

Foundation.

<sup>1</sup>J. J. Quinn and K. W. Chiu, in Taormina Research Conference on the Structure of Matter—POLARITONS 1972 (to be published); K. W. Chiu and J. J. Quinn, *Nuovo Cimento* **10**, 1 (1972); K. W. Chiu and J. J. Quinn, *Phys. Rev. Lett.* **29**, 600 (1972); J. J. Brion, R. F. Wallis, A. Hartstein, and E. Burstein, *Phys. Rev. Lett.* **28**, 1455 (1972); K. W. Chiu and J. J. Quinn, *Phys. Rev. B* **5**, 4707 (1972).

<sup>2</sup>See, for example, A. P. Protogenov and V. Ya. Dimikhovski, *Pis'ma Zh. Eksp. Teor. Fiz.* **14**, 518 (1971) [*JETP Lett.* **14**, 356 (1971)].

<sup>3</sup>V. I. Baibakov and V. N. Datsko, *Zh. Eksp. Teor. Fiz.* **15**, 195 (1972) [*JETP Lett.* **15**, 135 (1972)].

<sup>4</sup>We choose an uncompensated plasma because the sample used in Ref. 3 was *n*-type (though at room temperature it is almost intrinsic), and therefore has more electrons than holes. In addition, for the sake of simplicity, we consider the collision time  $\tau$  to be infinite, except for a brief discussion of the effect of collisions on the low-frequency surface mode. In the absence of collisions, bulk helicon propagation can only

occur in an uncompensated plasma, and the bulk mode discussed in Ref. 2 only occurs if  $n_1 \neq n_2$ .

<sup>5</sup>It is logically inconsistent to use a local dielectric tensor in the collisionless limit considered throughout most of this paper. However, for the higher frequency modes it is possible to have  $\omega\tau \gg 1$  while  $ql$  is sufficiently small to justify use of a local theory.

<sup>6</sup>This dispersion relation has been derived previously by Chiu and Quinn, the second paper listed in footnote 1.

<sup>7</sup>For these values of  $\tau_1$  and  $\tau_2$  the real and imaginary parts  $q_z$  are roughly equal in magnitude. This may account for the fact that harmonics of the fundamental transmission resonance were apparently not observed experimentally.

<sup>8</sup>These values are larger by almost an order of magnitude than one would expect for InSb at room temperature. More realistic values, however, actually interchange the order of some of the curves of Fig. 2. Therefore, our results can only be taken as qualitative and suggestive of a possible explanation of the experimental results of Ref. 3.

## Random Two-Component One-Dimensional Ising Model for Heteropolymer Melting

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Heteropolymer melting corresponds to a low-temperature phase transition in a one-dimensional two-component Ising model. A leading-order approximation for an additive physical quantity in the melting region is introduced; it is intimately connected with the microscopic statistical heteropolymer structure. This allows one to derive the heteropolymer distribution function (over the length and composition of the sections) directly from experimental data.

In the simplest case, heteropolymer (HP) melting is described<sup>1</sup> by a two-component one-dimensional Ising model with Hamiltonian

$$H = \frac{1}{2} \sum_{k=1}^n [U(a_k)(1 + s_k) + (V/4)(L - s_k s_{k+1})]; \quad s_{N+1} = s_1, \quad V > (1, U); \quad (1)$$

$$a_k = 1, 2; \quad s_k = \pm 1; \quad U(1) = U, \quad U(2) = -1, \quad U > 0.$$

Here  $a_1, a_2, \dots, a_N$  represent the fixed component sequence; the  $s_k$  determine the "thermodynamic state" of each link, i.e., all the  $\{s_k\}$  sets are included in the statistical sum;  $|U(2)| = 1$  defines the choice of energy units. We set  $s_{N+1} = s_1$  just for convenience;  $s_k = +1$  and  $s_k = -1$  represent the "helix" and "melted" (or "coiled") states (*h* and *c* states), respectively. A section which contains only *h* or *c* links is an *h* or *c* section (HS or CS); a CS which neighbors only with an HS is an "isolated" CS (ICS). The most probable state of a section is the one with the smallest value of  $H$  or (in the case of equal  $H$  values), it is a CS (see

below). In a HP, the energy  $V$  is much larger<sup>2</sup> than the thermal energy  $kT$ . This fact allows one to use the ground-state energy  $E$  as the leading order approximation (in  $kT/V$ ) for the free energy (this statement can be proved rigorously), and the problem then is to calculate  $E = \min(H)$  over all  $\{s_k\}$  sets.

Let us plot (see Fig. 1) the helix-state energy,  $H_M = UL_M - K_M$ , as a function of the number of links  $M$  ( $L_M$  and  $K_M$  are the numbers of component-1 and component-2 links, respectively, and  $L_M + K_M = M$ ; the points at Fig. 1 are joined by

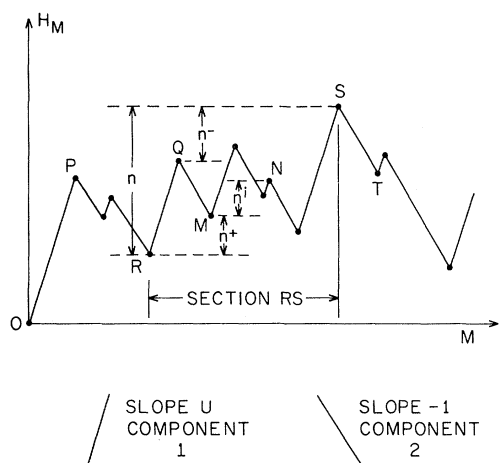


FIG. 1. The helix-heteropolymer energy  $H_M$  as a function of links number  $M$ .  $PQ$ ,  $MN$ , and  $ST$  are the new-born coiled sections;  $MN$  and  $ST$  heights equal  $V$ ,  $RQ$  height is less than  $V$ .  $V/2$  is the surface energy between helix and coiled sections.

straight lines). We shall describe any sections, e.g.,  $RS$  in Fig. 1, by its "height"  $n = H_S - H_R$ , and define the heights  $n^+ = H_M - H_R$ ,  $n^- = H_S - H_Q$ , and  $n^i = H_N - H_M$ , where  $M, N, Q$  are arbitrary inner points of the section (see Fig. 1). The same quantities for the left- (e.g.  $PR$ ) and right-hand (e.g.  $ST$ ) neighbor sections will be denoted by the subscripts  $+$  and  $-$ , respectively. It is clear from (1) that the change of a helix section to a coil section corresponds to the change of  $H$  variation at the boundaries by a  $Vp$  height jump, where  $p = 1$  or  $p = -1$  when both neighbors of the section are HS's or CS's, respectively, and  $p = 0$  when one of them is a CS and the other is an HS. Thus, a CS is more probable than an HS if the section height exceeds or equals  $Vp$ . It can be proved that the  $n$ -height ICS is the best one when, and only when, the conditions

$$\begin{aligned} n \geq V, \quad 0 \leq n^+ \leq n, \quad n^i \geq -V; \\ 0 > (n_-, n_+) \geq -V, \quad n_{\pm} < -V \end{aligned} \quad (2)$$

are met. The inequality  $n \geq V$  makes a CS better than an HS; the conditions  $n^+ \geq 0$ ,  $n^- \geq 0$  (the latter is equivalent to  $n^+ \leq n$ ), and  $n^i \geq -V$  prevent the existence of an  $h$  state of the appropriate ( $+$ ,  $-$ , and  $i$ ) segments. The inequalities  $n_{\pm} < -V$ ,  $(n_-, n_+) \geq -V$  give the exact specification of the neighbor sections. (The section will have just one neighbor if we choose its left-hand boundary for the first link of the HP; this is possible because  $s_{N+1} = s_1$ . If this single neighbor has  $n_-^+$

$\geq -V$ , it will be coiled and the basic section will not be an ICS.) The specification of the neighbor sections together with  $(n_-, n_+) < 0$  makes them HS's.

Any failure of the conditions discussed either destroys the completely coiled state of the basic section, or coils the neighbor segment (or segments). The geometrical meaning of (2) is evident. If we call "regular" a section which has  $0 \leq n^+ \leq n$  (or  $0 \geq n^+ \geq n$  for  $n < 0$ ), and "strictly regular" a section which has  $0 < n^+ < n$  (or  $0 > n^+ > n$  for  $n < 0$ ), then the section will be an ICS (for the given  $U$ ) if (1) its height exceeds or equals  $V$ , (2) it is regular, and (3) both its neighbors are strictly regular until their heights for the first time become less than  $-V$ . If  $U$  increases monotonically, all the heights increase or remain unaltered. Therefore the first four inequalities of (2) cannot be violated (while the next ones can). Thus, a CS remains a CS and may grow only by the coiling of the links of the neighbor sections.

The birth of a CS can be investigated on the basis of formula (2). An ICS can appear in one of four possible ways determined by which one of the inequalities (2) is satisfied last (or simultaneously with any of the following inequalities) as  $U$  increases. (All but the first four inequalities can fail but cannot become valid as  $U$  increases.) The new-born CS (or CS's) is easily ascertained. If  $U = U_0$  is the point of appearance of an ICS, then the ICS segment (or segments) which is a helix at  $U = U_0 - 0$  is just the new-born CS at  $U = U_0$ . Suppose the first inequality in (2),  $n = V$ , is the one satisfied last (or one of the last). Then the new-born section appears as a whole (e.g., section  $MN$  in Fig. 1) and is the " $p = 1$ " type section.

If it is the second inequality that defines the type of the new-born segment, i.e., if  $n > V$ ,  $\min(n^+) = 0$ , then the new-born segment forms the left-hand part of the ICS, its right boundary being the last ICS point where  $n^+ = 0$ . This may be called a " $p = 0, q = 1$ " segment, with

$$\begin{aligned} \tilde{n} = 0, \quad 0 \leq \tilde{n}^+ \leq V; \quad \tilde{n}_+ < -V, \quad 0 > \tilde{n}_+^- \geq -V; \\ \tilde{n}_- > V, \quad 0 < \tilde{n}^+ \leq V. \end{aligned} \quad (3)$$

[Here and below, a tilde denotes a new-born segment and its neighbors, as in (3).] The segment and its right-hand neighbor (3) form only part of the ICS in the general case. The rest of the ICS, as well as the ICS right-hand-neighbor section, does not influence the birth of the segment, but it can provide the simultaneous births of the next

type of CS. If  $n > V$ ,  $n^+ > 0$ , but  $\max(n^+) = n$  [i.e.,  $\min(n^-) = 0$ ], the new-born " $p = 0, q = -1$ " segment (e.g.,  $PQ$  in Fig. 1) forms the right-hand part of the new-born ICS and is quite analogous to the previous type of segment.

The last possible case corresponds to  $n > V$ ,  $0 < n^+ < n$ , and  $\min(n^-) = -V$ . The longest segments of those whose height equals  $-V$  are the new-born segments (e.g.,  $ST$  in Fig. 1) of " $p = -1$ " type. (If there are some of them, they have different heights of starting points.) The  $p$ -type and  $q$ -type new-born CS's are described by the conditions

$$\begin{aligned} \bar{n} &= pV, \quad 0 \leq m_p^q \bar{n}^+ \leq V; \quad m_p^{zq} \bar{n}_z^- < -V, \\ 0 > m_p^{zq} \bar{n}_z^{-z} &\geq -V, \end{aligned} \tag{4}$$

where

$$m_p^s \equiv p + (1 - p^2)s, \quad z = \pm 1.$$

These definitions allow the overlapping of the new-born CS's neighbor sections, but exclude the overlapping of the new-born CS's themselves.

The geometrical sense of the relations (4) is easily understood [as soon as they are written separately for each  $p$  or  $q$ —see, e.g., (3)] and is as simple as that of the relations (2). The first equality from (4) defines  $U_p = (K + pV)/L = \bar{U} + pVL$ , where  $(L, K)$  refers to the new-born CS. It allows one to write the conditions of CS birth in the terms of segment composition only ( $y_{1,2}$  define  $p = \pm 1$  and  $y_{3,4,5}$  define  $p = 0$ ):

$$\begin{aligned} y_1 &= \max[-p\bar{n}^+L/L^+, -p\bar{n}_z^{-z}(1 + L_z^{-z}/L)^{-1}, p\bar{n}^+(1 - L^+/L)^{-1}] \leq V; \\ y_2 &= \max[p\bar{n}_z(1 + L_z/L)^{-1}, p\bar{n}_z^{-z}L/L_z^{-z}] < -V; \quad y_3 = \max(\bar{n}^+q, -rq\bar{n}_z^{-z}) \leq V; \\ y_4 &= \max(rq\bar{n}_z) < -V; \quad y_5 = \max(-q\bar{n}^+ - 0, rq\bar{n}_z^{-z}) < 0; \quad z = \pm 1. \end{aligned} \tag{5}$$

The bar over the  $n$ 's denotes the heights at  $U = \bar{U}$ ; maxima are taken over all the variable points and over all the figures in parenthesis.

Let us calculate  $y_{2,\dots,5}$  for any HP section (e.g.,  $QN$  in Fig. 1) together with its arbitrary (but fixed) neighbors (e.g.,  $RQ$  and  $NT$  in Fig. 1,  $R$  and  $T$  are arbitrary), and let us construct the distribution function  $R_p(L, K; y_1, y_2)$ ,  $p = \pm 1$ ;  $R_0(x; y_3, y_4, y_5)$ ,  $x = L/(L + K)$ , of the total number of links of all the appropriate sections [i.e., the middle  $(L, K)$  sections of three consequent sections which are characterized by  $y_{1,2}$  or (for any  $q$ )  $y_{3,4,5}$ ]. (Of course in this way any link may be calculated more than once.) If conditions are satisfied, the section  $(L, K)$  is a ( $p$ - or  $q$ -type) newborn CS, and vice versa. Thus, the integration of the  $R$ 's over the regions (5) gives the distribution functions  $Q_p(L, K; V)$  and  $Q_0(x; V)$  of the total number of links of the  $p$ -type new-born CS ( $p = \pm 1, 0$ ).

These three smooth functions of the four variables  $L, K, V$ , and  $x$  are enough for the exhaustive description of the ground state of quite arbitrary component sequences. [Analogous functions, but depending on a larger number of variables, describe excitations and thermodynamics with the accuracy  $\exp(-V/kT)$ .] The condition  $U_p < U$  determines the CS; thus, the numbers of  $a$  links in a  $c$  state ( $N_a$ ) and of boundaries between CS and HS are given by

$$\begin{aligned} N_a(U, V) &= \sum L_a^{(p)}(L^{(p)} + K^{(p)})^{-1} Q_p(L^{(p)}, K^{(p)}; V) + \int x_a Q_0(x; V) dx; \\ N_b(U, V) &= 2p(L^{(p)} + K^{(p)})^{-1} Q_p(L^{(p)}, K^{(p)}; V); \\ L_1^{(p)} &= L^{(p)}, \quad L_2^{(p)} = K^{(p)}, \quad x_1 = x, \quad x_2 = 1 - x; \quad K^{(-1)} \geq 0, \quad L^{(-1)} \geq (K^{(-1)} + V)/U; \\ L^{(-1)} &\geq 0, \quad K^{(-1)} \leq L^{(-1)}U + V; \quad x \geq (U + 1)^{-1}; \quad p = \pm 1; \end{aligned} \tag{6}$$

summation is performed over the indicated  $p$ ,  $L^{(p)}$ ,  $K^{(p)}$ . When  $V = \text{const}/U$  and  $1/U \rightarrow 0$ , then  $N_1 \rightarrow L_N$ ,  $N_2 \rightarrow K_N$ , and  $N \rightarrow 0$ . Any additive physical quantity (per link)  $G$ , which equals  $g_a^s$  at an  $a$  link in  $s$  state and equals  $g_b$  at the state boundaries, can be written as

$$\begin{aligned} G &= G^+ + G', \quad G' = -\sum_a g_a n_a + g_b n_b; \\ g_a &= g_a^+ - g_a^-; \quad n_a = N_a/N, \quad n_b = N_b/N, \end{aligned} \tag{7}$$

where  $G^+$  is the  $G$  value in the HP  $h$  state. [For example, in the case of energy,  $g_a = U(a)$ ,  $g_b = V/2$ ; the relative total number of the  $c$  links, which determines<sup>2</sup> the optical density, corresponds to  $g_a = I$ ,  $g_b = 0$ .]

If three physical quantities are measured for given  $U, V$ , then Equations (7) allow one to find  $n_a$  and  $n_b$ . They determine (for these  $U, V$ ) the relative number of links of the CS ( $n = n_1 + n_2$ ), the

average CS-component concentration  $x = n_1/n$ , and the length  $l = 2n/n_b$ . The specification of  $U, V$  determines the CS distribution function  $n = n(\bar{x}, l)$ .

If the component sequence is known, one can calculate directly  $Q_p, Q_0$  when one notices that Fig. 1 represents a one-dimensional Markov process of  $M$  steps (the "coordinate"  $H_M$  varies with "time"  $M$ ); thus, the number of links  $N_M(n)$  at the height  $n$  after  $M$  steps is  $N_M(n) = wN_{M-1}(n-U) + (1-w)N_{M-1}(n)$  ( $n=1$ ), where  $w$  is the probability (depending on the sequence correlations) of the  $l$  component at the previous place. The relations (4) determine the boundary conditions. For instance, the boundaries  $n=0, V$  are not intersected if  $N_M(n) = (1-w)N_{M-1}(n+1)$  for  $n < U$  and  $N_M(n) = wN_{M-1}(n-U)$  for  $n > V-1$ . When  $V \gg (1, U)$ , the differential form of the equations for  $N_M$  is a well known system of diffusion equations (as  $w$ , and thus  $N_M$ , depend not only on  $n$ , but also on the component environment) with boundary conditions at  $n=0, V$ . If  $N_0(n) = \delta(n)$ , then  $N_M(n)$  is the probability density of the appropriate section.

The calculations of  $Q_p, Q_0$  are then straightforward. The case of a random sequence corresponds to  $w = \text{const}$ ; its first description by Brownian motion was given by Vedenov and Dykhne.<sup>1</sup> The solution of the general case of arbitrary component numbers and interaction is quite analogous to the one described and allows one to obtain the

distribution function over the CS length and composition (which is as detailed as is allowed by the interaction radius). For  $V \gg (1, U)$  (as is the case, e.g., for DNA), the CS corresponds to the essential composition fluctuations, and only the most probable CS, which have almost definite length and composition, are significant. In this case, the  $Q$ 's depend mainly on  $L, K$  in the approximation which is logarithmic in  $V^2/(U \pm 1)^2$ . Within this accuracy one can extract the ready-made HP distribution function over the length and component of the sections directly from the experimental data.<sup>3</sup> The main feature of this investigation method is the possibility to study the long-range many-particle correlation relations, while all other methods<sup>4</sup> refer to the short-range correlations.

<sup>1</sup>A. A. Vedenov and A. M. Dykhne, Zh. Eksp. Teor. Fiz. 55, 357 (1968) [Sov. Phys. JETP 28, 187 (1969)].

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<sup>3</sup>M. Ya. Azbel', to be published.

<sup>4</sup>D. M. Gray and I. Tinoco, Jr., Biopolymers 9, 223 (1970).