Journal of Statistical Physics, Vol. 19, No. 4, 1978

The Theory of Melting in Heteropolymers. II. Correlated Chains

I. Simon[1] and A. Vilenkin[1]

Received April 17, 1978

Equations are derived for the calculation of the ground-state melting curves for polynucleotide sequences with correlation between the nearest neighbors. The case of arbitrary correlated sequences is also considered. The effect of correlations in the sequence on the width and on the intrinsic fine structure of melting curves is discussed.

KEY WORDS: Helix–coil transition; heteropolymers; Ising model; melting; correlated sequences.

1. INTRODUCTION

In the first paper of this series[(1)] a method was developed for treating the melting of heteropolymers with a random sequence of components. Assuming strong cooperativity, the problem was reduced to studying the ground state of the polymer. The ground-state energy E and the fraction of broken bonds η were then expressed in terms of probabilities of certain Brownian trajectories of a fictitious particle. Systems of difference equations were obtained for determining these probabilities. (It should be mentioned that this method originated from the ideas of Azbel'[(2,3)] and Lifshitz.[(4)]) In the second paper of this series[(5)] this method was used for studying the intrinsic fine structure of melting curves. In the present work we shall generalize the method for sequences with correlation between the nearest neighbors and also obtain some results for arbitrary correlated sequences.

The melting of nonrandom polymers has been studied by several authors. Lehmann and McTague[(6)] reduced the problem to the solution of an integral equation, which, however, cannot be solved analytically, and thus numerical

---

Work supported in part by NSF Material Research Laboratory at Case Western Reserve University.

[1] Department of Physics, Case Western Reserve University, Cleveland, Ohio.

methods have to be used. Lacombe and Simha(7) derived recurrent relations for the calculation of melting curves on computers. Lifshitz(4) obtained an approximate analytic solution of the problem, which, however, is valid only close to the melting temperature. Our method reduces the calculation of melting curves to the solution of a system of linear difference equations. An analytic solution cannot be obtained in the general case. However, the equations can be solved at certain values of parameters, providing valuable information about the melting curves. Our results reduce to the results of Lifshitz in the corresponding approximation. In the general case, our equations can be conveniently used for a direct calculation of melting curves on computers.

2. CORRELATION BETWEEN THE NEAREST NEIGHBORS

Let us consider a heteropolymer consisting of links of two different types, which we shall label by the numbers 1 and 2. The concentrations of links of the two types are defined as $w_\alpha = \mathcal{N}_\alpha/\mathcal{N}$, where $\alpha = 1, 2$; $\mathcal{N}_\alpha$ is the number of links of type α in the chain, $\mathcal{N}$ is the total number of links, $w_1 + w_2 = 1$. If there is a correlation between the nearest neighbors, one can introduce the conditional probabilities $w_{\alpha\beta} = \mathcal{N}_{\alpha\beta}/\mathcal{N}_\alpha$, where $\mathcal{N}_{\alpha\beta}$ is the number of pairs (α, β) in the chain; $\alpha, \beta = 1, 2$. The quantity $w_{\alpha\beta}$ is the probability that a link of type α is followed by a link of type β. From the relation $\mathcal{N}_{\alpha\beta} = \mathcal{N}_{\beta\alpha}$ we find that $w_{\alpha\beta}w_\alpha = w_{\beta\alpha}w_\beta$ and

$$w_1 = w_{21}(w_{21} + w_{12})^{-1}, \qquad w_2 = w_{12}(w_{21} + w_{12})^{-1} \tag{1}$$

The probabilities $w_{\alpha\beta}$ satisfy

$$\sum_{\beta=1}^{2} w_{\alpha\beta} = 1 \tag{2}$$

To define the correlation radius, we note that the determinant $\det(w_{\alpha\beta}) \equiv \Delta = w_{11} - w_{21} = w_{22} - w_{12}$ has the meaning of "order parameter." For a random sequence $\omega_{\alpha\beta} = \omega_\beta$ and $\Delta = 0$. If $w_{\alpha\beta}^{(M)}$ is the probability that two links separated by a distance M are of types α and β, respectively, then we can define the correlation radius R by the relation

$$\det(w_{\alpha\beta}^{(R)}) = e^{-1} \tag{3}$$

It is easily seen that $\det(w_{\alpha\beta}^{(M)}) = \Delta^M$ and thus

$$R = -(\ln|\Delta|)^{-1} \tag{4}$$

R differs significantly from 1 only if $1 - |\Delta| \equiv \delta \ll 1$. In this case $R \approx \delta^{-1}$.

Now let us turn to the discussion of the melting of heteropolymers with correlation between the nearest neighbors. As in Refs. 1 and 5, we can introduce the probabilities $\mathscr{P}_m^+$, $\mathscr{P}^+$, $\mathscr{P}^-$, $\tilde{\mathscr{P}}^-$, q_k, and q_0 and the average lengths L_m^+, l_k, and l_0 (the definitions are given in Refs. 1 and 5). One would think that now the probabilities will have indices corresponding to the type of the preceding link. However, this is not so. The links preceding sections corresponding to $\mathscr{P}_m^+$ and $\mathscr{P}^+$ are always of type 2 and the links preceding sections of type $\mathscr{P}^-$, q_k, and q_0 are always of type 1. The probability $\tilde{\mathscr{P}}^-$ is defined as a nonconditional probability of a corresponding section.

The expressions obtained in Refs. 1 and 5 for the ground-state energy per link E, the fraction of melted links η, and the jumps $\Delta\eta_A$, $\Delta\eta_B$, $\Delta\eta_C$ can be easily generalized to take account of the nearest neighbor correlations (we use the notations of Refs. 1 and 5):

$$E = h^l - U\tilde{\mathscr{P}}^- \sum_{m=0}^{r-1} \mathscr{P}_m^+ \left[\delta N + m + (\mathscr{P}^-)^{-1} \sum_{k=1}^{r} kq_k\right] \tag{5}$$

$$\eta = \frac{\varpi_2}{\varpi_{12}} \sum_{m=0}^{r=1} \mathscr{P}_m^+ \left[(1 - q_0)\mathscr{P}^- L_m^+ + (1 - q_0) \sum_{k=1}^{r} q_k l_k + \mathscr{P}^- q_0 l_0\right] \tag{6}$$

$$\Delta\eta_A = (\varpi_2/\varpi_{12})(\mathscr{P}^-)^2 \mathscr{P}_0^+ [(1 - q_0)L_0^+ + q_0 l_0] \tag{7}$$

$$\Delta\eta_B = 2(\varpi_2/\varpi_{12})(\mathscr{P}^-)^2 \mathscr{P}^+ q_0 l_0 \tag{8}$$

$$\Delta\eta_C = (\varpi_1/\varpi_{21})(\mathscr{P}^+)^2 \mathscr{P}_0^- [(1 - q_0)L_0^- + q_0 l_0] \tag{9}$$

(note that the expression for E has not changed at all).

The probabilities $\mathscr{P}^-$, $\tilde{\mathscr{P}}^-$, q_k, and q_0 satisfy the identities

$$\mathscr{P}^- + \sum_{k=1}^{r} q_k = 1, \qquad \varpi_2(1 - q_0)\mathscr{P}^- = \varpi_{12}\tilde{\mathscr{P}}^- \tag{10}$$

which can be proved from their definitions. One can also show that in the case $r = 1$

$$(1 - q_0)q_1 = \varpi_{11} \qquad (r = 1) \tag{11}$$

3. EQUATIONS FOR PROBABILITIES AND AVERAGE LENGTHS

Following the method discussed in detail in Refs. 1 and 5, let us consider the motion of a fictitious particle that can step r units up (r-step) or s units down (s-step) with certain probabilities. Let ϖ_{11} be the probability that after an r-step the particle makes another r-step, ϖ_{12} the probability that after an r-step the particle makes an s-step, etc. Calculation of $\mathscr{P}_m^+$ and L_m^+ results in the problem of Brownian motion of the particle between two absorbing boundaries, $n = 0$ and $n = N$, with n the coordinate of the particle, which can assume arbitrary integral values. The corresponding equations are

$$\begin{aligned} \phi^+_{M,n} &= w_{12}\phi^-_{M-1,n+s} + w_{22}\phi^+_{M-1,n+s} \qquad (0 \leqslant n \leqslant N - s - 1) \\ \phi^-_{M,n} &= w_{11}\phi^-_{M-1'n-r} + w_{21}\phi^+_{M-1,n-r} \qquad (r \leqslant n \leqslant N - 1) \end{aligned} \tag{12a}$$

$$\begin{aligned} \phi^+_{M,n} &= 0 \qquad (n \geqslant N - s) \\ \phi^-_{M,n} &= 0 \qquad (n \leqslant r - 1) \end{aligned} \tag{12b}$$

$$\begin{aligned} \phi^+_{0,n} &= \delta_{0n} \\ \phi^-_{0,n} &= 0 \end{aligned} \tag{12c}$$

$$\mathscr{P}_m{}^+ = w_{11} \sum_{M=0}^{\infty} \phi^-_{M,N+m-r} + w_{21} \sum_{M=0}^{\infty} \phi^+_{M,N+m-r} \qquad (m = 0, 1,\ldots, r - 1) \tag{13}$$

$$\mathscr{P}_m{}^+ L_m{}^+ = w_{11} \sum_{M=0}^{\infty} (M + 1)\phi^-_{M,N+m-r} + w_{21} \sum_{M=0}^{\infty} (M + 1)\phi^+_{M,N+m-r} \tag{14}$$

Here $\phi^+_{M,n}$ is the probability that at "time" M the "particle" has "coordinate" n, its last step being of s-type; $\phi^-_{M,n}$ is the probability of having "coordinate" n at "time" M, the last step being of r-type.

Similar equations can be derived for q_k, l_k:

$$\begin{aligned} \phi^+_{M,n} &= w_{12}\phi^-_{M-1,n+s} + w_{22}\phi^+_{M-1,n+s} \qquad (-N \leqslant n \leqslant -s) \\ \phi^-_{M,n} &= w_{11}\phi^-_{M-1,n-r} + w_{21}\phi^+_{M-1,n-r} \qquad (-N + r \leqslant n \leqslant 0) \end{aligned} \tag{15a}$$

$$\begin{aligned} \phi^+_{M,n} &= 0 \qquad (n \geqslant -s + 1) \\ \phi^-_{M,n} &= 0 \qquad (n \leqslant -N + r - 1) \end{aligned} \tag{15b}$$

$$\begin{aligned} \phi^+_{0,n} &= 0 \\ \phi^-_{0,n} &= \delta_{0n} \end{aligned} \tag{15c}$$

$$q_k = w_{11} \sum_{M=0}^{\infty} \phi^-_{M,k-r} + w_{21} \sum_{M=0}^{\infty} \phi^+_{M,k-r} \qquad (k = 1, 2,\ldots, r) \tag{16}$$

$$q_k l_k = w_{11} \sum_{M=0}^{\infty} (M + 1)\phi^-_{M,k-r} + w_{21} \sum_{M=0}^{\infty} (M + 1)\phi^-_{M,k-r} \tag{17}$$

and for q_0, l_0:

$$\begin{aligned} \phi^+_{M,n} &= w_{12}\phi^-_{M-1,n+s} + w_{22}\phi^+_{M-1,n+s} \qquad (-N \leqslant n \leqslant -s - 1) \\ \phi^-_{M,n} &= w_{11}\phi^-_{M-1,n-r} + w_{21}\phi^+_{M-1,n-r} \qquad (-N + r \leqslant n \leqslant -1) \end{aligned} \tag{18a}$$

$$\begin{aligned} \phi^+_{M,n} &= 0 \qquad (n \geqslant -s;\ M \neq 0) \\ \phi^-_{M,n} &= 0 \qquad (n \leqslant -N + r - 1) \end{aligned} \tag{18b}$$

$$\begin{aligned} \phi^{+}_{0,n} &= w_{12}\delta_{n,-s} \\ \phi^{-}_{0,n} &= 0 \end{aligned} \tag{18c}$$

$$q_0 = w_{11} \sum_{M=0}^{\infty} \phi^{-}_{M,-r} + w_{21} \sum_{M=0}^{\infty} \phi^{+}_{M,-r} \tag{19}$$

$$q_0 l_0 = w_{11} \sum_{M=0}^{\infty} (M+2)\phi^{-}_{M,-r} + w_{21} \sum_{M=0}^{\infty} (M+2)\phi^{+}_{M,-r} \tag{20}$$

The probabilities $\mathscr{P}^-$ and $\tilde{\mathscr{P}}^-$ can be found from the identities (10).

Equations (6), (10), and (12)–(20) can be used for the direct calculation of melting curves on computers. Of course, in this case the summation over M in Eqs. (13), (14), etc., has to be cut off at some value M_0 which is much larger than the corresponding average length.

4. SPECIAL CASE: $r = s = 1$

Equations (12)–(20) can be easily solved in the case $r = s = 1$. We shall sketch the method of solution, which has been discussed in detail in Refs. 1 and 5. Introducing $\phi_n{}^{\pm} = \sum_{M=1}^{\infty} \phi^{\pm}_{M,n}$ and summing Eqs. (12a) with $r = s = 1$ over M from $M = 1$ to infinity, we get equations for $\phi_n{}^{\pm}$. Then, looking for solutions of the form $\phi_n{}^{\pm} = \sum_k A_k{}^{\pm} x_k{}^n$, we obtain a relation between $A_k{}^+$ and $A_k{}^-$, $A_k{}^+ = w_{21}^{-1}(x_k - w_{11})A_k{}^-$, and an equation for x_k,

$$w_{11}x_k^{-1} + w_{22}x_k = w_{11} + w_{22} \tag{21}$$

This quadratic equation has two solutions: $x_1 = 1$ and $x_2 = w_{11}/w_{22}$. The coefficients $A_k{}^{\pm}$ can be obtained from the initial and boundary conditions, Eqs. (12b), (12c). The final result for $\mathscr{P}_0{}^+$ is

$$\mathscr{P}_0{}^+ = w_{21}(x_2^{-1} - 1)/(w_{12}x_2^{-N} - w_{21}) \tag{22}$$

Similarly, one can find

$$\begin{aligned} \mathscr{P}^- &= \frac{w_{12}(x_2 - 1)}{w_{21}x_2^{N+1} - w_{12}}; \qquad \tilde{\mathscr{P}}^- = w_{22}w_2 \frac{x_2 - 1}{w_{21}x_2{}^N - w_{12}} \\ q_1 &= x_2 \frac{w_{21}x_2{}^N - w_{12}}{w_{21}x_2^{N+1} - w_{12}}; \qquad q_0 = \frac{w_{12}w_{21}(x_2{}^N - 1)}{w_{21}x_2{}^N - w_{12}} \end{aligned} \tag{23}$$

and

$$E = h^I - U\frac{w_1(w_{22} - w_{11})}{w_{22}x_2^{-N} - w_{21}} \tag{24}$$

To obtain an approximate expression for E near the melting temperature for arbitrary U_1 and U_2, we introduce $\Delta = w_{11} - w_{21} = w_{22} - w_{12}$ and $\theta = w_1 U_1 - w_2 U_2$. At the melting point, $\theta = 0$, and near the melting temperature, $\theta \ll U_1, U_2$. In the case $U_1 = U_2 = U$, $\theta/U = (w_{21} - w_{12})/(w_{21} + w_{12}) \ll 1$. Now we can express all the probabilities $w_{\alpha\beta}$ in terms of Δ and θ/U:

$$\begin{aligned} w_{11} &= 1 - w_{12} = \tfrac{1}{2}[1 + \Delta + (1 - \Delta)\theta/U] \\ w_{22} &= 1 - w_{21} = \tfrac{1}{2}[1 + \Delta - (1 - \Delta)\theta/U] \end{aligned} \tag{25}$$

Substituting Eqs. (25) in Eq. (24) and noticing that

$$\begin{aligned} x_2^{-N} &\approx \left(1 + \frac{1 - \Delta}{1 + \Delta}\frac{2\theta}{U}\right)^{-N} = \exp\left[-N \ln\left(1 + \frac{1 - \Delta}{1 + \Delta}\frac{2\theta}{U}\right)\right] \\ &\approx \exp\left(-\frac{\theta V}{\beta}\frac{1 - \Delta}{1 + \Delta}\right) \end{aligned} \tag{26}$$

where $\beta = U^2/2$, we get

$$E = h^l - \theta\left[1 - \exp\left(-\frac{\theta V}{\beta}\frac{1 - \Delta}{1 + \Delta}\right)\right]^{-1} \tag{27}$$

Comparing this expression with Eq. (67) of Ref. 1, we see that in the case of arbitrary U_1 and U_2 we have to put $\beta = U_1 U_2/2$, where the values of U_1 and U_2 are taken at the melting temperature.

It can be shown that in the case of correlation between the nearest neighbors, the result obtained by Lifshitz[(4)] is equivalent to Eq. (27). Of course our argument does not give a strict derivation of Eq. (27). In the next section we shall obtain this equation in a different way.

The fraction of melted links can be found by differentiation of E:

$$\eta = -\frac{\partial E}{\partial \theta} \tag{28}$$

Assuming a linear temperature dependence of U_1 and U_2, $U_1 = a(T - T_1)$, $U_2 = -a(T - T_2)$, we get for the width of the melting curve

$$\Delta T \equiv \left|\frac{\partial \eta}{\partial T}\right|^{-1}_{T=T_m} = \frac{1 + \Delta}{1 - \Delta}\frac{6\beta}{aV} = \frac{w_{11} + w_{22}}{w_{12} + w_{21}}\frac{6\beta}{aV} \tag{29}$$

We see that ΔT is rather sensitive to the correlations in the sequence. If $w_{11}, w_{22} \gg w_{12}, w_{21}$, then the polymer consists of long, pure component-1 and component-2 sections which melt out at temperatures close to T_1 and T_2, respectively, and the width of the melting curve is much larger than that for a random sequence. In the opposite limiting case ($w_{11}, w_{22} \ll w_{12}, w_{21}$)

the sequence of components is only slightly different from 121212..., and most of the links melt near $T_m = \frac{1}{2}(T_1 + T_2)$, so that ΔT is much smaller than ΔT for a random sequence.

To study the effect of the correlations in the sequence on the intrinsic fine structure of melting curves, one has to calculate the average lengths $L_0{}^+$, l_0, and l_1 (in the case $r = s = 1$). However, the expressions one gets for the average lengths and the resulting expressions for $\Delta\eta_{\text{A,B,C}}$ are rather complicated and difficult to analyze. To have an idea of the dependence of the fine structure on $w_{\alpha\beta}$, we calculated the magnitude of the principal peak $\Delta\eta_{\text{A}}$ and its width δT_{A} in two limiting cases: $w_{11}, w_{22} \ll w_{12}, w_{21}$ and $w_{11}, w_{22} \gg w_{12}, w_{21}$. To simplify the answers, we shall assume also that $w_{11} = w_{22}$, $w_{12} = w_{21}$, and $N \gg 1$. Then in the first case ($w_{11} \ll w_{12}$), $L_0{}^+ = N^2/3w_{11}$, $l_0 = 2$, and

$$\Delta\eta = 1/6N \tag{30}$$

The average length of a newborn section of type (A) equals (see Ref. 5)

$$L_{\text{A}} = L_0{}^+ + q_0 l_0 (1 - q_0)^{-1} N^2/3w_{11} \tag{31}$$

and the width of the peak is given by

$$\delta T_{\text{A}} = 4T/aL_{\text{A}} = 12w_{11}TU^2/aV^2 = 4T\Delta T/V \tag{32}$$

where $\Delta T = 3w_{11}U^2/aV$ is the width of the melting curve. In the second limiting case ($w_{12} \ll w_{11}$), $L_0{}^+ = N$, $q_0 l_0 \to 0$, and we get

$$\Delta\eta_{\text{A}} = \tfrac{1}{2}w_{12}^2 N \tag{33}$$

$$L_{\text{A}} = N, \qquad \delta T_{\text{A}} = 4w_{12}T\Delta T/3U \tag{34}$$

where $\Delta T = 3U^2/w_{12}aV$. From Eqs. (30)–(34) we see that the magnitudes and widths of the peaks are sensitive to the correlations in the sequence. On the other hand, the positions of the peaks are independent of $w_{\alpha\beta}$ and determined only by U_1, U_2, and V. The conditions for the principal peaks are the same as for a random sequence (see Ref. 5).

5. ARBITRARY CORRELATED SEQUENCES

Let us now assume that there is a correlation between $m + 1$ nearest neighbors. In this case the sequence is completely characterized by the quantities

$$w_{\alpha_1\alpha_2\cdots\alpha_{m+1}} \equiv \mathcal{N}_{\alpha_1\cdots\alpha_{m+1}}/\mathcal{N}_{\alpha_1\cdots\alpha_m} \tag{35}$$

where $\alpha_i = 1$ or 2. Here $w_{\alpha_1\cdots\alpha_{m+1}}$ is the probability that a section $(\alpha_1,\dots,\alpha_m)$

is followed by a link of type α_{m+1}. The total probability of a section $(\alpha_1, \ldots, \alpha_k)$ is given by

$$W_{\alpha_1 \cdots \alpha_k} \equiv \mathscr{N}_{\alpha_1 \cdots \alpha_k} / \mathscr{N} = w_{\alpha_1 \cdots \alpha_k} w_{\alpha_1 \cdots \alpha_{k-1}} \cdots w_{\alpha_1} \tag{36}$$

The probabilities $w_{\alpha_1 \cdots \alpha_i}$ and $W_{\alpha_1 \cdots \alpha_k}$ satisfy the identities

$$\sum_{\beta=1}^{2} w_{\alpha_1 \cdots \alpha_i \beta} = 1 \tag{37}$$

$$\sum_{\alpha_1=1}^{2} W_{\alpha_1 \alpha_2 \cdots \alpha_k} = W_{\alpha_2 \cdots \alpha_k} \tag{38}$$

$$\sum_{\alpha_k=1}^{2} W_{\alpha_1 \cdots \alpha_{k-1} \alpha_k} = W_{\alpha_1 \cdots \alpha_{k-1}} \tag{39}$$

$$\sum_{\alpha=1}^{2} w_{\alpha\beta \cdots \gamma\delta} W_{\alpha\beta \cdots \gamma} = W_{\beta \cdots \gamma\delta} \tag{40}$$

To describe the Brownian motion corresponding to our sequence, we have to introduce 2^m functions $\phi_{M,n}^{\alpha_1 \cdots \alpha_m}$ satisfying the equations

$$\phi_{M,n}^{\alpha \cdots \beta\gamma} = \sum_{\kappa=1}^{2} w_{\kappa\alpha \cdots \beta\gamma} \phi_{M-1, n - r\delta_{\gamma 1} + s\delta_{\gamma 2}}^{\kappa\alpha \cdots \beta} \tag{41}$$

where $\delta_{\mu\nu}$ is the Kronecker symbol. The probabilities $\mathscr{P}_n{}^{+}$, q_k, and q_0 will now have subscripts and superscripts; for example, $(\mathscr{P}_n{}^{+})_{\alpha_1 \cdots \alpha_m}^{\beta_1 \cdots \beta_m}$. The subscripts correspond to the links preceding the section and the superscripts correspond to the last m links of the section. The probability $\mathscr{P}^{-}$ has only subscripts and $\tilde{\mathscr{P}}^{-}$ has only superscripts. One can think of $\mathscr{P}_m{}^{+}$, q_k, and q_0 as operators in 2^m-dimensional vector space. Then $\mathscr{P}^{-}$ and $\tilde{\mathscr{P}}^{-}$ are ket and bra vectors, respectively.

The expressions for E, η, and $\Delta\eta_{\mathrm{A,B,C}}$ are easily found in the case $r = 1$ (cf. Refs. 1 and 5):

$$\begin{aligned} E &= h^I - U\langle \tilde{\mathscr{P}}^{-} | \hat{\mathscr{P}}_0{}^{+} \sum_{n=0}^{\infty} n \hat{q}_1{}^{n} | \mathscr{P}^{-} \rangle \\ &= h^I - U\langle \tilde{\mathscr{P}}^{-} | \hat{\mathscr{P}}_0{}^{+} \hat{q}_1 (\hat{I} - \hat{q}_1)^{-2} | \mathscr{P}^{-} \rangle \end{aligned} \tag{42}$$

where $\hat{I}$ is the unit operator. The equations for η and $\Delta\eta$ become more complicated:

$$\begin{aligned} \eta = \langle \tilde{\mathscr{P}}^{-} | \{ (\widehat{\mathscr{P}_0{}^{+} L_0{}^{+}}) + \hat{\mathscr{P}}_0{}^{+} (\hat{I} - \hat{q}_1)^{-1} (\widehat{q_1 l_1}) \\ + \hat{\mathscr{P}}_0{}^{+} (\hat{I} - \hat{q}_0)(\widehat{q_0 l_0}) \} (\hat{I} - \hat{q}_1)^{-1} | \mathscr{P}^{-} \rangle \end{aligned} \tag{43}$$

$$\Delta\eta_{\mathrm{A}} = \langle \tilde{\mathscr{P}}^{-} | (\widehat{\mathscr{P}_0{}^{+} L_0{}^{+}}) + \hat{\mathscr{P}}_0{}^{+} (\hat{I} - \hat{q}_0)^{-1} (\widehat{q_0 l_0}) | \mathscr{P}^{-} \rangle \tag{44}$$

where the operator $\widehat{(AB)}$ is defined as component by component product of operators $\hat{A}$ and $\hat{B}$. (Note that the average lengths $L_0{}^+$, l_1, and l_0 also have subscripts and superscripts, i.e., they are operators.)

If $r \neq 1$, then there are a number of operators $\hat{q}_k$ that do not commute with each other. In this case the equation

$$\sum_{n_1=0}^{\infty} \cdots \sum_{n_r=0}^{\infty} \left[\left(\sum_{k=1}^{r} n_k \right)! \prod_{k=1}^{r} \frac{q_k^{n_k}}{n_k!} \right] = \left(1 - \sum_{k=1}^{r} q_k \right)^{-1}$$

which has been used in Refs. 1 and 5, is no longer correct, and we fail to obtain closed expressions for E, η, and $\Delta\eta$. Equations (42) and (43) are not sufficient to calculate the melting curves, since they give the values of E and η only for certain values of temperature corresponding to $r = 1$. On the other hand, Eq. (44) and similar equations for $\Delta\eta_{\mathrm{B,C}}$ and $L_{\mathrm{A,B,C}}$ can be used for the calculation of the magnitudes and widths of the principal peaks on the differential melting curve corresponding to $U_1/U_2 = 1, 1/2, 1/3, \ldots$.

As in Ref. 1 and in the previous section of this paper, one can try to obtain an approximate expression for the ground-state energy E near the melting temperature. Summing Eq. (41) over all M from $M = 1$ to infinity and introducing

$$\phi_n^{\alpha\cdots\beta} = \sum_{M=1}^{\infty} \phi_{M,n}^{\alpha\cdots\beta} \tag{45}$$

we get

$$\phi_n^{\alpha\cdots\beta\gamma} = \sum_{\kappa=1}^{2} \omega_{\kappa\alpha\cdots\beta\gamma} \phi_{n-r\delta_{\gamma1}+s\delta_{\gamma2}}^{\kappa\alpha\cdots\beta} \tag{46}$$

Looking for solutions of Eq. (46) of the form

$$\phi_n^{\alpha\cdots\beta} = A^{\alpha\cdots\beta} x^n \tag{47}$$

we get a system of homogeneous linear equations for $A^{\alpha\cdots\beta}$:

$$A^{\alpha\cdots\beta\gamma} = \sum_{\kappa=1}^{2} \omega_{\kappa\alpha\cdots\beta\gamma} A^{\kappa\alpha\cdots\beta} x^{-r\delta_{\gamma1}+s\delta_{\gamma2}} \tag{48}$$

The values of x are determined by the equation

$$D(x) = 0 \tag{49}$$

where $D(x)$ is the determinant of the system.

Our analysis of random sequences$^{(1)}$ suggests that only one of $2^m(r + s)$ roots of Eq. (49) is important near the melting temperature, namely the root that is close to 1: $x = e^{\alpha}$, $|\alpha| \ll 1$. The ground-state energy is then given by[2]

$$E = h^l - \theta[1 - \exp(-\alpha N)]^{-1} \tag{50}$$

Expanding Eq. (49) in powers of α near $\alpha = 0$, we get

$$\alpha D'(\alpha = 0) + \tfrac{1}{2}\alpha^2 D''(\alpha = 0) + \cdots = 0 \tag{51}$$

In the first approximation

$$\alpha = 2D'(0)/D''(0) \tag{52}$$

It can be shown that

$$D'(0) = \text{const} \times (w_1 r - w_2 s) \tag{53}$$

Therefore we can write $\alpha N = \kappa\theta V/\beta$, where $\beta = U_1 U_2/2$ and $\kappa = \kappa(w_{\alpha\cdots\beta}, r/s)$. In our approximation we can take the value of r/s at the melting point: $r/s = w_2/w_1$, and κ becomes a constant. The width of the melting curve is given by

$$\Delta T = 6\beta/\kappa a V \tag{54}$$

In the case of random sequences ($m = 0$), $\kappa = 1$. If there is a correlation between the nearest neighbors ($m = 1$), a simple calculation gives[3]

$$\kappa = \frac{w_{12} + w_{21}}{w_{11} + w_{12}} \qquad (m = 1) \tag{55}$$

In the case $m = 2$ we get a rather complicated expression:

$$\begin{aligned}\kappa = {} & [w_{221}(w_{211} + w_{112}) + w_{112}(w_{221} + w_{122})][2(1 + w_{112} + w_{221} \\ & + w_{112}w_{221} - w_{212}w_{121}) - (2 + w_{211} + w_{112})w_{221}w_2/w_1 \\ & - (2 + w_{221} + w_{122})w_{112}w_1/w_2]^{-1}\end{aligned} \tag{56}$$

where

$$\begin{aligned}w_1 = 1 - w_2 = {} & w_{221}(w_{211} + w_{112})[w_{221}(w_{211} + w_{112}) \\ & + w_{112}(w_{122} + w_{221})]^{-1}\end{aligned} \tag{57}$$

Note that one can get expressions for κ for the cases $m = 1$ and $m = 0$ by dropping one or both of the first two indices in $w_{\alpha\beta\gamma}$ in Eq. (56). In the general case κ can be calculated by computer.

---

[2] Taking into account only one of the roots of Eq. (49) is equivalent to using the diffusion differential equation instead of the difference equations (46). Lifshitz(4) has shown that the diffusion equation approach leads to Eq. (50) (see also Ref. 1). Note that this approach is justified only if $R \ll L$, where R is the correlation radius and L is the average length of a melted section.

[3] Note that Eq. (50) with κ given by Eq. (55) is identical to Eq. (27).

REFERENCES

1. A. Vilenkin, *Biopolymers* **16**:1657 (1977).
2. M. Ya. Azbel', *Zh. Eksp. Teor. Fiz. Pis'ma Red.* **16**:183 (1972) [*Sov. Phys.—JETP Lett.* **16**:128 (1972)].
3. M. Ya. Azbel', *Phys. Rev. Lett.* **31**:589 (1973).
4. I. M. Lifshitz, *Zh. Eksp. Teor. Fiz.* **65**:1100 (1973) [*Sov. Phys.—JETP* **38**:545 (1974)].
5. A. Vilenkin, *J. Stat. Phys.*, this issue, preceding paper.
6. G. W. Lehmann and J. P. McTague, *J. Chem. Phys.* **49**:3170 (1968).
7. R. H. Lacombe and R. Simha, *J. Chem. Phys.* **58**:1043 (1973).