Phase Transitions under Pressure in Collagenous Material

U. Sandler* and A. Wyler†
Jerusalem College of Technology, P.O. Box 16031, Jerusalem, Israel

(Received 24 June 1994)

We have developed a theory of a phase transition under pressure in materials made from fibers. Using the path integral technique the free energy of the system is calculated. It is shown that a first order phase transition takes place and that the behavior of the thermodynamic parameters in the ordered phase are in accordance with scaling laws. Experimental data for leather agree qualitatively with the theory.

PACS numbers: 83.80.Lz, 64.60.Cn, 64.70.Md, 81.40.Vw

A novel material has been developed by exerting high pressure and moderate temperature on natural leather. The resulting material is thermoplastic. For this new phase of leather the name *pleather* has been coined.

By using common plastic forming techniques it is possible to make complicated shapes from pleather. With specially prepared leather, pleather can be used as a promising medical implanation material. On the other hand, furniture and packaging material can be made from pleather, and thus could replace plastics or expensive leather. It is important to note that pleather is "ecologically friendly."

Some of the biochemical [1] and mechanical [2] properties of pleather, and scanning electron microscope (SEM) micrographs of the internal structure, have been published elsewhere [3].

In order to develop the properties of pleather in a rational way, and to design pleather with desirable properties, an understanding of the physical mechanism of the phase transitions in leather is essential. At first it was thought that there are two phases: leather and pleather. We now realize that there are three different phases: *leather, compressed leather,* and *pleather.*

In this Letter we will present a description of a theoretical model for the transition which takes place between *leather* and *compressed leather* under high pressure. Our approach is based on a combination of the theory of phase transitions in liquid crystals [4] with some ideas from the theory of polymers [5]. This combination allows us to describe the phase transitions between the leather and the compressed leather, and to calculate some important thermodynamic properties of the system near the phase transitions.

Leather is made up of about 90% macromolecules of collagen which combine in fiber bundles of about 5–10 μm diam. The fiber bundles are built with a hierarchic structure: *collagen molecules, microfibrils, fibrils, primitive fibers,* and *fiber bundles.* Here we deal only with fiber bundles which are called *fibers* for short, as basic units.

At low pressure the fibers intermingle in a disordered way (see Fig. 1), the volume fraction of fibers, c, is relatively small, and the fibers interact only at a relatively small number of points. When the pressure is increased the fiber 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 (which can be clearly seen in Fig. 1), there will be a tendency for the fibers to align themselves in parallel straight pieces, instead of the disordered crossings of fibers in natural leather. This means that between low and high pressures a phase transition from a disordered to an ordered state takes place.

If we designate a typical coefficient of elasticity per unit of length of fiber as γ, the persistence length (quasistraight pieces) l_p will be of order γ/T, where T is the temperature. The condition, that l_p is much longer than the diameter D of the fibers, can be expressed as $DT/\gamma \ll 1$. It can also be seen from the SEM micrographs [3] that the typical length of fiber L is much longer than l_p, so $LT/\gamma \gg 1$.

The energy of one fiber consists of its elastic energy and the energy of interaction with other fibers. It follows from experimental data [2,3] that an ordered phase appears for quite a large value of the fiber's volume fraction. In this case repulsive short-range forces between fibers are dominant. It is obvious also that the interaction

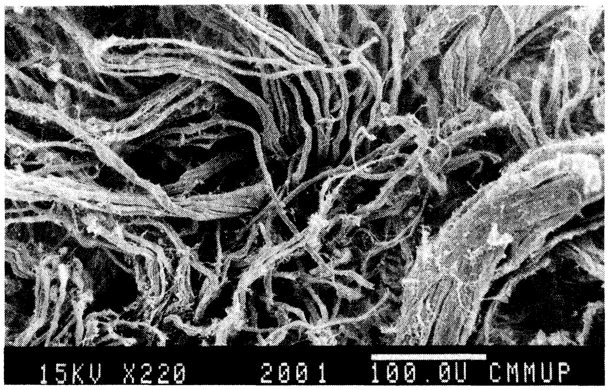

FIG. 1. SEM micrograph of the internal structure of leather.

0031-9007/95/74(15)/3073(4)$06.00

between two quasistraight pieces depends on the angle between them.

In the mean field approximation (MFA) the angular dependent part of the energy of interaction between one fiber and the others can then be represented in the form

$$\Delta U_i = \int_0^L dl\, U[\vec{s}_i(l)],$$

where

$$U(\vec{s}) = \frac{Tc}{D} \int_{\vec{n}^2=1} d\vec{n}\, S(\vec{n}) f(\vec{s};\vec{n}) . \tag{1}$$

Here $\vec{s}_i(l)$ is the unit tangent vector of the fiber (i) at a distance l from the beginning of the fiber, $S(\vec{n})$ is the average fraction of quasistraight pieces of the fibers that are directed in the direction $\vec{n}$, and $Tcf(\vec{s},\vec{n})/D$ is the angular dependent interaction between two pieces of fibers.

If we assume the simplest form for the elastic energy of the fibers (isotropic approximation), the part of the MFA energy of the system which depends on the local orientation of the fiber pieces will be

$$\Delta\mathscr{E}_{\mathrm{MFA}} = \frac{1}{2} \sum_i^N \int_0^L dl \left\{ \gamma \left(\frac{\partial \vec{s}_i}{\partial l} \right)^2 + U(\vec{s}_i(l)) \right\}, \tag{2}$$

where N is the total number of fibers.

The free energy of the system is

$$\mathcal{F} = \mathcal{F}_0 - T \ln Z , \tag{3}$$

where Z can be expressed as path integral over all the possible shapes of the fibers,

$$Z = \int \prod_i \mathcal{D}\{\vec{s}_i(l)\} \exp\left(-\frac{\Delta\mathscr{E}_{\mathrm{MFA}}}{T} \right), \tag{4}$$

and $\mathcal{F}_0$ is the part of free energy which does not depend on the elasticity and shapes of the fibers in the MFA.

In the usual way the path integral (4) may be written in the form

$$Z = \left(\sum_n \exp - E_n L \right)^N , \tag{5}$$

where E_n is the eigenvalue of the Schrödinger-like equation associated with this path integral,

$$\frac{\partial \psi}{\partial l} = \frac{T}{2\gamma} \nabla_{\vec{s}}^2 \psi - \frac{U(\vec{s})}{2T} \psi ; \tag{6}$$

here $\vec{s}$ is a unit vector and $\nabla_{\vec{s}}^2 = \partial^2/\partial\theta^2 + \tan^{-1}\theta\, \partial\theta + \sin^{-2}\theta\, \partial^2/\partial\varphi^2$ is the angular part of the Laplacian operator.

In the ordered phase the "depth of the potential well" $(U_{\max} - U_{\min})/2T$ is large compared to the "kinetic energy" $T/2\gamma$ because the phase transition to the ordered phase occurs for $c \sim 1$ [2] and

$$\max\left(\frac{\gamma}{T^2} U \right) \sim \frac{c\gamma}{DT} \sim c \frac{l_p}{D} \gg 1 ,$$

while $\min(U) \approx 0$. On the other hand, in a disordered phase $S(\vec{n}) \equiv 1/4\pi$ and $U(\vec{s}) = \mathrm{const}$. In both cases the energy spectrum will be discrete and the gap between the ground state and the first excited state will be about

$$E_1 - E_0 \sim T/\gamma .$$

As $LT/\gamma \sim L/l_p \gg 1$, the ground state is dominant, and we obtain for the free energy per unit volume

$$F = F_0 + \frac{Tc}{D^2} E_0 , \tag{7}$$

and, for $S(\vec{n})$,

$$S(\vec{n}) = |\psi_0(\vec{n})|^2 = \Psi^2(\vec{n}) . \tag{8}$$

E_0 can be obtained by using the variation principle from which we find that

$$F = F_0 + \frac{Tc}{2D^2} \int d\vec{s} \left[\frac{T}{\gamma} \left(\frac{\partial \Psi}{\partial \vec{s}} \right)^2 + \frac{c}{D} \int d\vec{n}\, \Psi^2(\vec{s}) f(\vec{s};\vec{n}) \Psi^2(\vec{n}) \right]; \tag{9}$$

this is a well known Ψ^4 field Hamiltonian.

The function $\Psi(\vec{s})$ must be found by minimizing F under the restriction

$$\int d\vec{s}\, \Psi^2 = 1 . \tag{10}$$

This can be done in many ways. Here we will use the simple approximation, which Onsager used in his treatment of liquid crystals [4]. In this approximation it is assumed that $\Psi(\vec{s})$ is a narrow peaked function in an ordered phase:

$$\Psi(\vec{s}) = \phi[\alpha(\vec{s} \cdot \vec{s}_0)] \qquad (\alpha \gg 1) , \tag{11}$$

where $\vec{s}_0$ is the direction of an average orientation of quasistraight pieces, while in a disordered phase $\Psi(\vec{s}) \equiv \sqrt{1/4\pi}$ (this means that in a disordered phase $\alpha = 0$) [6]. The parameter α is found by minimizing F.

The difference between the free energy in ordered and disordered phases is

$$\Delta F \simeq \frac{Tc^2}{2D^3} \left\{ g\left(\frac{TD}{\gamma c} \right) - 1 \right\}, \tag{12}$$

where the specific form of the function $g(x)$ depends on the behavior of $f(\vec{s},\vec{n})$ near $\vec{s} \approx \vec{n}$. If it is assumed that near $\vec{s} \approx \vec{n}$ the behavior of $f(\vec{s},\vec{n})$ is of the form

$$f \propto \rho[1 - (\vec{s} \cdot \vec{n})^2]^\nu \tag{13}$$

[ρ is a constant $O(1)$], then in the Onsager approximation one finds [7]

$$g(x) \approx (ax)^{\nu/(1+\nu)}, \tag{14}$$

with

$$a \approx (4\nu\rho)^{1/\nu}\left(k_1 + \frac{k_2}{\nu}\right)^{(1+\nu)/\nu}. \tag{15}$$

The numerical coefficients k_1 and k_2 are $O(1)$ and depend on the explicit form of the test function (11).

It is obvious from (12) that for fixed T and a specific value of the fiber fraction

$$c_* = T/T_*, \tag{16}$$

where

$$T_* = \gamma/aD,$$

the material undergoes a first order phase transition from the disordered to the ordered phase. The ordered phase is stable for $T < T_*$. This phase transition is from leather to the ordered state that we call compressed leather.

The order parameter S that describes the ordering in the orientation of the fibers can be defined as

$$S \approx \frac{1}{2}\left(3\int d\vec{n}\, S(\vec{n})\,(\vec{n}\cdot\vec{s}_0)^2 - 1\right). \tag{17}$$

In the ordered phase using (8) with $\Psi(\vec{n})$ from (11) one obtains

$$S \approx 1 - \frac{3}{\alpha} \approx 1 - 3(4\nu a)^{-1/(1+\nu)}\left(\frac{T}{T_* c}\right)^{1/(1+\nu)} \tag{18}$$

(in the disordered phase $S = 0$). The difference between thermodynamic parameters of the ordered and the disordered phases can be obtained as follows:

$$Q \sim \frac{T_*}{D^3}\frac{\nu}{1+\nu}\left(\frac{T}{T_*}\right)^3, \tag{19}$$

$$\Delta C \sim \frac{1}{D^3}\frac{\nu(1+2\nu)}{(1+\nu)^2}\left(\frac{T}{T_*}\right)^{\nu/(1+\nu)} c^{(2+\nu)/(1+\nu)}, \tag{20}$$

$$\Delta K_B \sim \frac{Tc^2}{D^3}\left[1 - \frac{2+\nu}{2(1+\nu)^2}\left(\frac{T}{T_* c}\right)^{\nu/(1+\nu)}\right], \tag{21}$$

where Q is the latent heat, C is the specific heat, K_B is the bulk modulus, and Δ indicates the difference between ordered and disordered phases. In general, the ordered phase consists of domains with different fiber orientation (see Fig. 2), but the energy of the domain boundaries gives a small contribution to ΔF.

It should be noted that for large volume fractions of the collagen fibers the form of their cross sections changes, and therefore so do the effective diameter and elasticity. Furthermore, the elasticity of the fiber bundles and coefficient ρ in the expression (12) depend on temperature, so that we must consider $T_* = T_*(T, c)$. If T is less than T_{d1} (T_{d1} is the lowest temperature of collagen denaturation: $T_{d1} \sim 350$ K) the inner structure of the fibers almost does not change and the dependence $T_* = T_*(T, c)$ is quite weak. In general, such dependence does not change the expressions for the free energy and order parameter, but additional terms appear in the other thermodynamic quantities. However, as most of the expressions contain T_* in a low power they are relatively insensitive to its variations. It is not anticipated that a change from the isotropic approximation for the elastic energy to a more realistic approximation would produce changes of any significance.

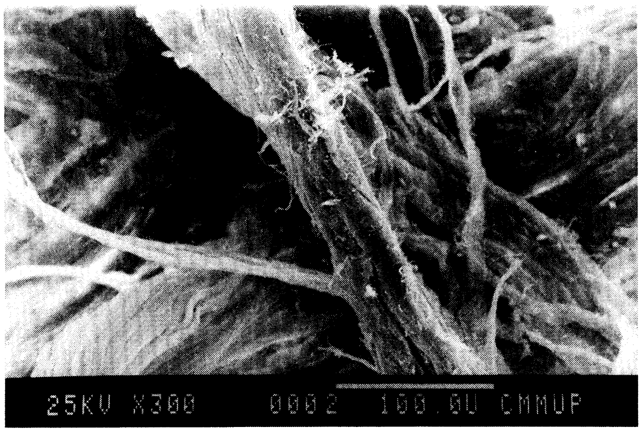

FIG. 2. SEM micrograph of compressed leather at room temperature. Pressure: 750 atm.

Consider now the compressed leather at some temperature T_0 and $c_0 > T_0/T_*$. If we increase the temperature for fixed $c = c_0$, then at a temperature above

$$T_{(c)} = cT_*$$

a first order phase transition from the ordered to the disordered phase takes place [see Eq. (12)]. For $T_{(c)} < T < T_{(d1)}$ this phase will be leather. A more complex situation appears for $T > T_{(d1)}$. In this case the partial denaturation (or "melting") of collagen takes place and for high enough temperature the dependence $\gamma(T, c)$ may be complex and, besides that, the nature of the contact between fibers may change [8]. For such temperatures the disordered phase will be pleather and the theoretical consideration for this phase transition must be essentially revised. (A detailed theory for pleather will be published in a forthcoming article.)

The MFA is the most important approximation in our theory but it is a reasonable one because, first, each quasistraight piece of a fiber interacts with a large number of neighbors [$n_{\text{neighb}} \sim c(l_p/D)^3(1-S) \sim c^{\nu/(1+\nu)}(l_p/D)^{(2+3\nu)/(1+\nu)} \gg 1$], and therefore fluctuations of the concentration of fibers are irrelevant; second, the phase transition is strong first order ($S \sim 1$) and so fluctuations of the order parameter are small.

The low pressure and high pressure phases can be seen in photographs in Fig. 1 and Fig. 2, respectively. In a qualitative way the transition from a disordered phase (leather) to an ordered phase (compressed leather) is clearly seen. At room temperature and ν between 10^{-1} and 1 (in the Onsager approximation $\nu = 0.5$ [4]) the critical volume fraction of fibers $c_* = aTD/\gamma \sim aD/l_p \sim 1$, which agree qualitatively with experimental data [2].

The above mentioned arguments show that this theory is able to give a reasonable description of the phase transitions in real leather under high pressure. However, our assumption that the persistence length of fiber is much bigger than the diameter, while the typical length of a fiber is much longer than the persistence length, and our concrete choice of the form of the angular dependent interaction between fibers are general enough to apply the theory to a whole class of compressed materials made from other biological or man-made fibers.

The theory gives us an explicit prediction for the behavior of the thermodynamic properties. For example, sensitivity of the transition to a uniaxial stress [8] and temperature and volume fraction dependence of the thermodynamic properties can be tested by experiment.

We would like to express our gratitude to Professor C. Domb for his interest in the work and for critically reading the manuscript, and to Professor P. G. De Gennes for some important remarks.

---

*Electronic address: SANDLER@MATH.JCT.AC.IL

†Electronic address: WYLER@HAGIGA.JCT.AC.IL

[1] B. de Castro, M. Ferreira, R. T. Markus, and A. Wyler, J. Macromolecular Sci. Pure Appl. Chem. (to be published).

[2] A. Wyler, R. T. Markus, H. J. Wagner, and B. de Castro, J. Mater. Res. **7**, 1990 (1992).

[3] A. Wyler, R. T. Markus, and B. de Castro, B. J. Soc. Leather Technol. Chem. **75**, 52 (1991).

[4] P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon Press, Oxford, 1974).

[5] P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell Univ. Press, Ithaca, London, 1979).

[6] Onsager used the function ϕ in the form $\phi(x) = A\cosh(\alpha x)$, but the final results are weakly sensitive to the concrete form of $\phi(x)$ [see Eq. (15)].

[7] The parameter α here is

$$\alpha = \begin{cases} \left(4\nu ac\,\frac{T_*}{T}\right)^{1/(1+\nu)} \gg 1 & \text{if } T < T_*c\,, \\ 0 & \text{if } T > T_*c\,, \end{cases}$$

which justifies the use of the approximation (11).

[8] P. G. de Gennes (private communication).

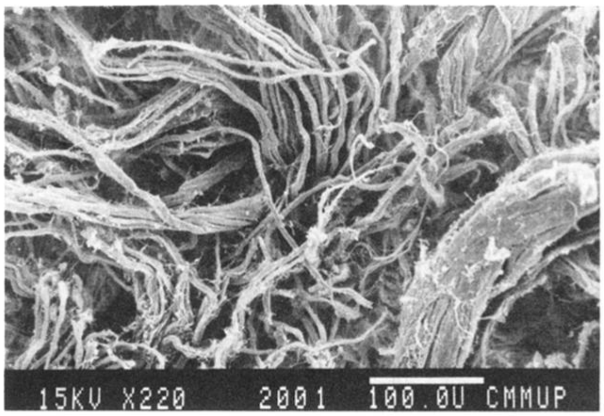

FIG. 1. SEM micrograph of the internal structure of leather.

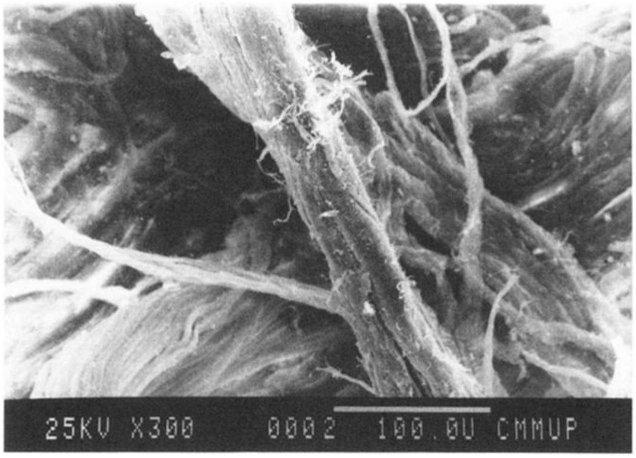

FIG. 2. SEM micrograph of compressed leather at room temperature. Pressure: 750 atm.