

## Phase transitions in fiber materials

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We propose a theory for the phase transitions in materials made from natural fibers. At heating, the theory predicts structural phase transitions of the first order. The normalized thermodynamical characteristics show the universal behavior of a scaling law, which is unusual for first order phase transitions. The scaling exponents depend only on the exponent of the energy of small-angle interaction between fiber segments. We consider here some specific fibers like collagen which “melt” (denaturate) at higher temperature and we found explicit expressions for the thermodynamics characteristics, which can be verified by experiment.

*Introduction.* In crystals, liquid crystals, and molecular liquids the energy of intramolecular interaction is much higher than the characteristic temperatures of phase transitions. For these materials the structural transformations are determined by a competition between the intermolecular interactions which force the material to order and the tendency of the entropy to increase. The basic units of these systems are microscopic and interact with their neighbors by short-range interaction. Because the effective number of neighbors is small, mean-field approximation is problematic and higher approximations are required. On the other hand, the relevant parameters of the intermolecular interaction depend on details of the molecular structure and correct estimation of them requires a complex quantum-mechanical calculation. Both these factors complicate the theory so much that only huge numerical calculation may lead to satisfactory results for a real case. In certain cases, however, we can avoid these difficulties by the replacement of the microscopic basic units by quasimacroscopic ones. This approach was successfully used in the renormalization-group theory of critical phenomena and in polymer physics—the concepts of “quasimonomers”<sup>1</sup> and “blobs.”<sup>2</sup> In all these cases such a replacement was successful because of the existing long-range correlations in the system.

In this paper we would like to propose still another model, where the concept of quasimacroscopic basic units is natural. It is a system that consists of quasistable macromolecules or molecular aggregates in which the energy of the relevant intraunits interactions is of the same order as the characteristic temperature of the phase transformations. In such a case, the structure of the material is determined by a competition between the interunit interactions and the temperature-dependent change of the internal structure of the units. Because of the macroscopic nature of the units, most of the details of the internal structure of the units are irrelevant for an effective interunit interaction and this can be approximated by using simple expressions in the mean-field approximation. Therefore, the theory simplifies and most of the thermodynamic characteristics can be calculated analytically.

We will discuss here a concrete case of collagen made material—natural leather. Leather is made up of fibers, which are built from collagen molecules in “helix” (spiral) form. The collagen molecule in helix form has a length of 3000 Å and a diameter of 15 Å. The three folded spirals are

bonded by relatively weak, mainly hydrogen, bonds. The spiral consists of about 300 segments and each one contains approximately 3 amino-acid residues with 20–30 carbon and nitrogen atoms.<sup>3</sup> If the temperature is low ( $T \ll T_{d1}$ , where  $T_{d1} \approx 310$  K) the helix form is stable. At higher temperature, hydrogen and other weak bonds, which stabilize the helix form, become unstable and the helix breaks down to random coils.<sup>3</sup> This transition, however, is not sharp, but spreads over a temperature interval of 30–40 K. This indicates that a cooperative process takes place and not a real phase transition.<sup>4</sup> For higher temperature ( $T \geq T_{d2}$ ,  $T_{d2} \approx 350$  K) collagen molecules are “melted” completely. This process of the breakdown of the ordered helix structure, held together by noncovalent bonds, to a randomly coiled phase is called denaturation. The organized fibers are stable for  $T \ll T_{d1}$  and break down for  $T \geq T_{d2}$ .

At low temperature the fibers are stable and can be considered as basic units. When the pressure is increased, the number of fibers per volume fraction increases and the interaction between the fibers becomes important. As the fibers have a certain rigidity and their quasistraight pieces are much longer than their diameter, there will be a tendency for the fibers to align themselves in parallel straight pieces. It has been shown in Ref. 5 that the free energy of such a system has the form of the  $\Psi^4$  field Hamiltonian on a sphere and that at low temperature between low and high pressures a phase transition from a disordered to an ordered state takes place. For the explicit expressions of the density and temperature dependencies of the other thermodynamic parameters, see Ref. 5.

*Theory.* If we increase the temperature of compressed material with fixed  $c$ , to a temperature higher than  $T_0 = cT_*$ , a first-order phase transition from the ordered to the disordered phase takes place. As long as  $T_0 \ll T_{d1}$  this will be the initial disordered phase.

A more complex situation occurs for  $T_0 > T_{d1}$ . If the temperature is higher than  $T_{d1}$ , the helix form of the collagen molecule becomes unstable, the molecules melt, and the fibers are destroyed. The approach of the previous section fails, because the variation in the internal free energy of the fibers plays a major role.<sup>6</sup> The structure of the material for  $T \geq T_{d1}$  is determined by the competition between the melting and ordering of the collagen molecules. We will describe the behavior of the material by using the following model.

In a first approximation the leading term of the free energy can be represented as

$$F = F_0 + cf_{\text{mol}} + Tce_{\text{orien}} + F_{\text{int}}, \quad (1)$$

where  $f_{\text{mol}}$  is the free energy of a single collagen molecule,  $e_{\text{orien}}$  is the orientation dependent part of the entropy, and  $F_{\text{int}}$  is the energy of intermolecular interaction. In order to calculate  $f_{\text{mol}}$  we use an approximation which is close to the well-known Zimm-Bragg model. The latter is in good agreement with the real behavior of the collagen molecules (see, for example Ref. 4).

Consider a collagen molecule that contains  $sN$  segments in helix form and  $pN$  boundaries between ‘‘helix’’ and ‘‘coil’’ parts of the molecule (in the literature  $s$  is called spirality), where  $N$  is the number of segments in the molecule.  $N$  is large. Let us call the free energy of a segment in helix form  $-\varepsilon_h$ , in coil form  $-\varepsilon_c$  and the energy of segments on the boundary between helix and coil parts as  $\varepsilon_s$  [ $\varepsilon_h - \varepsilon_c = \Delta U - T\Delta S \equiv \Delta S(T_m - T)$ , where  $\Delta U$  and  $\Delta S$  are the differences between the internal energy and entropy of a spiral and a melted segment]. As the collagen molecule can be considered as a one-dimensional system, we can calculate the free energy  $f_{\text{mol}}$  in an analogous way as for the one-dimensional (1D) Ising model. The result is Ref. 4:

$$f_{\text{mol}} = -(\varepsilon_c - \varepsilon_h)s + \varepsilon_s p - T\{s \ln s + (1-s)\ln(1-s) - 2p \ln p - (s-p)\ln(s-p) - (1-s-p)\ln(1-s-p)\}. \quad (2)$$

The last two terms in Eq. (1) we obtain in the mean-field approximation (MFA):<sup>13</sup>

$$e_{\text{orien}} = s \int_{\vec{n}^2=1} d\vec{n} g(\vec{n}) \ln(4\pi g(\vec{n})); \quad (4)$$

$$F_{\text{int}} = \frac{c^2}{2} \left\{ s^2 \int_{\vec{n}^2=1} d\vec{k} d\vec{n} g(\vec{k}) g(\vec{n}) U(\vec{k}; \vec{n}) + 2T\chi_{sh}s(1-s) + T\chi_{ss}(1-s)^2 \right\}, \quad (5)$$

where  $g(\vec{n})$  is the average fraction of the segments in helix form that are directed in the direction  $\vec{n}$ . The first term in Eq. (5) corresponds to the interaction between helix-helix segments, while the others describe the interaction between helix-coil and coil-coil segments, respectively.

The energy of interaction between spiral segments we write in the form

$$U(\vec{k}; \vec{n}) \approx T\chi_{hh}u(\vec{k}; \vec{n}). \quad (6)$$

We assume as above, that near  $\vec{k} \approx \vec{n}$

$$u \propto |\vec{k} \times \vec{n}|^{2\omega}, \quad (7)$$

which corresponds to a repulsive interaction in an excluded-volume approximation.<sup>7</sup> In this approximation,  $\omega=0$  corresponds to the bundles made from hard spheres,  $\omega=0.5$  to the bundles made from hard bars and larger  $\omega$  may be used for archlike ‘‘hemstitch’’ units.

We will also assume that in a first approximation the coefficients  $\chi_{hh} \approx \chi_{hs} \approx \chi_{ss} \approx n_s \chi$  are of the same order.  $n_s$  is the number of atoms in the segments.

Using the Onsager approximation for  $g(\vec{k})$  (Ref. 13) and integrating formula (5) over  $\vec{n}$  and  $\vec{k}$ , we obtain for  $\lambda \gg 1$

$$Tce_{\text{orien}} + F_{\text{int}} \approx Tc \left\{ s(\ln \lambda - 1) + s^2 \frac{cn_s \chi}{2} \zeta(\omega) \lambda^{-\omega} - s^2 \frac{cn_s \chi}{2} \right\} + \frac{Tc^2 n_s \chi}{2}, \quad (8)$$

where coefficient  $\zeta(\omega)$  is

$$\zeta(\omega) = 2^{2\omega+1} \pi^{-1/2} \Gamma(\frac{3}{2} + \omega).$$

In the disordered phase  $g(\vec{k}) \equiv 1/4\pi$  and the interaction term in this approximation

$$F'_{\text{int}} = \frac{Tc^2}{2} \{ \chi_{hh}s^2 + 2\chi_{sh}s(1-s) + \chi_{ss}(1-s)^2 \} \approx \frac{Tc^2 n_s \chi}{2} \quad (9)$$

does not depend on spirality. In the ordered phase the quantities  $s, p$  and  $\lambda$  have to be found by minimizing Eq. (1). This gives

$$\lambda = (c/c_0)^{1/\omega} s^{1/\omega}, \quad (10)$$

$$\frac{(1-s-p)s}{(s-p)(1-s)} = \frac{\lambda}{\tau} \exp \frac{2}{\omega} \left( -\frac{c}{\zeta c_0} s + 1 - \frac{\omega}{2} \right), \quad (11)$$

$$\frac{p^2}{(s-p)(1-s-p)} = \sigma, \quad (12)$$

where

$$\tau = \exp \frac{\varepsilon_c - \varepsilon_h}{T} \equiv \exp \Delta S \frac{T_m - T}{T}, \quad (13)$$

$$\sigma = \exp -\varepsilon_s/T, \quad (14)$$

$$c_0 = 2/\chi n_s \omega \zeta \quad (15)$$

(for collagen  $\varepsilon_s \gg T_m$ ,  $\omega \approx 0.5$ ,  $n_s \sim 2 \times 10^1$  and  $\Delta S \sim 10$ ). If  $cs \ll c_0$ ,  $\lambda$  is small and the above used approach fails. For such  $c$  and  $s$ , however, the angle-dependent interaction between molecules becomes irrelevant, and the system will be in the disordered phase. In this phase  $\lambda=0$  and the free energy  $F'$  can be calculated in an explicit form. The result is<sup>4</sup>

$$F' \approx F_0 - cT \ln \frac{\tau + 1 + \sqrt{(\tau-1)^2 + 4\sigma\tau}}{2} + \frac{Tc^2 n_s \chi}{2}. \quad (16)$$

The order parameter in the ordered phase is

$$Q \approx 1 - \frac{3}{\lambda} + o\left(\frac{1}{\lambda^2}\right) \approx 1 - 3\left(\frac{c_0}{c}\right)^{1/\omega} s^{-1/\omega}. \quad (17)$$

Note, that we have here

$$\frac{\partial \ln(1-Q)}{\partial \ln c} = \frac{\partial \ln(1-Q)}{\partial \ln s} \approx -\frac{1}{\omega}, \quad (18)$$

while for the phase transition under pressure at low temperatures it is obtained in Ref. 5 that

$$\frac{\partial \ln(1-Q)}{\partial \ln c} \approx -\frac{1}{1+\omega}. \quad (19)$$

So in Eq. (18) the dependence of  $Q$  on  $c$  is much stronger for small  $\omega$ , than in Eq. (19). These derivations depend only on  $\nu$  and thus measurement of  $Q$  gives important information on the type of interfiber interaction.

The solution of the system (10)–(12) that corresponds to large  $\lambda$ , is

$$1-s \approx \frac{1}{\tau} \left[ \left( \frac{c}{c_0} \right) \exp \left( -\frac{2c}{\zeta c_0} + 2 - \omega \right) \right]^{1/\omega} \ll 1, \quad (20)$$

$$Q \approx 1 - 3 \left( \frac{c}{c_0} \right)^{-1/\omega}. \quad (21)$$

The phase transition temperature  $T_c$  is found from the condition  $F_{\text{order}}(T_c) = F'_{\text{disorder}}(T_c)$ . So we obtain

$$\Delta S \frac{T_c - T_m}{T_c} \approx \xi \left( \omega, \frac{c}{c_t} \right) - \ln \left( 1 + \frac{\sigma e^{-2\xi}}{1 - e^{-\xi}} \right), \quad (22)$$

$$\xi \approx \frac{\rho(\omega)(c/c_t - 1) - \ln(c/c_t)}{\omega}, \quad (23)$$

$$\rho = \ln \rho + \ln \zeta(\omega) e^{1-\omega}, \quad (24)$$

$$c_t = \zeta \rho c_0. \quad (25)$$

The ordered phase can be stable only if  $c > c_t = \zeta \rho c_0$ . Thus  $\lambda > (\zeta \rho)^{1/\omega}$  and the above used approximation (6) is valid, because  $\zeta \rho > 1$ .

The derivative of the transition temperature to the pressure

$$\frac{\partial T_c}{\partial P} \propto \frac{\partial T_c}{\partial c} \sim \frac{T_c^3}{q \omega T_m} \left( 1 + \sigma \frac{(2 - e^{-\xi}) e^{-2\xi}}{(1 - e^{-\xi})^2} \right) \left( \frac{c_t}{c} \right) \left( \rho \frac{c}{c_t} - 1 \right) > 0 \quad (26)$$

is positive. The latent heat and the jump in compressibility for this case are

$$q \sim c_t T_c \Delta S, \quad (27)$$

$$\Delta \kappa \propto \frac{c_t T_c}{\omega} \left( 1 - 2 \rho \frac{c}{c_t} \right) < 0. \quad (28)$$

For the jumps in the orientation order parameter and in the spirality we have

$$\Delta Q \approx 1 - 3 \left( \frac{c_t}{\zeta \rho c} \right)^{1/\omega}, \quad (29)$$

$$\Delta s \approx 1 - \exp \frac{1}{\omega} \left( 1 - \rho \frac{c}{c_t} \right), \quad (30)$$

so the phase transition is of first order. Note, that in our approximation these jumps strongly depend on the exponent of the small-angle interaction between the molecules segments.

The restriction  $c_t \leq 1$  leads to

$$n_s \geq n_{s0}(\omega) = 2\rho/\chi\omega \quad (31)$$

and for  $n_s < n_{s0}(\omega)$  the phase transition does not exist. The numerical solution of the system (10)–(12) is shown in Fig. 1.

On the left hand side ( $c < c_t$ ) cooperative ‘‘melting’’ takes place, while on the right hand side ( $c > c_t$ ) a first order phase transition can clearly be seen. The intermolecular interaction transforms the cooperative ‘‘melting’’ to the phase transition of the first order.

*Discussion and concluding remarks.* The MFA is the most crucial approximation in our theory but it is a reasonable one. At low temperatures each quasistraight piece of a

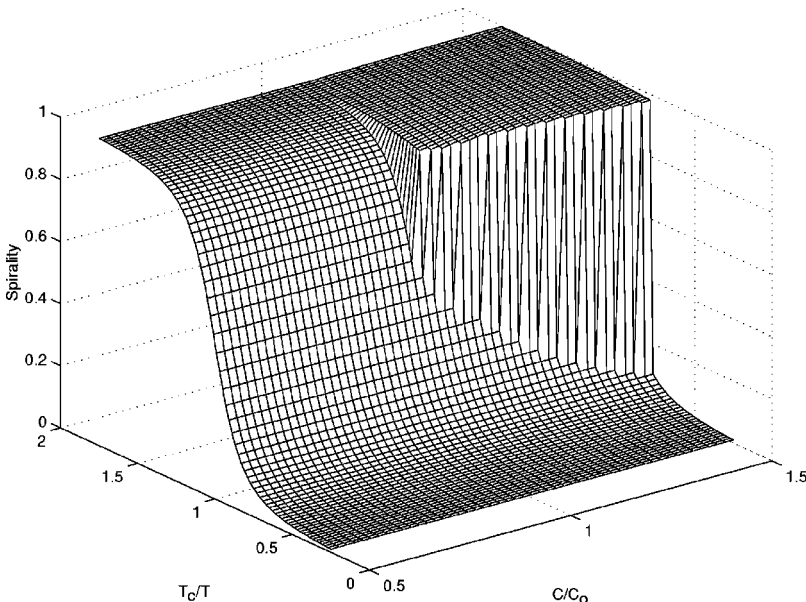


FIG. 1. Spirality as a function of the normalized inverse temperature and density.

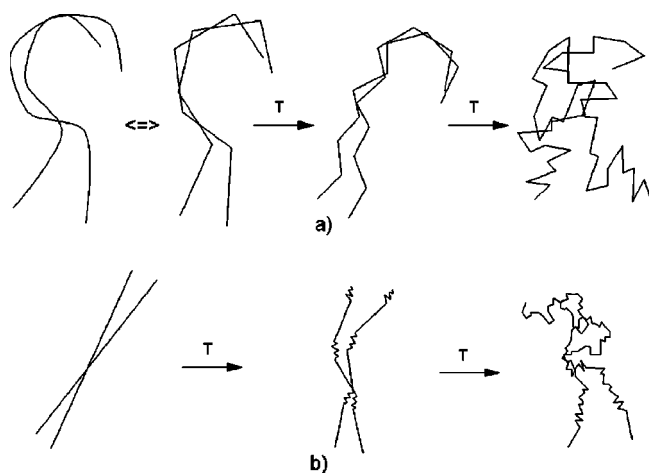


FIG. 2. Change of basic unit structure as function of the temperature. (a) fibers, (b) collagen molecules.

fiber or collagen molecule interacts with a large number of neighbors and, therefore, fluctuations of the concentration are irrelevant. On the other hand, the phase transitions are of the first order and fluctuations of the order parameter are therefore small.

In spite of the different analytical expressions obtained in Ref. 5 and here, there is a close relationship between the corresponding models. In Ref. 5 our basic units were fibers. We can roughly consider the fiber as a chain with the straight-piece segments being of persistent length. Because the persistent length is inverse proportional to the temperature the unit structure changes as function of the temperature as shown in Fig. 2(a) (see also the concept of “quasimonomers” in Ref. 1). In this paper our basic units were collagen molecules. In the temperature interval, where the collagen molecule denatures, it can be considered as a chain built up from straight-helix pieces interspersed with denatured coil pieces. Because the fraction of helix segments decreases with increasing temperature the unit structure changes as shown

in Fig. 2(b). It is clear that Figs. 2(a) and 2(b) are comparable.

For low pressure, heating leads to destruction of the leather, but for high pressure it leads to the appearance of an amorphous material (see Fig. 3 in Ref. 5). This transformation corresponds to the transition described here. For this transition the jump of Young’s modulus, which is strongly correlated with the jump in the compressibility [see Eq. (28)], was observed in Ref. 8. The theory predicts the stabilization of the spiral form of the collagen molecules at high pressure and the sensitivity of the transition to an uniaxial stress.<sup>6</sup> The spiral form stabilization has been found already in an aqueous solution of collagen,<sup>9</sup> while the sensitivity to an uniaxial stress should be tested by experiment.

In fact, it has been shown in Refs. 10–12, that a novel material can be developed by exerting high pressure and temperature on natural leather material. The production is done in an oxygen poor environment in order to prevent burning of the leather. The resulting material, which was called *pleather*, is thermoplastic.

It should be noted, that in the real material the phase transition under heating is not reversible and after cooling the system does not return to the initial low-temperature phase. This effect is connected with the cross links between collagen molecules in the coil form. These cross links are not important for the behavior under heating, because until the phase transition the spirality of collagen is large. However, if we cool the material after phase transition the cross links prevents spiralization and, therefore, stabilize the disordered phase.

Our main assumptions are general enough to apply the theory to a class of compressed materials made from various fibers. It could be used, for example, for implant materials made from actin myofibrils or for artificial wood made from natural cellulose fibrils.

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<sup>1</sup>A. Khohlov, *Polymer* **9**, 1387 (1978).

<sup>2</sup>P.G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, 1979).

<sup>3</sup>P. Kronick, in *Fundamentals of Leather Manufacturing*, edited by E. Heideman (Edward Roether, Darmstadt, Germany, 1993), Chap. 4.

<sup>4</sup>A.A. Vedenov, *The Physics of Solutions* (Science, Moscow, 1984); D. Poland and H.A. Scheraga, *Theory of Helix-Coil Transitions in Biopolymers* (Academic Press, New York, 1970).

<sup>5</sup>U. Sandler and A. Wyler, *Phys. Rev. Lett.* **74**, 3073 (1995).

<sup>6</sup>P.G. de Gennes (private communication).

<sup>7</sup>In fact,  $U(\vec{k}; \vec{n})$  must include the term that corresponds to an attractive interaction. This term has the form  $\delta U \sim - (p/s) \mu u_{\text{attr}}(\vec{k}; \vec{n})$ . In our theory  $\delta U$  can be neglected for the following reasons: for  $s \ll 1$  and  $\varepsilon_s \gg \varepsilon_c - \varepsilon_h$ ,  $\delta U$  is small be-

cause  $p \ll s$ . On the other hand, if  $s \ll 1$  and  $p \sim s$  the whole term  $s^2 \int_{\vec{n}^2=1} d\vec{k} d\vec{n} g(\vec{k}) g(\vec{n}) U(\vec{k}; \vec{n})$  in Eq. (5) is small and can be neglected. Note, however, that attractive interaction has to be considered in the cases of collapse or segregation in pleather.

<sup>8</sup>A. Wyler (unpublished).

<sup>9</sup>K. Gekko and M. Fukamizu, *Int. J. Biol. Macromol.* **13**, 299 (1991).

<sup>10</sup>B. de Castro, M. Ferreira, R.T. Markus, and A. Wyler, *J. Macromol. Sci., Pure Appl. Chem. A* **34**(1), 109 (1997).

<sup>11</sup>A. Wyler, R.T. Markus, H.J. Wagner, and B. de Castro, *J. Mater. Res.* **7**, 1990 (1992).

<sup>12</sup>A. Wyler, R.T. Markus, and B. de Castro, *J. Soc. Leather Technol. Chem.* **75**, 52 (1991).

<sup>13</sup>P.G. de Gennes, *The Physics of Liquid Crystals* (Clarendon, Ithaca, 1979).