaluated at $s = 0$. Doing this yields

$$I_1(y^*) + I_2(y^*) \sim \frac{4\pi^{1/2}\mathrm{e}^{-\lambda f(y^*)}}{3(y^*)^{1/2}}\left(\frac{\lambda}{(-f(y^*))}\right)^{1/3} \frac{\mathrm{Ai}(0)\mathrm{Bi}(0)}{[\lambda(-f'(y^*)]^{1/2}} \int_{-f(y^*)}^{\infty} \mathrm{e}^{-\lambda\mathcal{F}(s)}\,\mathrm{d}s \tag{75}$$

so that we finally obtain for $\eta = 0$

$$f_N(y^*) \sim \frac{4\pi}{3}\frac{\mathrm{Ai}(0)\mathrm{Bi}(0)}{y^*}\left(\frac{\lambda}{(-f'(y^*))}\right)^{1/3}. \tag{76}$$

Zone III. This zone corresponds to η negative. For $3\lambda\zeta/2 > \mathrm{O}(1)$, or $|\eta| > \mathrm{O}(\lambda^{-2/3})$, the Airy functions may be written down in their large argument (trigonometric) form. We then find, to leading order, that

$$I_1(x) + I_2(x) \sim \frac{\mathrm{e}^{-\lambda f(y^*)}}{\pi^{1/2}x}\int_{\eta}^{\infty} \mathrm{d}s\, \mathrm{e}^{-\lambda\mathcal{F}(s)} \frac{\cos(\lambda\zeta + \pi/4)\sin(\lambda\zeta + \pi/4)}{(s - \eta)^{1/2}}\{I_g + I_{gg}\} \tag{77}$$

and evaluating the I_g and I_{gg} integrals, as per usual, yields

$$I_1(x) + I_2(x) \sim \frac{\mathrm{e}^{-\lambda f(y^*)}}{\pi^{1/2}x}\int_{\eta}^{\infty} \mathrm{d}s\, \mathrm{e}^{-\lambda\mathcal{F}(s)} \frac{\cos(\lambda\zeta + \pi/4)\sin(\lambda\zeta + \pi/4)}{(s - \eta)^{1/2}[\lambda(-f'(x_s))]^{1/2}} x_s^{1/2}\,. \tag{78}$$

The s-integral we are left with now is somewhat different to what we had before. We still have the $e^{-\lambda\mathcal{F}(s)}$ factor which is dominated by s near zero. The cos and sin functions oscillate rapidly at $s = 0$. These oscillations will tend to cancel each other out and thus diminish the size of the integral [17]. The oscillations die out at $s = \eta$ but in this region the exponential term will make the integrand exponentially small. To evaluate the asymptotic behaviour of this integral explicitly is a complicated exercise.

However, we do not need to evaluate this integral explicitly. We can, in fact, put an upper bound on it. Since we will eventually compare this integral with $\mathcal{N}$, we find that $f_N(x) \leqslant O(\lambda^{-1/2})$. Hence for $|\eta| > O(\lambda^{-2/3})$ and negative, we find

$$f_N(x) \sim o(1)\,. \tag{79}$$

3.4. Description of $f_N(x)$

We have now determined the leading-order functional behaviour of $f_N(x)$ over the entire x-range. In zone I, which corresponds to $y^* - x > O(\lambda^{-2/3})$, we have found

$$f_N(x) \sim \frac{1}{2x[f_N(x) - f_N(y^*)]^{1/2}}\,. \tag{80}$$

Close to the origin $f_N(x) \gg f_N(y^*)$, so that we obtain the result

$$f_N(x) \sim \frac{1}{(2x)^{2/3}}\,. \tag{81}$$

Manipulating the functional form (80) yields

$$xf_N(x) \sim \frac{1}{2[f_N(x) - f_N(y^*)]^{1/2}}\,. \tag{82}$$

Integrating both sides with respect to x, from zero to y^*, then implies

$$\int_0^{y^*} xf_N(x)\,\mathrm{d}x \sim \frac{1}{2}\int_0^{y^*} \frac{\mathrm{d}x}{[f_N(x) - f_N(y^*)]^{1/2}}\,. \tag{83}$$

To be strictly correct we should write $y^* - O(\lambda^{-2/3})$ as the upper limit in (83). However, the error in replacing this with y^* is at most $O(\lambda^{-2/3})$ so that as $N \to \infty$, equation (83) is correct. Now if $B(y^*)$ is zero, this implies the right-hand side of the above asymptotic equation is one. Thus we obtain

$$\int_0^{y^*} xf_N(x)\,\mathrm{d}x \sim 1 \tag{84}$$

which is a normalization condition on $f_N(x)$. This condition implies that all the monomers, to leading order, are contained within a circle of radius y^* around the origin. If this is correct, we should find for $x > y^*$ that $f_N(x)$ is zero. The above normalization condition is a verification of our result in the region $x > y^*$, equation (79). Therefore, in the neighbourhood of y^* there must exist a sharp decay in the scaled density $f_N(x)$. Correspondingly, $f_N'(y^*)$ should be large and negative.

The point y^* is in the middle of the decay region and so the above discussion implies $f_N(y^*)$ is at most an O(1) number. Equation (76) gives the leading terms for $f_N(y^*)$. Clearly, if $f_N'(y^*) \sim O(\lambda)$, $f_N(y^*)$ is an O(1) number as required. The problem will be completed once we determine $f_N'(y^*)$, since the two, as yet undetermined, parameters y^* and $f_N(y^*)$ may then be calculated using the normalization condition (84), together with (76).

We now verify that the leading-order form of $f_N(x)$ is consistent with our assumptions on $B(x)$. For x close to the origin we may use (81) for $f_N(x)$. Substituting this into the definition of $B(x)$ and evaluating the resulting integral yields

$$B(x) \sim 1 - \beta x^{4/3} \tag{85}$$

where β is a positive constant. Thus, close to the origin $B(x)$ is a monotonically decreasing function of x. Furthermore, one can show that as long as $f_N(x)$ is a monotonically decreasing function, $B(x)$ is also a monotonically decreasing function. Our derived form for the scaled density implies that all the monomers, to leading order, are contained within a circle of radius y^* around the origin. Thus using (83) we can see that our derived functional form for $f_N(x)$ is consistent with our initial definition that y^* is the first zero of $B(x)$, and that this zero corresponds to the minimum of $A(x)$.

Finally, we consider determining the derivative of the scaled density at the point y^*. However, before embarking on this complicated exercise we point out that if $f'_N(y^*) \sim \mathrm{O}(\lambda)$, as we have alluded to above, this would imply WKB solutions are invalid in the neighbourhood of y^*. That is, the higher-order terms in the WKB series that we could previously neglect are now non-negligible. We have, in fact, evaluated $f'_N(y^*)$, by formally differentiating $I_1(x)$ and $I_2(x)$, and have found that the leading-order λ terms cancel exactly, giving the result $f'_N(y^*) \sim \mathrm{o}(\lambda)$. Although this result contradicts our earlier description of $f_N(x)$, it is not unexpected in view of the breakdown of WKB theory near y^*. We now discuss the implications of this result.

4. Discussion

We initially consider the implications of the breakdown in the WKB solution at $x = y^*$. Consider the validity of our solutions well away from y^*. In this region the WKB solution, as far as the x variable is concerned, is correct. However, the complete solution involves y, which is integrated over all space. Thus y must pass through the neighbourhood of y^*. However, note, to leading order, that the implicit y dependence in $D_N(x)$ is the same as the y dependence in $\mathcal{N}$. Since we integrate over all space, and ultimately divide $D_N(x)$ by $\mathcal{N}$, any error in not approximating y properly at y^* will therefore be cancelled, to leading order. All that we have to be certain about is that our y integrals are dominated by the neighbourhood of y^*.

The WKB solutions for y well away from y^* are correct since $f_N(x)$ does not vary rapidly there. The contribution to the integrals $D_N(x)$ and $\mathcal{N}$ from these regions were negligible compared with the contribution from y near y^*, so that the integrals are, in fact, dominated by the neighbourhood of y^*. Thus from this discussion we believe that our solutions in the region $|y^* - x| > \mathrm{O}(\lambda^{-2/3})$ are correct.

Next consider the validity of (76) for $f_N(y^*)$. As far as the y integration is concerned by comparing (64) and (72), for $\mathcal{N}$ and $D_N(x)$, respectively, one can see that the leading-order y dependence is the same. Thus the arguments we used above concerning the cancellation of errors in the y integrals in $D_N(x)$ and $\mathcal{N}$ still hold. As far as x is concerned there are higher-order terms in the WKB series that we should not have neglected. If $f'_N(y^*) \sim \mathrm{O}(\lambda)$ these higher-order terms are O(1). Since these terms are in the exponent and O(1), they will only affect the coefficient of $[\lambda/(-f'_N(y^*)]^{1/3}$. Thus $f_N(y^*)$ will still be O(1), although not the same O(1) number that (76) implies.

The same reasoning that we applied to $f_N(y^*)$ now applies to $f'_N(y^*)$. That is, the higher-order terms in the WKB series are not negligible for x near y^* and so they affect the coefficient of λ. Thus although our analysis implies the coefficient of λ is zero we

believe proper consideration of the higher-order terms in the WKB series would rectify this inconsistency.

This discussion is merely meant to give a qualitative reasoning for the inconsistency in our solutions. To remedy the WKB solutions in the neighbourhood of y^* we must solve (40) exactly in the decay region. The exact Green's function solution must be matched into the WKB solutions which are valid well away from y^* in a manner analogous to the method we used to obtain our solutions in the region $x < \mathrm{O}(\lambda^{-3/2})$ (see equations (42)–(45)) and to the turning point analysis. We have attempted to do this under the assumption that $f_N(x)$ is given by

$$f_N(x) \sim f_N(y^*) + \mathrm{O}(\lambda)(y^* - x) \tag{86}$$

in the decay region. However, matching the Green's function solutions into the regions well away from y^* is not possible. It becomes apparent that one must give a more complete description of the functionality of $f_N(x)$ in this region, i.e. how $f_N(x)$ behaves near the boundaries of the decay region. Assuming a more complex form for $f_N(x)$, however, makes it difficult to obtain an exact solution of (40) in the decay region. Nevertheless, it is felt, if such a solution can be found, a complete self-consistent solution of the excluded volume problem is possible.

5. Conclusions

In this study we have used a self-consistent mean-field method to determine the configurational properties of long-chain polymers under the excluded volume interaction. The formalism that we have presented is, in fact, quite general so that it may be extended to three dimensions and to more general interactions.

Using a scaling argument, we verify the Flory result for excluded volume polymers in 2D, i.e. $R_N \sim N^{3/4}$. We have found that the asymptotics of the problem are dominated by the neighbourhood of the turning point. By obtaining a uniformly valid Green's function solution to the differential equations we are able to show that there exists a point y^*, where y^* is an O(1) number, in the neighbourhood of which the polymer density decays rapidly. We believe the rate of decay is $\mathrm{O}(\lambda)$. This result causes the Green's function solutions to be incorrect in the neighbourhood of y^*. In spite of this, we believe, due to the structure of the problem, that our solutions for $|y^* - x| > \mathrm{O}(\lambda^{-2/3})$ (equations (79) and (80)) are still valid. This is based on the fact that any Green's function solution must necessarily match with the WKB solutions well away from y^*. To obtain a complete self-consistent solution for the problem we require to solve the differential equations exactly in the neighbourhood of y^*. Although this is a difficult task we are currently pursuing this objective.

Acknowledgments

We would like to thank Robert Bursill for useful discussions and the financial support of an Australian Postgraduate Research Award and a NSTB Post-doctoral Fellowship is gratefully acknowledged.

Appendix

In this appendix we consider obtaining the function $G_0(x, y)$ and construct the function $D_N(x)$. To obtain $G_0(x, y)$ we must solve the scaled versions of (23)–(25) along the

negative real axis. To do this we write $G_0(x, y) = g_0(x, y)/y^{1/2}$ and hence solve the following equations for $g_0(x, y)$:

$$\frac{\partial^2 g_0}{\partial y^2} + \frac{1}{y}\frac{\partial g_0}{\partial y} - \lambda^2\left[f(y) + \mathrm{e}^{\pm \mathrm{i}\pi} f(x_s) - \frac{1}{(2\lambda y)^2}\right] g_0 = 0 \qquad y \neq x \tag{A1}$$

subject to the boundary conditions:

$$\left.\frac{\partial g_0}{\partial y}\right|_{y=x_+} - \left.\frac{\partial g_0}{\partial y}\right|_{y=x_-} = \frac{-2}{x^{1/2}} \tag{A2}$$

and

$$g_0|_{y=x_+} = g_0|_{y=x_-} \tag{A3}$$

along the upper and lower branches of the branch cut. The general solution is given by

$$g_{0,\pm}(x, y) = A_\pm(x)\mathrm{ai}(x_s, y) + B_\pm(x)\mathrm{bi}(x_s, y) \tag{A4}$$

for $y < x$, and

$$g_{0,\pm}(x, y) = C_\pm(x)\mathrm{ai}(x_s, y) + D_\pm(x)\mathrm{bi}(x_s, y) \tag{A5}$$

for $y > x$. We have four arbitrary complex constants to determine while, at the moment, we only have two boundary conditions so that another two are required. These two conditions are given by (i) insisting that as $y \to \infty$, for fixed x, that $g_{0,\pm}(x, y)$ has the same y dependence as $g_\pm(y)$ and (ii) imposing the reversibility property of Green's functions which implies $\lim_{y\to 0}(g_{0,\pm}(x, y)/y^{1/2}) = g_\pm(x)/x^{1/2}$. To obtain the boundary conditions as $y \to 0$ we must make use of both solutions $G^{(1)}(x)$ and $G^{(2)}(x)$ given by (44) and (45). Solving for all four boundary conditions then gives the particular solutions for $g_{0,\pm}(x, y)$ along the upper and lower branches:

$$g_{0,\pm}(x, y) \sim \frac{\pi}{\lambda x^{1/2}}[\mathrm{bi}(x_s, x) \mp \mathrm{i}\,\mathrm{ai}(x_s, x)][\mathrm{ai}(x_s, y) - \mathrm{e}^{-2\lambda w_1}(\mathrm{bi}(x_s, y) \mp \mathrm{i}\,\mathrm{ai}(x_s, y))] \tag{A6}$$

for $y < x$, and

$$g_{0,\pm}(x, y) \sim \frac{\pi}{\lambda x^{1/2}}[\mathrm{bi}(x_s, y) \mp \mathrm{i}\,\mathrm{ai}(x_s, y)][\mathrm{ai}(x_s, x) - \mathrm{e}^{-2\lambda w_1}(\mathrm{bi}(x_s, x) \mp \mathrm{i}\,\mathrm{ai}(x_s, x))] \tag{A7}$$

for $y > x$. We can see that this function is symmetric in x and y as required for a Green's function.

To construct $D_N(x)$ defined by (58) we follow the same procedure as outlined to construct $\mathcal{N}$. The function $g_\pm(x)$ is given in (50). $D_N(x)$ is formed by multiplying $g_+(x)$ and $g_{0,+}(x, y)$ on the upper branch and multiplying $g_-(x)$ and $g_{0,-}(x, y)$ on the lower branch and then taking the integral of their difference. When this is done we find the resulting dominant terms in $D_N(x)$ are given by

$$D_N(x) \sim I_1(x) + I_2(x) \tag{A8}$$

where

$$\begin{aligned} I_1(x) = {} & \frac{\pi^{1/2}\gamma_N}{x}\left(\frac{3\pi}{4\lambda}\right)^{1/2} \\ & \times \left\{\int_0^{f(x)} \mathrm{d}(f(x_s))\,\mathrm{e}^{-\lambda[w_1 + f(x_s)]} 2\mathrm{ai}(x_s, x)\mathrm{bi}(x_s, x)\int_0^x \mathrm{ai}(x_s, y) y^{1/2}\,\mathrm{d}y \right. \\ & + \int_{f(x)}^{\infty} \mathrm{d}(f(x_s))\,\mathrm{e}^{-\lambda[w_1 + f(x_s)]} 2\mathrm{ai}(x_s, x)\mathrm{bi}(x_s, x)\int_0^{x_s} \mathrm{ai}(x_s, y) y^{1/2}\,\mathrm{d}y \\ & \left. + \int_{f(x)}^{\infty} \mathrm{d}(f(x_s))\,\mathrm{e}^{-\lambda[w_1 + f(x_s)]} 2\mathrm{ai}(x_s, x)\mathrm{bi}(x_s, x)\int_{x_s}^x \mathrm{ai}(x_s, y) y^{1/2}\,\mathrm{d}y \right\} \end{aligned} \tag{A9}$$

and

$$I_2(x) = \frac{\pi^{1/2}\gamma_N}{x}\left(\frac{3\pi}{4\lambda}\right)^{1/2} \times \left\{ \int_0^{f(x)} \mathrm{d}(f(x_s))\, \mathrm{e}^{-\lambda[w_1+f(x_s)]}\mathrm{ai}(x_s,x)\mathrm{bi}(x_s,x) \int_x^{x_s} \mathrm{ai}(x_s,y)y^{1/2}\,\mathrm{d}y + \int_0^{f(x)} \mathrm{d}(f(x_s))\, \mathrm{e}^{-\lambda[w_1+f(x_s)]}\mathrm{ai}(x_s,x)\mathrm{bi}(x_s,x) \int_{x_s}^{\infty} \mathrm{ai}(x_s,y)y^{1/2}\,\mathrm{d}y + \int_{f(x)}^{\infty} \mathrm{d}(f(x_s))\, \mathrm{e}^{-\lambda[w_1+f(x_s)]}\mathrm{ai}(x_s,x)\mathrm{bi}(x_s,x) \int_x^{\infty} \mathrm{ai}(x_s,y)y^{1/2}\,\mathrm{d}y + \int_0^{f(x)} \mathrm{d}(f(x_s))\, \mathrm{e}^{-\lambda[w_1+f(x_s)]}\mathrm{ai}^2(x_s,x) \int_x^{x_s} \mathrm{bi}(x_s,y)y^{1/2}\,\mathrm{d}y + \int_0^{f(x)} \mathrm{d}(f(x_s))\, \mathrm{e}^{-\lambda[w_1+f(x_s)]}\mathrm{ai}^2(x_s,x) \int_{x_s}^{\infty} \mathrm{bi}(x_s,y)y^{1/2}\,\mathrm{d}y + \int_{f(x)}^{\infty} \mathrm{d}(f(x_s))\, \mathrm{e}^{-\lambda[w_1+f(x_s)]}\mathrm{ai}^2(x_s,x) \int_x^{\infty} \mathrm{bi}(x_s,y)y^{1/2}\,\mathrm{d}y \right\}. \tag{A10}$$

Finally, we make the change of variables defined by (63) and by $\eta = f(x) - f(y^*)$ on these integrals. We then find

$$I_1(x) = \frac{\pi^{1/2}\mathrm{e}^{-\lambda f(y^*)}}{x} \left\{ \int_{-f(y^*)}^{\eta} \mathrm{d}s\, \mathrm{e}^{-\lambda\mathcal{F}(s)} 2\left(\tfrac{3}{2}\lambda\xi\right)^{1/3} \frac{\mathrm{Ai}\left[\left(\frac{3}{2}\lambda\xi\right)^{2/3}\right]\mathrm{Bi}\left[\left(\frac{3}{2}\lambda\xi\right)^{2/3}\right]}{(\eta-s)^{1/2}} \times \int_{\infty}^{\eta} \frac{\mathrm{d}\epsilon\, y^{1/2}(\epsilon)}{f'(y(\epsilon))} \left(\tfrac{3}{2}\lambda\Gamma\right)^{1/6} \frac{\mathrm{Ai}\left(\frac{3}{2}\lambda\Gamma\right)^{2/3}]}{(\epsilon-s)^{1/4}} + \int_{\eta}^{\infty} \mathrm{d}s\, \mathrm{e}^{-\lambda\mathcal{F}(s)} 2\left(\tfrac{3}{2}\lambda\zeta\right)^{1/3} \frac{\mathrm{Ai}\left[-\left(\frac{3}{2}\lambda\zeta\right)^{2/3}\right]\mathrm{Bi}\left[-\left(\frac{3}{2}\lambda\zeta\right)^{2/3}\right]}{(s-\eta)^{1/2}} \times \int_{\infty}^{s} \frac{\mathrm{d}\epsilon\, y^{1/2}(\epsilon)}{f'(y(\epsilon))} \left(\tfrac{3}{2}\lambda\Gamma\right)^{1/6} \frac{\mathrm{Ai}\left[\left(\frac{3}{2}\lambda\Gamma\right)^{2/3}\right]}{(\epsilon-s)^{1/4}} + \int_{\eta}^{\infty} \mathrm{d}s\, \mathrm{e}^{-\lambda\mathcal{F}(s)} 2\left(\tfrac{3}{2}\lambda\zeta\right)^{1/3} \frac{\mathrm{Ai}\left[-\left(\frac{3}{2}\lambda\zeta\right)^{2/3}\right]\mathrm{Bi}\left[-\left(\frac{3}{2}\lambda\zeta\right)^{2/3}\right]}{(s-\eta)^{1/2}} \times \int_{s}^{\eta} \frac{\mathrm{d}\epsilon\, y^{1/2}(\epsilon)}{f'(y(\epsilon))} \left(\tfrac{3}{2}\lambda G\right)^{1/6} \frac{\mathrm{Ai}\left[-\left(\frac{3}{2}\lambda G\right)^{2/3}\right]}{(s-\epsilon)^{1/4}} \right\} \tag{A11}$$

and

$$I_2(x) = \frac{\pi^{1/2}\mathrm{e}^{-\lambda f(y^*)}}{x} \left\{ \int_{-f(y^*)}^{\eta} \mathrm{d}s\, \mathrm{e}^{-\lambda\mathcal{F}(s)} \left(\tfrac{3}{2}\lambda\xi\right)^{1/3} \frac{\mathrm{Ai}\left[\left(\frac{3}{2}\lambda\xi\right)^{2/3}\right]\mathrm{Bi}\left[\left(\frac{3}{2}\lambda\xi\right)^{2/3}\right]}{(\eta-s)^{1/2}} \times \int_{\eta}^{s} \frac{\mathrm{d}\epsilon\, y^{1/2}(\epsilon)}{f'(y(\epsilon))} \left(\tfrac{3}{2}\lambda\Gamma\right)^{1/6} \frac{\mathrm{Ai}\left[\left(\frac{3}{2}\lambda\Gamma\right)^{2/3}\right]}{(\epsilon-s)^{1/4}} + \int_{-f(y^*)}^{\eta} \mathrm{d}s\, \mathrm{e}^{-\lambda\mathcal{F}(s)} \left(\tfrac{3}{2}\lambda\xi\right)^{1/3} \frac{\mathrm{Ai}\left[\left(\frac{3}{2}\lambda\xi\right)^{2/3}\right]\mathrm{Bi}\left[\left(\frac{3}{2}\lambda\xi\right)^{2/3}\right]}{(\eta-s)^{1/2}} \times \int_{s}^{-f(y^*)} \frac{\mathrm{d}\epsilon\, y^{1/2}(\epsilon)}{f'(y(\epsilon))} \left(\tfrac{3}{2}\lambda G\right)^{1/6} \frac{\mathrm{Ai}\left[-\left(\frac{3}{2}\lambda G\right)^{2/3}\right]}{(s-\epsilon)^{1/4}}$$

$$
\begin{aligned}
&+\int_{\eta}^{\infty} \mathrm{d}s\, \mathrm{e}^{-\lambda\mathcal{F}(s)}\left(\tfrac{3}{2}\lambda\zeta\right)^{1/3}\frac{\mathrm{Ai}\left[-\left(\tfrac{3}{2}\lambda\zeta\right)^{2/3}\right]\mathrm{Bi}\left[-\left(\tfrac{3}{2}\lambda\zeta\right)^{2/3}\right]}{(s-\eta)^{1/2}}\\
&\times\int_{\eta}^{-f(y^*)}\frac{\mathrm{d}\epsilon\, y^{1/2}(\epsilon)}{f'(y(\epsilon))}\left(\tfrac{3}{2}\lambda G\right)^{1/6}\frac{\mathrm{Ai}\left[-\left(\tfrac{3}{2}\lambda G\right)^{2/3}\right]}{(s-\epsilon)^{1/4}}\\
&+\int_{-f(y^*)}^{\eta}\mathrm{d}s\, \mathrm{e}^{-\lambda\mathcal{F}(s)}\left(\tfrac{3}{2}\lambda\xi\right)^{1/3}\frac{\mathrm{Ai}^2\left[\left(\tfrac{3}{2}\lambda\xi\right)^{2/3}\right]}{(\eta-s)^{1/2}}\\
&\times\int_{\eta}^{s}\frac{\mathrm{d}\epsilon\, y^{1/2}(\epsilon)}{f'(y(\epsilon))}\left(\tfrac{3}{2}\lambda\Gamma\right)^{1/6}\frac{\mathrm{Bi}\left[\left(\tfrac{3}{2}\lambda\Gamma\right)^{2/3}\right]}{(\epsilon-s)^{1/4}}\\
&+\int_{-f(y^*)}^{\eta}\mathrm{d}s\, \mathrm{e}^{-\lambda\mathcal{F}(s)}\left(\tfrac{3}{2}\lambda\xi\right)^{1/3}\frac{\mathrm{Ai}^2\left[\left(\tfrac{3}{2}\lambda\xi\right)^{2/3}\right]}{(\eta-s)^{1/2}}\\
&\times\int_{s}^{-f(y^*)}\frac{\mathrm{d}\epsilon\, y^{1/2}(\epsilon)}{f'(y(\epsilon))}\left(\tfrac{3}{2}\lambda G\right)^{1/6}\frac{\mathrm{Bi}\left[-\left(\tfrac{3}{2}\lambda G\right)^{2/3}\right]}{(s-\epsilon)^{1/4}}\\
&+\int_{\eta}^{\infty}\mathrm{d}s\, \mathrm{e}^{-\lambda\mathcal{F}(s)}\left(\tfrac{3}{2}\lambda\xi\right)^{1/3}\frac{\mathrm{Ai}^2\left[\left(\tfrac{3}{2}\lambda\xi\right)^{2/3}\right]}{(\eta-s)^{1/2}}\\
&\times\int_{\eta}^{-f(y^*)}\frac{\mathrm{d}\epsilon\, y^{1/2}(\epsilon)}{f'(y(\epsilon))}\left(\tfrac{3}{2}\lambda G\right)^{1/6}\frac{\mathrm{Bi}\left[-\left(\tfrac{3}{2}\lambda G\right)^{2/3}\right]}{(s-\epsilon)^{1/4}}\Bigg\}. \qquad \text{(A12)}
\end{aligned}
$$

References

[1] Flory P J 1948 *J. Chem. Phys.* **17** 303
Flory P J 1971 *Principles of Polymer Chemistry* (Ithaca, NY: Cornell University Press)
[2] Freed K F 1971 *J. Chem. Phys.* **55** 3910
Gillis H P and Freed K F 1975 *J. Chem. Phys.* **63** 852
Kosmas M K and Freed K F 1978 *J. Chem. Phys.* **68** 4878
[3] Edward S F 1965 *Proc. Phys. Soc.* **85** 613
[4] Reiss H 1967 *J. Chem. Phys.* **47** 186
[5] Pereira G G 1995 *Physica* **219A** 290
[6] Pereira G G 1993 *PhD Thesis* The University of Melbourne
[7] Shannon S R, Choy T C and Fleming R J 1996 *Phys. Rev.* B **53** 2175
[8] Yamakawa H 1971 *Modern Theory of Polymer Solutions* (New York: Harper and Row)
[9] Hughes B D 1995 *Random Walks and Random Environments* vol 1 (Oxford: Oxford University Press)
[10] Whittaker E T and Watson G N 1927 *A Course of Modern Analysis* 4th edn (Cambridge: Cambridge University Press)
[11] Copson E T 1935 *An Introduction to the Theory of Functions of a Complex Variable* (Oxford: Clarendon)
[12] Titchmarsh E C 1932 *The Theory of Functions* (Oxford: Clarendon)
[13] de Gennes P G 1979 *Scaling Concepts in Polymer Physics* (Ithaca, NY: Cornell University Press)
[14] Fisher M E 1966 *J. Chem. Phys.* **44** 616
[15] Barber M N and Ninham B W 1970 *Random and Restricted Walks* (New York: Gordon and Breach)
[16] Bender C M and Orszag S A 1978 *Advanced Mathematical Methods for Scientists and Engineers* (New York: McGraw-Hill)
[17] Olver F W J 1974 *Asymtotics and Special Functions* (New York: Academic)
[18] Abramowitz M and Stegun I A 1970 *Handbook of Mathematical Functions* (New York: Dover)