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AN IDEAL POLYMER CHAIN IN ARBITRARY DIMENSIONS NEAR AN ATTRACTIVE SITE

S.N. MAJUMDAR
Tata Institute of Fundamental Research, Homi Bhabha Road, Bombay 400005, India

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We study a lattice model of an ideal (no self-exclusion) polymer chain in d dimensions in the presence of an attractive site. For very long chains, we calculate analytically, for all dimensions, the partition function, the average energy per monomer unit and the probability distribution of the end-to-end length of the chain. For $d \geq 3$, the system undergoes a phase transition from the low-temperature adsorbed phase to a high-temperature extended phase. This transition is continuous for $d \leq 4$ and first order for $d > 4$. We determine the finite-size scaling functions near the transition for all $d \neq 4$. For $d = 4$, there is no scaling form due to the existence of logarithmic corrections.

1. Introduction

The statistical mechanics of polymer molecules interacting with surfaces and interfaces is a subject of long standing interest. The potential of important technological applications has motivated much theoretical and experimental research in this area. Recent experimental studies [1–3] have revealed the complexity of the phenomena involved. One particularly interesting phenomenon is the *adsorption–desorption* transition of a polymer chain near an attractive surface from the low-temperature *adsorbed* phase where the polymer is collapsed (staying close to the surface), to a high-temperature *desorbed* phase where it is extended (most of the monomers are not near the adsorbing surface).

Various theoretical models have been suggested for studying the equilibrium properties of this phenomenon. A particularly simple case where this transition still occurs is a system of highly dilute polymer solution near an attractive surface. This case is easier to deal with theoretically as it is sufficient to consider a single chain interacting with the surface. A random-walk lattice model of this system in 3D was considered by Rubin [4] in case of an ideal polymer chain (self-excluded-volume effect not taken into account). He calcu-

lated analytically the average number of monomer units in the surface layer and the mean extent of the chain in the direction normal to the surface. He also considered [5] the adsorption of a polymer chain to a long rigid rod-like molecule on a 3D cubic lattice. The behaviour of a long ideal chain interacting with two parallel surfaces in a 3D simple cubic lattice was investigated by Van Opheusden et al. [6]. They found an exact closed set of equations to determine the relevant thermodynamic quantities as a function of the interaction energy, temperature and the distance between the two plates. Eisenriegler et al. [7] considered a polymer chain in a d-dimensional lattice and interacting with a $(d-1)$-dimensional surface. For the ideal Gaussian chain, they evaluated the associated exponents and the scaling functions analytically.

When the self-excluded volume effect is taken into account, the problem becomes difficult to tackle analytically. For this case, general scaling ideas have been proposed [7–10] and Monte Carlo [11] and real-space renormalization [12] calculations have been done to estimate the exponents and the scaling functions near the transition point. Exact lattice SAW enumeration [13–15] and transfer matrix methods [16] have been used to study the behaviour of a single self-avoiding chain near surfaces and interfaces, and in two dimensions the exact critical exponents are known from conformal invariance arguments [17]. An exact solution for a class of directed SAW models of the adsorption transition in 2 and 3 dimensions has been recently obtained by Privman et al. [18, 19]. Using transfer matrix methods, they have evaluated quantities like the fraction of monomers at the substrate and the concentration profile of monomers as a function of the distance from the wall.

A natural generalization of the adsorption of a single chain in a d-dimensional lattice to a $(d-1)$-dimensional attractive surface would be the adsorption to a $d' < d$ dimensional subset of the lattice. This problem has been considered in detail for some fractal lattices [20] where d and d' are not integers. For integers d and d' and in case of a Gaussian chain, it is easy to see that this problem is reducible to that of the adsorption of a chain in a $(d-d')$-dimensional lattice to a 0-dimensional subset, i.e. a particular site of the lattice. Thus for the Gaussian chain it is sufficient to consider the chain in a d-dimensional lattice and interacting attractively to a particular lattice site.

The dynamic properties of a polymer chain near its adsorption–desorption transition are, however, as for most other physical systems [21, 22], relatively less understood compared to their static counterpart. The dynamics of dilute polymer solutions was first modelled by Rouse [23]. In this model the polymer is represented by a set of beads connected along a chain and having localized interactions only (excluded-volume effect not considered). The dynamics of the chain is modelled by the Brownian motion of the beads. A variant of this model was suggested by Verdier and Stockmayer [24]. They started with a

freely jointed chain and simulated its dynamics by allowing local jumps of the beads. We have been interested in studying the dynamics of a simple, ideal chain on a lattice near its adsorption–desorption transition as it provides one of the simplest examples where dynamical effects near a phase transition can be analytically studied. We have considered an ideal chain embedded in a d-dimensional hypercubic lattice and interacting with a single attractive site of the lattice. However, as a prerequisite, we have studied the equilibrium statistical mechanics of this model in some detail and calculated the exact scaling functions of various thermodynamic quantities near the transition temperature. We find that the thermodynamic properties of this model have an interesting, nontrivial dependence on the dimension d of the lattice. These results are summarized in this paper. We hope to deal with the dynamical properties of the chain in a future publication.

We consider a single polymer chain in a d-dimensional hypercubic lattice. The chain consists of n momomer units. One end of the chain is fixed at the origin of the lattice, the other end being free. The monomers are constrained to lie along the bonds of the lattice. The chain is ideal (no self-avoidance or other self-interactions). The origin is a special adsorbing site in the following sense. It associates a negative adsorption energy $-mE$ (with $E>0$) to a chain configuration with m returns to the origin. So, in equilibrium, the canonical weight to be associated with this configuration is y^m, where $y = e^{E/k_B T}$, where T is the temperature and k_B is the Boltzman constant. We calculate analytically the partition function, mean square end-to-end distance of the chain, average energy, the probability distribution of the position of the free end of the chain, etc., as a function of y (hence of T) in all dimensions, in the limit of a very long chain ($n \to \infty$).

In the long chain limit, the behaviour of various thermodynamic quantities shows some interesting features. For $d \geq 3$, we show that there exists a finite $T = T_c$ such that, for $T > T_c$, the mean square end-to-end distance $\bar{r}^2(y, n)$ of the chain increases linearly with n for large n. This is said to be the *extended* phase of the polymer chain. For $T < T_c$, $\bar{r}^2(y, n)$ remains finite even as n tends to infinity. The polymer is then said to be in the *localized* or *adsorbed* phase. In dimensions 1 and 2, the chain remains in the adsorbed phase at any finite temperature, and the critical temperature T_c is infinite.

The effect of the dimension of the space on the nature of the transition mentioned above is particularly interesting. As mentioned above, for $d \leq 2$ there is no phase transition. We show that the transition is *continuous* for $2 < d \leq 4$ and *first order* for $d > 4$. For finite n, we study the finite-size effects on different thermodynamic quantities including the partition function. Near $T = T_c$, all of them exhibit finite-size scaling behaviour in all dimensions, except for $d = 4$, where the corresponding quantities do not have a scaling form

due the appearance of logarithmic corrections to power-law forms. So, $d = 2$ and $d = 4$ turn out to be the special dimensions. We derive exact expressions for different scaling functions. In particular, for $d \geq 5$, this gives a simple, soluble example where finite-size scaling holds for first-order transitions [25] and the scaling functions can be computed explicitly.

The plan of the paper is as follows. In section 2, we introduce the notation and derive integral representations for the thermodynamic quantities of interest in terms of the generating functions of random walks on the lattice. In section 3, we derive an expression for T_c for $d \geq 3$ and show that $T_c = \infty$ for $d = 1$ and 2. Section 4 deals with the partition function in the large n limit and its scaling form near $T = T_c$. Explicit expressions for the mean square end-to-end distance and the corresponding scaling functions are derived in section 5. In sections 6 and 7, we investigate the scaling behaviour of the average energy and the probability distribution of the position of the chain-end, respectively. In the concluding section 8, we summarize and discuss the results. The mathematical details of the asymptotic analysis of some of the integrals are included in the three appendices.

2. Generating functions

Each n-step walk on a d-dimensional hypercubic lattice corresponds to a particular polymer configuration. The statistics of such walks can be studied by defining appropriate generating functions [26] as done below. We, then, express all the thermodynamic quantities in terms of these random-walk generating functions.

Let $C_m^r(\boldsymbol{x})$ be the number of r-stepped paths starting from the origin and finally arriving at $\boldsymbol{x}$ with m returns to the origin in between. Then

$$\begin{aligned} C(r) &= \sum_{\boldsymbol{x}} \sum_{m} C_m^r(\boldsymbol{x}) \\ &= \text{total number of } r\text{-stepped paths starting from the origin} \\ &= (2d)^r . \end{aligned}$$

Clearly, $C_m^r = 0$ if $m > r/2$. We define

$$P(\boldsymbol{x}, y, r) = \left(\sum_{m} y^m C_m^r(\boldsymbol{x}) \right) (2d)^{-r} . \tag{2.1}$$

If $y = 1$, $P(\boldsymbol{x}, y, r)$ is the probability that a random walk starting at the origin will end at $\boldsymbol{x}$ after r steps. The generating function for $P(\boldsymbol{x}, y, r)$ is defined as

$$G(\boldsymbol{x}, y, z) = \sum_{r=0}^{\infty} P(\boldsymbol{x}, y, r)\, z^r \,. \tag{2.2}$$

The random walk generating function $U(\boldsymbol{x}, z)$ is defined by

$$U(\boldsymbol{x}, z) = G(\boldsymbol{x}, y = 1, z) \,. \tag{2.3}$$

Let $F(z)$ be the generating function for the probability of a path starting at the origin and coming back there for the first time (this is usually called the first-passage probability) and $S(\boldsymbol{x}, z)$ be the generaing function for the probability of a path starting at the origin and arriving at $\boldsymbol{x}$ without coming back to the origin. Clearly

$$G(\boldsymbol{x}, y, z) = \sum_{k=0}^{\infty} [yF(z)]^k S(\boldsymbol{x}, z) = \frac{S(\boldsymbol{x}, z)}{1 - yF(z)} \,. \tag{2.4}$$

Since

$$U(\boldsymbol{x}, z) = G(\boldsymbol{x}, y = 1, z) = \frac{S(\boldsymbol{x}, z)}{1 - F(z)} \,, \tag{2.5}$$

we get

$$G(\boldsymbol{x}, y, z) = \left(\frac{1 - F(z)}{1 - yF(z)} \right) U(\boldsymbol{x}, z) \,. \tag{2.6}$$

The partition function for a chain of n monomers is defined as

$$\Omega(y, n) = \sum_{\boldsymbol{x}} P(\boldsymbol{x}, y, n) \,. \tag{2.7}$$

We define $\Gamma(\boldsymbol{\varphi}, y, z)$ to be the Fourier transform of $G(\boldsymbol{x}, y, z)$,

$$\Gamma(\boldsymbol{\varphi}, y, z) = \sum_{\boldsymbol{x}} \mathrm{e}^{\mathrm{i}\boldsymbol{\varphi}\cdot\boldsymbol{x}} G(\boldsymbol{x}, y, z) \,, \tag{2.8}$$

where the vector $\boldsymbol{\varphi}$ is a d-dimensional vector lying in the first Brillouin zone. Using (1.6), it is easy to show that

$$\Gamma(\boldsymbol{\varphi}, y, z) = \left(\frac{1 - F(z)}{1 - yF(z)} \right) \frac{1}{[1 - z\lambda(\boldsymbol{\varphi})]} \,, \tag{2.9}$$

where

$$\lambda(\boldsymbol{\varphi}) = \sum p(\boldsymbol{l})\, \mathrm{e}^{\mathrm{i}\boldsymbol{\varphi}\cdot\boldsymbol{l}} \,, \tag{2.10}$$

where the summation extends over all the nearest neighbour bonds $\boldsymbol{l}$, and $p(\boldsymbol{l})$ is the probability that the random walk will take place along that bond [26].

For an isotropic random walk on a hypercubic lattice of dimension d

$$p(\boldsymbol{l}) = \frac{1}{2d} \tag{2.11}$$

for each of the $2d$ bond directions $\boldsymbol{l}$ from any lattice site. Now

$$\Gamma(0, y, z) = \sum_{r=0}^{\infty} \Omega(y, r)\, z^r ,$$

whence

$$\Omega(y, n) = \frac{1}{2\pi \mathrm{i}} \oint_{C_0} \frac{\Gamma(0, y, z)}{z^{n+1}}\, \mathrm{d}z , \tag{2.12}$$

where C_0 is a closed contour in the complex-z plane enclosing only the pole at $z = 0$. The mean square end-to-end distance $\bar{r}^2(y, n)$ is defined as

$$\bar{r}^2(y, n) = \frac{1}{\Omega(y, n)} \sum_{\boldsymbol{x}} x^2 P(\boldsymbol{x}, y, n) . \tag{2.13}$$

Now

$$-\nabla_{\boldsymbol{\varphi}}^2 \Gamma(\boldsymbol{\varphi}, y, z)|_{\boldsymbol{\varphi}=\boldsymbol{0}} = \sum_{r=0}^{\infty} \left(\sum_{\boldsymbol{x}} x^2 P(\boldsymbol{x}, y, r) \right) z^r , \tag{2.14}$$

whence

$$\sum_{\boldsymbol{x}} x^2 P(\boldsymbol{x}, y, n) = \frac{1}{2\pi \mathrm{i}} \oint_{C_0} \frac{-\nabla_{\boldsymbol{\varphi}}^2 \Gamma(\boldsymbol{\varphi}, y, z)|_{\boldsymbol{\varphi}=\boldsymbol{0}}}{z^{n+1}}\, \mathrm{d}z . \tag{2.15}$$

The average energy $\bar{E}(y, n)$, in units of $k_{\mathrm{B}}T$, is given by

$$\bar{E}(y, n) = -y \log y\, \frac{\partial \log \Omega(y, n)}{\partial y} . \tag{2.16}$$

The normalized probability distribution of the position of the chain-end is defined as

$$Q(\boldsymbol{x}, y, n) = \frac{1}{\Omega(y, n)}\, P(\boldsymbol{x}, y, n) = \frac{1}{\Omega(y, n)}\, \frac{1}{2\pi \mathrm{i}} \oint_{C_0} \frac{1}{z^{n+1}}\, G(\boldsymbol{x}, y, z)\, \mathrm{d}z . \tag{2.17}$$

Using the expressions for $G(\boldsymbol{x}, y, z)$ and $\Gamma(\boldsymbol{\varphi}, y, z)$ from eqs. (2.6) and (2.9), respectively, and substituting them in (2.12), (2.15) and (2.16), respectively, we get the following integral representations:

$$\Omega(y, n) = \frac{1}{2\pi i} \oint_{C_0} \frac{1 - F(z)}{z^{n+1}[1 - yF(z)](1 - z)} \, dz \,, \tag{2.18}$$

$$\bar{r}^2(y, n) = \frac{1}{\Omega(y, n)\, 2\pi i} \oint_{C_0} \frac{1 - F(z)}{z^n[1 - yF(z)](1 - z)^2} \, dz \,, \tag{2.19}$$

$$\bar{E}(y, n) = -\frac{y \log y}{\Omega(y, n)\, 2\pi i} \oint_{C_0} \frac{F(z)\,[1 - F(z)]}{z^{n+1}[1 - yF(z)]^2(1 - z)} \, dz \,, \tag{2.20}$$

$$Q(\boldsymbol{x}, y, n) = \frac{1}{\Omega(y, n)\, 2\pi i} \oint_{C_0} \frac{1 - F(z)}{z^{n+1}[1 - yF(z)]} \, U(\boldsymbol{x}, z) \, dz \,. \tag{2.21}$$

3. Calculation of T_c

To compute the integrals in eqs. (2.18)–(2.21), we note the following behaviour of $F(z)$ as a function of z in different dimensions:

$$F(z) = \sum_{n=1}^{\infty} f_n z^n \,, \tag{3.1}$$

where f_n is the probability of coming back to the origin for the first time in n steps. For a hypercubic lattice, all odd terms in this expansion are zero and we get

$$F(z) = \sum_{n=1}^{\infty} f_{2n} z^{2n} \,. \tag{3.2}$$

As $f_{2n} \geq 0$, it obviously follows that along the real axis in the complex-z plane, $F(x)$ is an even function of x and for $x \geq 0$ it monotonically increases with x.

According to Polya's theorem [26]

$$\begin{aligned} F(1) &= 1 \,, \qquad d = 1, 2 \,, \\ &< 1 \,, \qquad d \geq 3 \,. \end{aligned} \tag{3.3}$$

So, for real x lying in [0, 1], the function $F(x)$ behaves qualitatively as sketched in fig. 1a and b respectively.

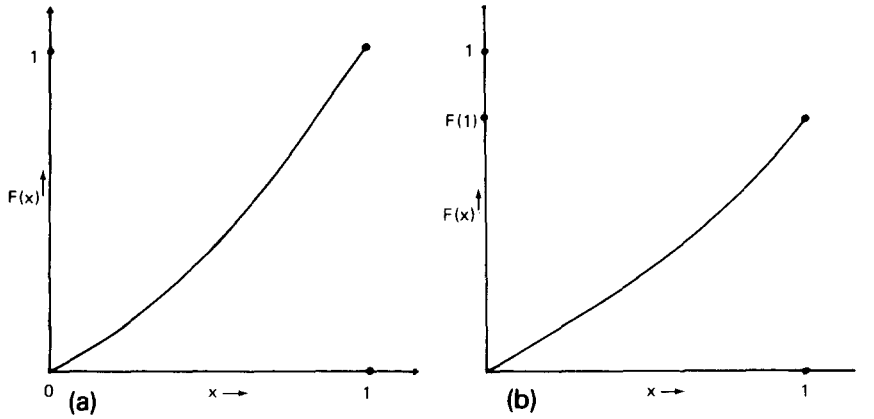

Fig. 1. The behaviour (schematic) of $F(x)$, the generating function for the first-passage probability, with real x lying in $[0, 1]$ for (a) $d \leq 2$, (b) $d \geq 3$.

Now, the singularities of the integrands in eqs. (2.18)–(2.21) occur at

(i) $z = 0$,

(ii) $z = 1$,

(iii) $z = \pm z_+$, where $F(z_+) = \frac{1}{y} \leq 1$ as $y \geq 1$.

For $d \leq 2$, there exists a pair of solutions $z = \pm z_+$ to $F(z) = 1/y$ with $z_+ < 1$ for all $y > 1$. Whereas, for $d \geq 3$, singularity of type (iii) occurs only if $y > y_c = 1/F(1)$. These give rise to different behaviours of the integrals in the two regions $y < y_c$ and $y > y_c$. So, the transition or the critical temperature is given by the equation

$$y_c = e^{E/k_B T_c} = \frac{1}{F(1)} . \tag{3.4}$$

In 1 and 2 dimensions, $F(1)$ is 1, which corresponds to infinite T_c.

4. Partition function

Here we compute the behaviour of the partition function in the limit of large n for the three distinct cases $T < T_c$, $T > T_c$ and $T = T_c$, respectively, in all dimensions of the lattice. Also, we deduce the scaling form of the partition function near $T = T_c$.

Case 1: $T < T_c$

There exists a pair of pole type singularities of the integrand in (2.18) in the

region $|z|<1$ at $\pm z_+$ given by

$$F(z_+) = \frac{1}{y} . \tag{4.1}$$

Also [26],

$$F(z) = 1 - \frac{1}{U(0, z)} . \tag{4.2}$$

The asymptotic expansion of $U(0, z)$ near $z \to 1$ in different dimensions are given by [27, 28]

$$U(0, z) = \begin{cases} \dfrac{1}{\sqrt{1-z^2}} & \text{for } d = 1 , \quad (4.3) \\ -\dfrac{1}{\pi} \ln(1-z) & \text{for } d = 2 , \quad (4.4) \\ u_3 - a_3(1-z)^{1/2} & \text{for } d = 3 , \quad (4.5) \\ u_4 + a_4(1-z)\ln(1-z) & \text{for } d = 4 , \quad (4.6) \\ u_d - a_d(1-z) + \mathcal{O}[(1-z)^\theta \ln(1-z), \theta > 1] & \text{for } d \geqslant 5 , \quad (4.7) \end{cases}$$

where u_n and a_n are positive numerical constants. Similar asymptotic analysis holds for $z \to -1$ with z replaced by $-z$ in the above expressions [27]. Thus, apart from the pole type singularities at $z = 0, 1$ and $\pm z_+$, there are branch-cut singularities at $z = \pm 1$.

In the limit of large n, the partition function is given by the following expression (the details of the calculation are given in appendix A):

$$\Omega(y, n) \approx \frac{1}{z_+^{n+1}} \frac{y-1}{y^2} \frac{1}{F'(z_+)} \left(\frac{1}{1-z_+} + \frac{(-1)^n}{1+z_+} \right) , \tag{4.8}$$

where z_+ is given by the solution of eq. (4.1) and $F'(z_+)$ is the derivative of $F(z)$ at $z = z_+$. As y goes to y_c from above, z_+ tends to 1. Then defining $\epsilon = (y - y_c)/y_c$ and substituting (4.3) to (4.7) and using it in (4.8), we get, for fixed y close to y_c and large n, the following asymptotic values of the partition function in different dimensions:

$$\Omega(y,n)\sim\begin{cases} 2\,\mathrm{e}^{\epsilon^2 n/2} & \text{for } d=1\,, \quad (4.9)\\ \dfrac{\pi}{\epsilon}\,\mathrm{e}^{n\,\mathrm{e}^{-\pi/\epsilon}} & \text{for } d=2\,, \quad (4.10)\\ \dfrac{2}{\epsilon}\left(\dfrac{y_c(3)-1}{y_c(3)}\right)\mathrm{e}^{n\epsilon^2 A_3} & \text{for } d=3\,, \quad (4.11)\\ \left(\dfrac{y_c(4)-1}{y_c^2(4)}\right)\dfrac{1}{(1-z_+)F'(z_+)\,z_+^{n+1}} & \text{for } d=4\,, \quad (4.12)\\ \left(\dfrac{y_c(d)-1}{y_c(d)}\right)\dfrac{1}{\epsilon}\,\mathrm{e}^{A_d n\epsilon} & \text{for } d\geqslant 5\,, \quad (4.13)\end{cases}$$

where $A_3 = u_3^4/y_c^2(3)\,a_3^2$ with $y_c(3) = u_3/(u_3-1)$ and $A_d = u_d^2/y_c(d)\,a_d$ with $y_c(d) = u_d/(u_d-1)$ and z_+ and $F(z_+)$ in (4.12) have to be obtained by solving (4.1), (4.2) and (4.6).

Case 2: $T > T_c$

For $d = 1, 2$, this phase does not exist as T_c is infinite. For other dimensions, we find, to leading order for large n (for details see appendix B), the following behaviour of the partition function:

$$\Omega(y,n)\sim -\left(\frac{y_c(d)-1}{y_c(d)}\right)\frac{1}{\epsilon}\,. \quad (4.14)$$

Case 3: $T = T_c$

For $d \leqslant 2$, $y_c = 1$. From eq. (2.18) it follows trivially that

$$\Omega(y=1,n) = 1\,. \quad (4.15)$$

For $d = 3$, substituting $y = y_c$ in eq. (2.18), it is shown in appendix B that

$$\Omega(y=y_c,n)\approx \frac{2}{a_3[y_c(3)-1]\sqrt{\pi}}\,n^{1/2}\,, \quad (4.16)$$

where $\approx$ indicates that only the leading order term in n has been kept.

For $d = 4$, putting $y = y_c$ in eq. (2.18), one gets

$$\Omega(y=y_c,n)\approx \frac{n}{a_4[y_c(4)-1]}\int_0^\infty \frac{\mathrm{e}^{-nx}}{x}\,\frac{1}{[(\ln x)^2+\pi^2]}\,\mathrm{d}x\,. \quad (4.17)$$

The function

$$I(n) = \int_0^\infty \frac{e^{-nx}}{x} \frac{1}{[(\ln x)^2 + \pi^2]} dx$$

is known as the *Ramanujan function* [29]. This function appears in other fields of physics also such as in the theory of transport of neutrons inside nuclear reactors [30]. The asymptotic analysis of this function shows [29] that $I(n)$ behaves as $1/\log n$ as $n \to \infty$. Using this in (4.17) we get

$$\Omega(y = y_c, n) \approx \frac{1}{a_4[y_c(4) - 1]} \frac{n}{\log n} . \tag{4.18}$$

For $d \geq 5$, again putting $y = y_c$ and following the same procedure, we get the following leading order term for large n:

$$\Omega(y = y_c, n) \approx \frac{n}{a_d[y_c(d) - 1]} . \tag{4.19}$$

We can calculate the partition function per link in the thermodynamic limit, $w(\epsilon)$, by the formula

$$w(\epsilon) = \lim_{n \to \infty} [\Omega(\epsilon, n)]^{1/n} . \tag{4.20}$$

Then the function $w(\epsilon)$ can be easily calculated and shown to be continuous at $\epsilon = 0$ for all $d \geq 3$. For $d \leq 2$, there is no $\epsilon < 0$ phase. The qualitative behaviour of the function $w(\epsilon)$ is shown in fig. 2a and b.

We now show that the partition function has a simple scaling form near $T = T_c$ in all dimensions except for $d = 4$.

For $d = 1$, we define the scaling variable $x = \epsilon(n/2)^{1/2}$ with $\epsilon = (y - y_c)/y_c = y - 1 \geq 0$ (for $d = 1$, $y_c = 1$) and perform the limiting operation $\lim[\epsilon \to 0,$

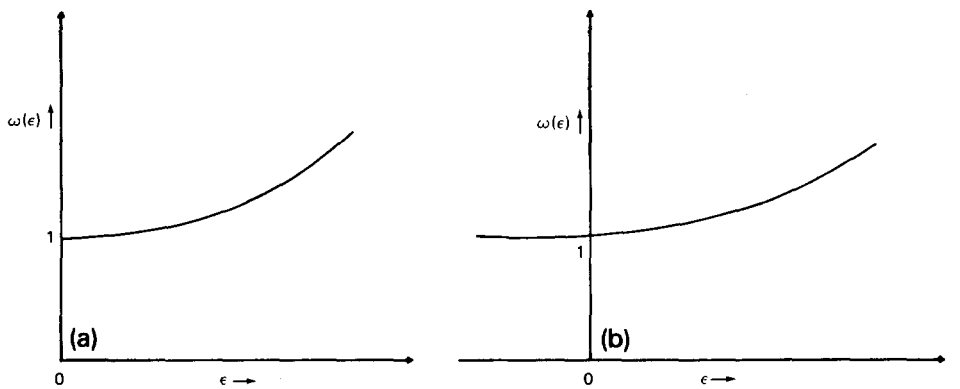

Fig. 2. The qualitative behaviour of $w(\epsilon)$, near $\epsilon = 0$, for (a) $d \leq 2$, (b) $d \geq 3$.

$n \to \infty$, x fixed] on the partition function $\Omega(\epsilon, n)$ to get the scaling function $\Omega(x)$. Using $F(z) = 1 - \sqrt{1 - z^2}$ for $d = 1$ [26] in eq. (2.18), we get after some algebra

$$\Omega(x) = \lim_{n \to \infty} [\Omega(x(n/2)^{-1/2}, n)] = e^{x^2}[1 + \mathrm{erf}(x)] . \tag{4.21}$$

It is easy to check that this scaling function has the proper limits as $x \to 0$ and $x \to \infty$ using the asymptotic expansion of erf(x) [31].

(i) As $x \to 0$, $\Omega(x) \to 1$, which agrees with (4.15).

(ii) As $x \to \infty$, erf$(x) \to 1$ and $\Omega(x) \to 2e^{x^2} = 2e^{\epsilon^2 n/2}$, which agrees with eq. (4.9) as expected.

For $d = 2$, we define the scaling variable $x = n\, e^{-\pi/\epsilon}$. In this case, the partition function $\Omega(\epsilon, n)$, with a proper prefactor ϵ/π, scales as follows:

$$\Omega(\epsilon, n) \approx \frac{\pi}{\epsilon} f(n\, e^{-\pi/\epsilon}) ,$$

where

$$f(x) = e^x - I(x) . \tag{4.22}$$

It is interesting to note that the Ramanujan function $I(x)$ appears here also. To check the proper limits we use the asymptotic analysis of the Ramanujan function as derived in appendix C and refs. [30, 31].

(i) As $x \to 0$, then $\Omega(x) \to -1/\log x = \epsilon/\pi$ (see appendix C) and hence $\Omega(\epsilon, n) \to 1$, which agrees with (4.15).

(ii) As $x \to \infty$, $I(x)$ varies as $1/\log x$ and hence $\Omega(\epsilon, n) \to (\pi/\epsilon)\, e^{n\, e^{-\pi/\epsilon}}$, which agrees with eq. (4.10).

For $d = 3$, the scaling variable is $x = \epsilon n^{1/2}\sqrt{A_3}$, where A_3 is defined in eq. (4.11). The scaling function is found to be

$$\Omega(\epsilon, n) \approx n^{1/2} f(\epsilon n^{1/2}\sqrt{A_3}) ,$$

where

$$f(x) = \frac{1}{a_3[y_c(3) - 1]} \frac{1}{x} \{e^{x^2}[1 + \mathrm{erf}(x)] - 1\} . \tag{4.23}$$

The limits $x \to 0, \pm\infty$ are easily seen to agree with eqs. (4.16), (4.11) and (4.14), respectively.

For $d = 4$, one cannot define a single scaling variable x as in the other cases and get a scaled function $f(x)$ independent of ϵ and n, because of the presence of the term $(1 - z)\ln(1 - z)$ in the denominator of the integrand in the integral representation of the partition function, as shown explicitly in appendix B. So, the partition function does not have a scaling form in $d = 4$.

For $d \geq 5$, defining the scaling variable $x = A_d \epsilon n$, and repeating the same analysis one obtains the following scaling function:

$$\Omega(\epsilon, n) \approx nf(A_d \epsilon n) ,$$

with

$$f(x) = \frac{1}{a_d(y_c - 1)} \left(\frac{e^x - 1}{x} \right) , \tag{4.24}$$

which can be easily verified to have the correct limits as $x \to 0, \pm\infty$ agreeing, respectively, with eqs. (4.19), (4.13) and (4.14).

5. Mean square end-to-end distance

The mean square end-to-end distance $\bar{r}^2(y, n)$ and the partition function $\Omega(y, n)$ are connected by the following simple equation:

$$\bar{r}^2(y, n) = \frac{1}{\Omega(y, n)} \sum_{n'=0}^{n} \Omega(y, n') . \tag{5.1}$$

This follows immediately from the relation

$$\sum_{\omega_n} x_n^2 P(\boldsymbol{x}, y, n) = \sum_{n'=0}^{n} \sum_{\omega_{n'}} P(\boldsymbol{x}, y, n') , \tag{5.2}$$

where Σ_{ω_n} refers to the sum over all possible n-stepped walks. This last equation can be easily derived by the method of induction. The expressions for $\Omega(y, n)$, derived in section 4, can be usd in eq. (5.1) to compute $\bar{r}^2(y, n)$ and its scaling function near T_c. Alternatively, they can be directly derived from the asymptotic analysis of (2.19) for large n.

Case 1: $T < T_c$

Exactly similar analysis of eq. (2.19) as in the case of the partition function yields, for large n, the following expression for the mean square end-to-end distance:

$$\bar{r}^2(y, n) = \begin{cases} \dfrac{1 + z_+^2}{1 - z_+^2} & \text{for } n \text{ odd} , \\ \dfrac{2z_+^2}{1 - z_+^2} & \text{for } n \text{ even} . \end{cases} \tag{5.3}$$

When $y \to y_c^+$, $z_+ \to 1^-$ and then for y close to y_c and large n, we get

$$\bar{r}^2(y,n) \approx \frac{1}{1-z_+} \approx \begin{cases} \dfrac{2}{\epsilon^2} & \text{for } d=1\,, \quad (5.4) \\ e^{\pi/\epsilon} & \text{for } d=2\,, \quad (5.5) \\ \dfrac{1}{A_3\epsilon^2} & \text{for } d=3\,, \quad (5.6) \\ \dfrac{1}{1-z_+}\,, \quad F(z_+)=\dfrac{1}{y} & \text{for } d=4\,, \quad (5.7) \\ \dfrac{1}{A_d\epsilon} & \text{for } d\geq 5\,, \quad (5.8) \end{cases}$$

where A_n's have been defined in (4.9)–(4.13).

Case 2: $T > T_c$

For $d = 1, 2$, this phase is absent as $T_c = \infty$. For $d \geq 3$, we integrate eq. (2.19) by parts to reduce the singularity at $z = 1$ from $(1-z)^{-2}$ to $(1-z)^{-1}$ and proceed as in the other cases to get the following leading order term for large n:

$$\bar{r}^2(y,n) \approx n\,. \tag{5.9}$$

Case 3: $T = T_c$

For $d = 1, 2$, $y_c = 1$, and this case corresponds to the noninteracting random walk on the lattice. Hence

$$\bar{r}^2(n, y=1) = n\,. \tag{5.10}$$

For $d = 3$, from eq. (4.5) and proceeding in a similar fashion we get, to leading order for large n,

$$\bar{r}^2(y = y_c(3), n) \approx \tfrac{2}{3}n\,. \tag{5.11}$$

For $d = 4$, similar asymptotic analysis for large n yields

$$\bar{r}^2(y = y_c(4), n) \approx \tfrac{1}{2}n\left(1 + \frac{1}{\log n} + \cdots\right). \tag{5.12}$$

For $d \geq 5$, integration by parts followed by large n analysis yields

$$\bar{r}^2(y = y_c(d), n) \approx \tfrac{1}{2}n\,. \tag{5.13}$$

Defining

$$R(\epsilon) = \lim_{n\to\infty}\left(\frac{\bar{r}^2(\epsilon, n)}{n}\right), \tag{5.14}$$

we find that, near $\epsilon = 0$, this function has the following behaviour:

$$R(\epsilon) = \begin{cases} 0 & \text{for } \epsilon > 0 \\ 1 & \text{for } \epsilon = 0 \end{cases} \quad (d = 1, 2),$$

$$= \begin{cases} 0 & \text{for } \epsilon > 0 \\ \frac{2}{3} & \text{for } \epsilon = 0 \\ 1 & \text{for } \epsilon < 0 \end{cases} \quad (d = 3),$$

$$= \begin{cases} 0 & \text{for } \epsilon > 0 \\ \frac{1}{2} & \text{for } \epsilon = 0 \\ 1 & \text{for } \epsilon < 0 \end{cases} \quad (d \geq 4).$$

So the function $R(\epsilon)$ is discontinuous at $\epsilon = 0$ in all dimensions.

We use the same combinations of ϵ and n, as used in case of the partition function, to define the scaling variable x in different dimensions (except for $d = 4$) and compute the following scaling function for the mean square end-to-end distance:

$$R(x) = \lim\left(\frac{\bar{r}^2(\epsilon, n)}{n}\right), \tag{5.15}$$

where "lim" denotes the limiting operation ($\epsilon \to 0$, $n \to \infty$, x fixed). Using eq. (5.1), $R(x)$, for all $d \neq 4$, can be expressed in terms of the corresponding $\Omega(x)$ derived in section 4. Here we give the results skipping algebraic details,

$$R(x) = \begin{cases} \dfrac{2}{x^2\Omega(x)} \displaystyle\int_0^x x'\Omega(x')\,dx' & \text{for } d = 1, \quad (5.16) \\ \dfrac{1}{x\Omega(x)} \displaystyle\int_0^x \Omega(x')\,dx' & \text{for } d = 2, \quad (5.17) \\ \dfrac{2}{x^3\Omega(x)} \displaystyle\int_0^x x'^2\Omega(x')\,dx' & \text{for } d = 3, \quad (5.18) \\ \dfrac{1}{x^2\Omega(x)} \displaystyle\int_0^x x'\Omega(x')\,dx' & \text{for } d \geq 5, \quad (5.19) \end{cases}$$

where $\Omega(x)$ is the scaling form of partition function in respective dimensions, as derived in section 4. For $d = 4$, as usual, $\bar{r}^2(\epsilon, n)/n$ does not have a scaling form. For other dimensions, these integrals can be easily performed to give closed form expressions and can be shown to have the correct asymptotic behaviour as $x \to 0, \pm\infty$.

6. Scaling function for average energy

In this section, first, we compute the average energy of the chain for the three different regions $T < T_c$, $T > T_c$ and $T = T_c$ in the limit of a large chain in all dimensions. We then calculate the scaling functions near $T = T_c$.

Case 1: $T < T_c$

Exactly similar analysis of eq. (2.20) as in the other cases yields to leading order in n the following expression for the average energy:

$$\bar{E}(y, n) = -\frac{\ln y}{y} \frac{n}{F'(z_+)} . \tag{6.1}$$

When $y \to y_c^+$, $z_+ \to 1^-$ and then using the asymptotic expansion of $U(0, z)$ near $z = 1$, from eqs. (4.3) to (4.7) we get

$$\bar{E}(y, n) \approx \begin{cases} -n\epsilon^2 & \text{for } d = 1 , \quad (6.2) \\ -\dfrac{\pi}{\epsilon} n\, e^{-\pi/\epsilon} & \text{for } d = 2 , \quad (6.3) \\ -\left(\dfrac{2u_3^4 \ln y_c(3)}{a_3^2 y_c^2(3)}\right) n\epsilon & \text{for } d = 3 , \quad (6.4) \\ \left(\dfrac{u_4^2 \ln y_c(4)}{y_c(4)\, a_4 \ln(1 - z_+)}\right) n & \text{for } d = 4 , \quad (6.5) \\ -\left(\dfrac{u_d^2 \ln y_c(d)}{y_c(d)\, a_d}\right) n & \text{for } d \geq 5 , \quad (6.6) \end{cases}$$

where u_n's and a_n's have been defined in (4.3)–(4.7).

Case 2: $T > T_c$

For $d \leq 2$, as usual, there is no $T > T_c$ phase. For $d \geq 3$, one gets

$$\bar{E}(y, n) \approx -\left(\frac{y \ln y}{y_c(d) - y}\right). \tag{6.7}$$

Case 3: $T = T_c$

For $d \leqslant 2$, $y_c = 1$ and hence from eq. (2.20), $\bar{E}(y = 1, n) = 0$. However, in these cases, the interesting quantity to calculate would be the *average number of returns to the origin*, $\bar{S}(y, n) = -\bar{E}(y, n)/(E/k_B T)$, and hence from (2.20), using $\Omega(y = 1, n) = 1$, we get

$$\bar{S}(y = 1, n) = \frac{1}{2\pi i} \oint_{C_0} \frac{F(z)}{z^{n+1}(1 - z)[1 - F(z)]} \, dz \,. \tag{6.8}$$

Asymptotic analysis ($n \to \infty$) of this integral can be shown to yield

$$\bar{S}(y = 1, n) \approx \begin{cases} \sqrt{\frac{2}{\pi}} \, n^{1/2} & \text{for } d = 1 \,, \quad (6.9) \\ \frac{1}{\pi} \log n & \text{for } d = 2 \,. \quad (6.10) \end{cases}$$

For $d \geqslant 3$, putting $y = y_c$ and hence $b_d = 0$ in the respective equations and using the large n expansion, as in the other cases, one obtains

$$\bar{E}(y = y_c, n) \approx \begin{cases} -\left(\frac{\sqrt{\pi} \, y_c \ln y_c}{2a_3(y_c - 1)^2}\right) n^{1/2} & \text{for } d = 3 \,, \quad (6.11) \\ -\left(\frac{y_c \ln y_c}{2a_4(y_c - 1)^2}\right) \frac{n}{\log n} & \text{for } d = 4 \,, \quad (6.12) \\ -\left(\frac{y_c \ln y_c}{2a_d(y_c - 1)^2}\right) n & \text{for } d \geqslant 5 \,. \quad (6.13) \end{cases}$$

Defining

$$E(\epsilon) = -\lim_{n \to \infty} \left(\frac{\bar{E}(\epsilon, n)}{n}\right) \tag{6.14}$$

we find that, near $\epsilon = 0$, the function has the following behaviour:

$$E(\epsilon) \sim \begin{cases} \epsilon^2 & \text{for } \epsilon > 0 \\ 0 & \text{for } \epsilon = 0 \end{cases} \qquad (d = 1) \,,$$

$$\approx \begin{cases} \frac{\pi}{\epsilon} e^{-\pi/\epsilon} & \text{for } \epsilon > 0 \\ 0 & \text{for } \epsilon = 0 \end{cases} \qquad (d = 2),$$

$$\approx \begin{cases} \left(\frac{2u_3^4 \ln y_c}{a_3^2 y_c^2}\right) \epsilon & \text{for } \epsilon > 0 \\ 0 & \text{for } \epsilon \leqslant 0 \end{cases} \qquad (d = 3),$$

$$\approx \begin{cases} -\left(\frac{u_4^2 \ln y_c}{y_c a_4}\right) \frac{1}{\ln(1 - z_+)} & \text{for } \epsilon > 0 \\ 0 & \text{for } \epsilon \leqslant 0 \end{cases} \qquad (d = 4),$$

$$\approx \begin{cases} \left(\frac{u_d^2 \ln y_c}{y_c a_d}\right) & \text{for } \epsilon > 0 \\ \left(\frac{y_c \ln y_c}{2a_d (y_c - 1)^2}\right) & \text{for } \epsilon = 0 \\ 0 & \text{for } \epsilon < 0 \end{cases} \qquad (d \geqslant 5).$$

The qualitative behaviour of the function $E(\epsilon)$, near $\epsilon = 0$, is sketched in fig. 3a, b and c, respectively.

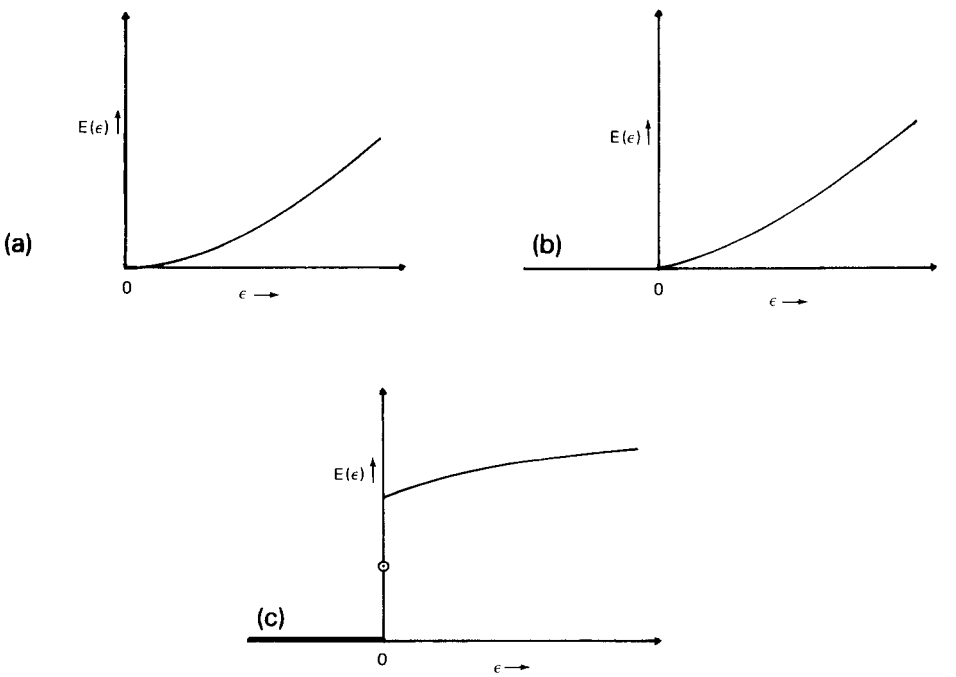

Fig. 3. The schematic sketch of $E(\epsilon)$, near $\epsilon = 0$, for (a) $d \leqslant 2$, (b) $d = 3, 4$, (c) $d \geqslant 5$.

Clearly, the function $E(\epsilon)$ is continuous at $\epsilon = 0$ for $d \leqslant 4$. Above $d = 4$, it becomes discontinuous at $\epsilon = 0$ and undergoes a jump signifying a first-order transition. In what follows, we show that exact finite-size scaling holds even for this first-order transition in $d \geqslant 5$ and the scaling function can be computed easily.

To compute the scaling function, we use the same combination of powers of ϵ and n to define the scaling variable x in different dimensions as used in the case of the calculation of the partition function. To avoid repetition, we just mention the results here, which can be easily verified.

For $d = 1$, the scaling function is given by

$$E(x) = \lim_{n\to\infty} \bar{E}(x(\tfrac{1}{2}n)^{-1/2}, n) = -\left(2x^2 + \frac{2}{\sqrt{\pi}}\, x\, \mathrm{e}^{-x^2}[1 + \mathrm{erf}(x)]^{-1}\right). \quad (6.15)$$

For $d = 3$, we get

$$E(x) = \lim_{n\to\infty} [n^{-1/2}\bar{E}(x(nA_3)^{-1/2}, n)]$$
$$= [\ln y_c(3)]\sqrt{A_3}\,\frac{1}{x}\left[1 - 2x^2 - \left(2x^2 + \frac{2x}{\sqrt{\pi}}\right)[\mathrm{e}^{x^2} + \mathrm{e}^{x^2}\,\mathrm{erf}(x) - 1]\right]. \quad (6.16)$$

For $d \geqslant 5$, the scaling function is

$$E(x) = \lim_{n\to\infty} [n^{-1}\bar{E}(x(nA_d)^{-1}, n)]$$
$$= \frac{u_d^2 \ln y_c(d)}{a_d y_c(d)}\,\frac{1}{x}\,[1 - x\,\mathrm{e}^x(\mathrm{e}^x - 1)^{-1}]. \quad (6.17)$$

These scaling functions, once again, have the correct limits, as can be checked easily. For $d = 4$, the average energy, like the other quantities, does not have a scaling form. Now $d = 2$ is somewhat different from the other dimensions so far as the scaling function of the average energy is concerned. In this case, we find

$$\bar{E}(\epsilon, n) - 1 \approx \frac{\pi}{\epsilon}\, E(n\,\mathrm{e}^{-\pi/\epsilon}),$$

where

$$E(x) = -\left(\frac{x\,\mathrm{e}^x - I_1(x)}{\mathrm{e}^x - I(x)}\right), \quad (6.18)$$

where $I(x)$ is, once again, the Ramanujan function and the function $I_1(x)$ is given by

$$I_1(x) = x \frac{\mathrm{d}I}{\mathrm{d}x} . \tag{6.19}$$

This scaling function can also be shown to have correct limits by using the asymptotic expansion of $I(x)$ and hence of $I_1(x)$.

7. Scaling functions for the probability distribution of the position of the chain-end

As before, the three distinct cases $T < T_c$, $T > T_c$ and $T = T_c$ are first considered for a large chain in all lattice dimensions and then the scaling functions in different dimensions are computed separately.

Case 1: $T < T_c$

To reach a point $\boldsymbol{x}$ on a hypercubic lattice, starting at the origin, one needs either odd or even number of steps depending upon whether $\Sigma_{i=1}^{d} x_i$ is odd or even. Hence

$$U(\boldsymbol{x}, -z) = (-1)^{\Sigma_{i=1}^{d} x_i} U(\boldsymbol{x}, z) . \tag{7.1}$$

Using this fact and eq. (2.21), it is easy to verify that for large n

$$Q(\boldsymbol{x}, y, n) \approx \eta(\boldsymbol{x}, n) \left(\frac{1}{1 - z_+} + \frac{(-1)^n}{1 + z_+} \right)^{-1} U(\boldsymbol{x}, z_+) , \tag{7.2}$$

where

$$\eta(\boldsymbol{x}, n) = [1 + (-1)^{n + \Sigma_{i=1}^{d} x_i}] \tag{7.3}$$

is an indicator function taking values 0 or 1 depending on the parity of n and $\boldsymbol{x}$.

The asymptotic expansion of $U(\boldsymbol{x}, z)$ to leading order, for large $|\boldsymbol{x}|$ and for $z \geqslant 0$, is given by [22]

$$U(\boldsymbol{x}, z) \approx \frac{D_d z^{-(d+2)/4} (1 - z)^{(d-2)/4}}{R^{d/2-1}} K_{d/2-1} \left(\sqrt{\frac{d(1 - z)}{z}} R \right) , \tag{7.4}$$

where $D_d = \pi^{-d/2} d^{(d+2)/4}$, $R = |\boldsymbol{x}|$ and K_ν is the modified Bessel function of second kind of order ν. Keeping R at a fixed large value and fixing y close to y_c (whence z_+ close to 1) we get, for large n,

$$Q(x,\epsilon,n)\approx\begin{cases}\eta(x,n)\,\dfrac{D_1\epsilon^{3/2}R^{1/2}}{2^{3/4}}\,K_{1/2}\left(\dfrac{\epsilon R}{\sqrt{2}}\right) & \text{for } d=1\,, \quad (7.5)\\[2ex] \eta(x,n)\,D_2\,\mathrm{e}^{-\pi/\epsilon}K_0(\sqrt{2}\,R\,\mathrm{e}^{-\pi/2\epsilon}) & \text{for } d=2\,, \quad (7.6)\\[2ex] \eta(x,n)\,\dfrac{D_3A_3^{5/4}\epsilon^{5/2}}{R^{1/2}}\,K_{1/2}(\sqrt{3A_3}\,\epsilon R) & \text{for } d=3\,, \quad (7.7)\\[2ex] \eta(x,n)\,\dfrac{D_4(1-z_+)^{3/2}}{R}\,K_1[2(1-z_+)^{1/2}R] & \text{for } d=4\,, \quad (7.8)\\[2ex] \eta(x,n)\,\dfrac{D_dA_d^{(d+2)/4}\epsilon^{(d+2)/4}}{R^{(d-1)/2}}\,K_{d/2-1}(\sqrt{dA_d}\epsilon\,R) & \text{for } d\geq 5\,. \quad (7.9)\end{cases}$$

Case 2: $T > T_c$

For $d \leq 2$, there is no $T > T_c$ phase. For other dimensions, we find, for fixed large R, fixed small ϵ and large n, such that $n/R^2 \gg 1$, the following asymptotic behaviour:

$$Q(x,\epsilon,n) \approx D'_d\eta(x,n)\,n^{-d/2}\,, \quad (7.10)$$

where D'_d are positive numerical constants.

Case 3: $T = T_c$

Here, again for, $n/R^2 \gg 1$, we get

$$Q(x,y=1,n)\approx\begin{cases}C_1\,\eta(x,n)\,n^{-1/2} & \text{for } d=1\,, \quad (7.11)\\[2ex] C_d\,\eta(x,n)\,\dfrac{1}{R^{d-2}n} & \text{for } d\geq 2\,. \quad (7.12)\end{cases}$$

While computing the scaling function for the probability distribution we note that $Q(x,y,n)=0$ unless $\eta(x,n)=1$. In this case, $Q(x,y,n)=2Q^+(x,y,n)$ where $Q^+(x,y,n)$ represents the contribution to the integral in (2.21) which comes from the pole at $z=z_+$ and the branch-cut across $z=1$ (see fig. A.1). In deriving the scaling form of $Q(x,y,n)$ we will always assume this to be the case. In other words, we will compute the scaling form of $Q^+(x,y,n)$.

For $d=1$, we define two scaling variables

$$x_1 = \epsilon n^{1/2}\,, \qquad x_2 = \epsilon x\,. \quad (7.13)$$

Next we define the limiting operation $\lim(\epsilon \to 0,\ n \to \infty,\ |\boldsymbol{x}| \to \infty$ with $x_1,\ x_2$ fixed). To carry out this limiting operation we use the general expression of $U(\boldsymbol{x}, z)$ in any dimension [26],

$$U_d(\boldsymbol{x}, z) = \frac{1}{(2\pi)^d} \int_{-\pi}^{\pi} \cdots \int_{-\pi}^{\pi} \frac{e^{i\boldsymbol{x}\cdot\boldsymbol{\theta}}}{1 - z \sum_{i=1}^{d} \cos\theta_i} \, d^d\boldsymbol{\theta} \,. \tag{7.14}$$

In $d = 1$, the scaling function defined as

$$G(x_1, x_2) = \lim_{n\to\infty} \left[Q\left(\frac{x_2 n^{1/2}}{x_1}, x_1 n^{-1/2}, n \right) \right] \tag{7.15}$$

can be computed to be

$$G(x_1, x_2) = \frac{2}{e^{x_1^2}[1 + \operatorname{erf}(x_1)]} \left(e^{x_1^2 - x_2} - I(x_1, x_2) + \frac{\partial I(x_1, x_2)}{\partial x_2} \right), \tag{7.16}$$

where

$$I(x_1, x_2) = \frac{1}{2\pi} \int_0^{\infty} \frac{e^{-x_1^2 y} \sin(\sqrt{y}\, x_2)}{y + 1} \, dy \,.$$

For $d = 2$, we define the scaling variables and the scaling function as follows:

$$x_1 = n\, e^{-\pi/\epsilon}, \qquad \boldsymbol{x}_2 = \boldsymbol{x}\, e^{-\pi/2\epsilon},$$

$$G(x_1, x_2) = \lim_{\epsilon\to 0} [\pi\, e^{\pi/\epsilon} Q(\boldsymbol{x}_2\, e^{\pi/2\epsilon}, \epsilon, x_1 e^{\pi/\epsilon})] \,.$$

Then the scaling function can be computed to be

$$G(x_1, x_2) = \frac{2}{e^{x_1} - I(x_1)} \left(2\, e^{x_1} K_0(\sqrt{2}\, x_2) - \pi \int_0^{\infty} \frac{e^{-x_1 y} Y_0(\sqrt{2y}\, x_2)}{[(\log y)^2 + \pi^2]} \, dy \right.$$
$$\left. + \int_0^{\infty} \frac{e^{-x_1 y} \ln y\, J_0(\sqrt{2y}\, x_2)}{[(\log y)^2 + \pi^2]} \, dy \right), \tag{7.17}$$

where $I(x_1)$ is the Ramanujan function and $J_n(x)$ and $Y_n(x)$ are the nth order Bessel functions of first and second kind, respectively.

For $d = 3$, we similarly define the scaling variables and the scaling function as follows:

$$x_1 = n^{1/2}|\epsilon|\sqrt{A_3}\,, \qquad x_2 = \sqrt{3A_3}\,|\epsilon| x\,,$$

$$G_{\pm}(x_1, x_2) = \lim_{n\to\infty}\left(\frac{n^{3/2}A_3 Q((x_2/x_1)(\tfrac{1}{3}n)^{1/2}, \pm x_1(nA_3)^{-1/2}, n)}{x_1^2}\right),$$

where $G_{\pm}(x_1, x_2)$ denotes the scaling functions in the region for $\epsilon > 0$ and $\epsilon < 0$, respectively, and A_3 has been defined in (4.11). In this case they cannot be matched by a single function as in the previous cases. These functions, computed in the same way, are as follows:

$$G_{+}(x_1, x_2) = \frac{D_3 x_1}{x_2\{e^{x_1^2}[1 + \mathrm{erf}(x_1)] - 1\}}\left(2e^{x_1^2 - x_2} - I(x_1, x_2) + \frac{\partial I(x_1, x_2)}{\partial x_2}\right),$$

$$G_{-}(x_1, x_2) = \frac{D_3 x_1}{x_2\{1 - e^{x_1^2}[1 - \mathrm{erf}(x_1)]\}}\left(I(x_1, x_2) + \frac{\partial I(x_1, x_2)}{\partial x_2}\right). \tag{7.18}$$

For $d = 4$, as usual, there is no scaling form for $Q(x, y, n)$.

For $d \geq 5$, scaled variables and the scaling function are defined as follows:

$$x_1 = n|\epsilon|A_d\,, \qquad x_2 = \sqrt{dA_d|\epsilon|}\,x\,,$$

$$G_{\pm}(x_1, x_2) = \lim_{n\to\infty}\left(\frac{n^{d/2}A_d^{d/2-1}Q(x_2(n/dx_1)^{1/2}, \pm x_1/nA_d, n)}{x_1^{(d-2)/2}}\right),$$

where the functions $G_{\pm}(x_1, x_2)$ are the form of the same scaling function on either side of $\epsilon = 0$ and are given by

$$G_{+}(x_1, x_2) = \frac{2C_d x_1}{(e^{x_1} - 1)x_2^{(d-2)/2}} \times\left(e^{x_1}K_{d/2-1}(x_2) - \frac{1}{2}\int_0^{\infty}\frac{e^{-x_1 y}y^{(d-2)/4}J_{d/2-1}(x_2\sqrt{y})}{y+1}\,dy\right),$$

$$G_{-}(x_1, x_2) = \frac{2C_d x_1}{(1 - e^{-x_1})x_2^{(d-2)/2}} \times\left(-\tfrac{1}{2}\pi e^{-x_1}Y_{d/2-1}(x_2) - \frac{1}{2}\int_0^{\infty}\frac{e^{-x_1 y}y^{(d-2)/4}J_{d/2-1}(x_2\sqrt{y})}{y-1}\,dy\right), \tag{7.19}$$

where $C_d = \pi^{-d/2}d^{d/2}A_d^{(d-2)/2}$ and $Y(x)$, $J(x)$ and $K(x)$ are different kinds of Bessel functions, as have already been defined.

8. Summary and discussion

In summary, in this paper we have studied the critical behaviour of an ideal polymer chain undergoing the adsorption–desorption transition. Our lattice model, though idealized and not completely realistic, has the advantage that various finite-size scaling functions can be computed exactly in all dimensions (except at $d=4$). An interesting feature of the model is that the transition changes from being second order for $d \leq 4$ to first order for $d > 4$. The scaling behaviour of a critical system undergoing a first-order phase transition is not well understood. Our model represents a simple physical system exhibiting finite-size scaling near a first-order transition in $d > 4$.

An important feature of the problem deserves comment at this point. A naive, qualitative argument would suggest that in the collapsed phase the system has only one natural length scale $\bar{L}$ denoting the average number of steps between two successive returns to the origin. Then one would expect that e, the average energy per monomer unit, goes as $\bar{L}^{-1}$ and the mean square end-to-end distance $\bar{r}^2 \sim \bar{L}$. This would imply that $\bar{r}^2 e \sim 1$. However, our calculation shows that $\bar{r}^2 e$ diverges near T_c. It is easy to see where exactly the qualitative argument goes wrong. Let $P(L)$ denote the probability distribution of the number of steps between two successive returns to the origin. Then, one finds

$$e \sim \frac{1}{\int P(L)\, L\, \mathrm{d}L} \quad \text{and} \quad \bar{r}^2 \sim \frac{\int P(L)\, L^2\, \mathrm{d}L}{\int P(L)\, L\, \mathrm{d}L},$$

so that

$$\bar{r}^2 e \sim \frac{\overline{L^2}}{\bar{L}^2}.$$

Thus $\bar{r}^2 e \sim 1$ when the system has strictly one length scale $\bar{L}$. However, in our problem, $P(L)$ typically is an exponentially decaying function with an amplitude decaying with a power law. For example, in 3D, one finds, $P(L) \sim L^{-3/2} \exp(-L/\xi)$ with $\xi \sim \epsilon^{-2}$ where $\epsilon = (y - y_c)/y_c$. Then $\overline{L^2} \gg \bar{L}^2$, which agrees with our calculation. Thus we find that fluctuations at all length scales less than or equal to ξ are important near the critical point, which essentially leads to the divergence of $\bar{r}^2 e$ as $T \to T_c$. This emphasizes the role of fluctuations at various length scales in our problem and a simple, heuristic argument assuming only one length scale fails to predict the correct critical behaviour.

Acknowledgement

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Appendix A

To calculate the partition function from eq. (2.18) for the case $y > y_c$ or $T < T_c$, we make the choice of contour in the complex-z plane as shown in fig. A.1. The contour C_0 encloses the origin. $C_\pm$ enclose the poles at $\pm z_+$, respectively. C_1 consists of a circular part with radius $1 + \delta$ and an indentation around the branch points at $z = \pm 1$ where δ is a small positive number. Now

$$\oint_{C_0} = -\oint_{C_+} - \oint_{C_-} + \oint_{C_1} . \tag{A.1}$$

We first evaluate $\oint_{C_\pm}$ and show that $\oint_{C_1}$ is negligible compared to them in the limit of large n. Since the integrand in eq. (2.18) has simple poles at $\pm z_+$ for $y > y_c$, one easily gets

$$-\oint_{C_+} = \frac{1}{z_+^{n+1}} \frac{1 - F(z_+)}{y(1 - z_+)F'(z_+)} , \tag{A.2}$$

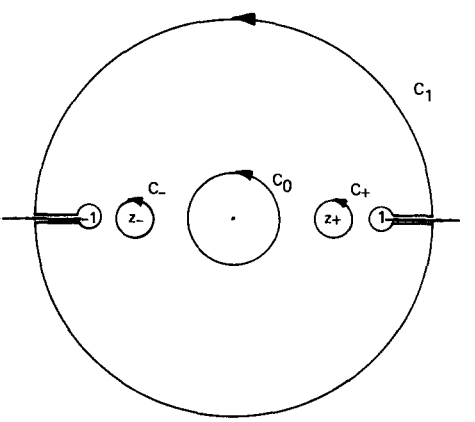

Fig. A.1. The choice of the contour in the complex-z plane for $T < T_c$.

$$-\oint_{C_-} = (-1)^n \frac{1}{z_+^{n+1}} \frac{1-F(z_+)}{y(1+z_+)F'(z_+)} . \tag{A.3}$$

Thus the integrals along $C_\pm$ are proportional to the $(n+1)$th power of a number which is larger than unity as $z_+ < 1$. It can be easily seen that in case of C_1, the integral around the circular part of the contour is proportional to $(1+\delta)^{-n}$, which is an exponentially small number for large n. The integral around the remaining part of the contour C_1 is bounded in magnitude by a number independent of n. Hence, in the limit of $n \to \infty$, we get the following expression of the partition function:

$$\Omega(y, n) \approx \frac{y-1}{z_+^n y^2 F'(z_+)} \left(\frac{1}{1-z_+} + \frac{(-1)^n}{1+z_+} \right), \tag{A.4}$$

where we have used the fact that $yF(z_+) = 1$.

Appendix B

In order to calculate the partition function for the case $y < y_c$ or $T > T_c$, we note that the only poles of the integrand in eq. (2.18) are at $z = 0, 1$ with branch point singularities at $z = \pm 1$. The contour is chosen as shown in fig. B.1. Consequently

$$\oint_{C_0} = \oint_{C_1} .$$

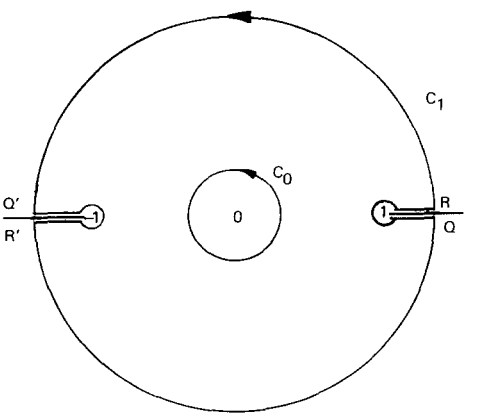

Fig. B.1. The choice of the contour in the complex-z plane for $T \geqslant T_c$.

The contour integral around C_1 is approximately equal to the integral from Q to R and Q′ to R′ (see fig. B.1) around the cut for large n. The contribution of the circular part of the contour is exponentially small for large n. Also the contribution of the QR part is much larger than the Q′R′ part because of the extra pole type singularity at $z = 1$ in the integrand of eq. (2.18). Using this argument and substituting (4.2) in (2.18) we get

$$\Omega(y, n) \approx \frac{1}{(y-1)2\pi i} \int_{Q}^{R} \frac{1}{z^{n+1}(1-z)\left(\frac{y}{y-1} - U(0, z)\right)} \, dz \, . \tag{B.1}$$

Using the asymptotic expansion for $U(0, z)$ near $z = 1$ as given by eqs. (4.3)–(4.7), we get the following expressions for the partition function in different dimensions.

For $d = 3$ we have

$$\Omega(y, n) \approx \frac{1}{a_3(y-1)2\pi i} \int_{Q}^{R} \frac{1}{z^{n+1}(1-z)[b_3 + (1-z)^{1/2}]} \, dz \, , \tag{B.2}$$

where

$$b_3 = \frac{y_c(3) - y}{a_3(y-1)[y_c(3) - 1]} \, . \tag{B.3}$$

There are two contributions to this integral, one from the circular part around $z = 1$ and one from the flat portion parallel to the cut. The contribution of the circular part is trivially given by $1/a_3 b_3 (y-1)$. The contribution of the flat part I_f is given by (substituting $z = 1 + z'$ in eq. (B.2))

$$\begin{aligned} I_f &= \frac{1}{a_3(y-1)2\pi i} \int_{Q}^{R} \frac{1}{(1+z')^{n+1}(-z')[b_3 + (-z')^{1/2}]} \, dz' \\ &= -\frac{1}{\pi a_3(y-1)} \int_{0}^{\delta} \frac{x^{-1/2}}{(1+x)^{n+1}(b_3^2 + x)} \, dx \\ &\approx -\frac{1}{a_3 b_3^2 (y-1)\sqrt{\pi}\, n^{1/2}} \, . \end{aligned} \tag{B.4}$$

For the above asymptotic analysis, for large n, see the appendix of ref. [4]. So, to leading order for large n, we get

$$\Omega(y,n) \approx \frac{1}{a_3 b_3 (y-1)} \left[1 - \mathcal{O}(n^{-1/2})\right] . \tag{B.5}$$

The phase of $(-z')^{1/2}$ in eq. (B.4) is chosen so that it is real and positive for real, negative z'. Therefore, on the lower portion of the cut, $(-z')^{1/2} = \mathrm{i}x^{1/2}$, and on the upper side, $(-z')^{1/2} = -\mathrm{i}x^{1/2}$, where x is real and positive.

A similar analysis, for $d = 4$, gives

$$\Omega(y,n) \approx \frac{1}{a_4 (y-1) 2\pi \mathrm{i}} \int_{\mathrm{O}}^{\mathrm{R}} \frac{1}{z^{n+1}(1-z)[b_4 - (1-z)\ln(1-z)]} \, \mathrm{d}z , \tag{B.6}$$

where

$$b_4 = \frac{y_c(4) - y}{a_4 (y-1)[y_c(4) - 1]} . \tag{B.7}$$

We note that, for $y < y_c$, b_4 is positive. To leading order for large n, the main contribution, once again, comes from the circular part of the contour C_1 around the point $z = 1$ and is given by

$$\Omega(y,n) \approx \frac{1}{a_4 b_4 (y-1)} . \tag{B.8}$$

For $d \geq 5$, we get

$$\Omega(y,n) \approx \frac{1}{a_d (y-1) 2\pi \mathrm{i}} \int_{\mathrm{O}}^{\mathrm{R}} \frac{1}{z^{n+1}(1-z)[b_d - (1-z)]} \, \mathrm{d}z , \tag{B.9}$$

where

$$b_d = \frac{y_c(d) - y}{a_d (y-1)[y_c(d) - 1]} . \tag{B.10}$$

Again to leading order

$$\Omega(y,n) \approx \frac{1}{a_d b_d (y-1)} . \tag{B.11}$$

In general, for all $d \geq 3$, we get

$$\Omega(y,n) \approx \frac{1}{a_d b_d (y-1)} = \frac{y_c(d) - 1}{y_c(d) - y} . \tag{B.12}$$

We note that, for $d \leq 2$, there is no $T > T_c$ phase as the T_c itself is infinite.

Appendix C

In this appendix, we calculate the leading asymptotic behaviour of the Ramanujan function

$$I(x) = \int_0^\infty \frac{e^{-xy}}{y} \frac{1}{[(\ln y)^2 + \pi^2]} \, dy$$

in the limit $x \to 0$. In the limit $x \to \infty$, it is known that [29] $I(x) \to 1/\log x$ to leading order. To compute the $x \to 0$ limit, we make use of the following Ramanujan identity [30]:

$$I(x) = e^x - \nu(x) , \tag{C.1}$$

where

$$\nu(x) = \int_0^\infty \frac{x^t}{\Gamma(t+1)} \, dt . \tag{C.2}$$

Substituting $y = x^t$ in (C.2) and noting that for small x, $\lim_{t\to\infty} x^t = 0$ we get

$$\nu(x) = \frac{1}{|\log x|} \int_0^1 \frac{dy}{\Gamma(1 + |\log y|/|\log x|)} . \tag{C.3}$$

As $x \to 0$, for fixed y, the denominator of the integrand tends to $\Gamma(1)$. This leads to the following asymptotic behaviour of $\nu(x)$ as $x \to 0$:

$$\lim_{x\to 0} \nu(x) \approx \frac{1}{|\log x|} = -\frac{1}{\log x} . \tag{C.4}$$

Hence from eq. (C.1) we get the leading order asymptotic behaviour of $I(x)$ in the limit $x \to 0$,

$$I(x) \approx 1 + \frac{1}{\log x} . \tag{C.5}$$

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