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Thermodynamics of the quasiequilibrial growth of crazes

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By comparing the morphology and physical properties (averaged over the scale of 1 to 10 μm) of a crazed and uncrazed polymer, it can be concluded that crazing is a new phase development in the initially homogeneous material. The present study is based on recent work on the general thermodynamic explanation of the development of a damaged layer of material. The treatment generalizes the model of a crack-cut in mechanics. The complete system of equations for the quasiequilibrial craze growth follows from the conditions of local and global phase equilibrium, mechanical equilibrium and a kinematic condition. Constitutive equations of craze growth-equations are proposed that are between the geometric characteristics of a craze and generalized forces. It is shown that these forces, conjugated with the geometric characteristics of a craze, can be expressed through the known path independent integrals (*J, L, M,*). The criterion of craze growth is developed from the condition of global phase equilibrium.

F	Helmholtz's free energy
G	Gibb's free energy (thermodynamic potential)
f	density of F
g	density of G
T	absolute temperature
S	density of entropy
ϵ	strain tensor
$\epsilon_{\alpha\beta}$	components of ϵ
σ	stress tensor
$\sigma_{\alpha\beta}$	components of σ
σ_y	stress along the boundary of an active zone (yield stress)
σ_b	stress along the boundary of an inert zone
σ_∞	applied stress
σ_∞^0	value of σ_∞ at the moment of craze initiation
K	stress intensity factor
C	tensor of elastic moduli
C^{-1}	tensor of compliance
$\epsilon : C : \epsilon \overset{\text{def}}{=} \epsilon_{\alpha\beta} C_{\alpha\beta\gamma\delta} \epsilon_{\gamma\delta}$	internal tensorial product
V	volume occupied by sample
V_1	volume occupied by original material
V_2	volume occupied by crazed material
∂V	boundary of V
$\delta_\alpha(\partial V)$	vector δ-function localized on ∂V
$\chi(x)$	characteristic function of an area
$\delta\chi(x)$	variation of $\chi(x)$
$\psi(x)$	a finite function
$\epsilon_{\alpha\beta\gamma}$	tensor of alternation
v_α	components of the boundary displacement vector
l_α	components of the vector of translation
n_α	components of the normal to a boundary
ω_k	components of the vector of rotation
$e_{(\alpha\beta)}$	symmetric tensor of deviatoric deformation of an active zone
λ	expansion of an active zone
$J_\alpha^{(i)}, L_k^{(i)}, M^{(i)}, N_{\alpha\beta}^{(i)}$	partial derivatives of $G^{(i)}$ with respect to l_α, ω_k, λ and $e_{(\alpha\beta)}$, respectively
$[\ ]$	jump of the parameter inside the brackets.
δ	thickness of a craze
$2l$	length of a craze
$2b$	length of an active zone
l_c	distance between the geometrical centres of the active zone and the craze
δ^*	craze thickness on the boundary of an active and the inert zone
l^*	craze parameter (length dimension)
A	craze parameter (dimensionless)
λ^*	extension of craze material

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1. Introduction

The phenomenon of crazing in glassy (and in some crystalline) polymers has been reported in many studies. A recent review can be found in a monograph by Kaush [1].

Crazing is studied on different scale levels. Multiple works on morphology show different mechanisms of craze origination and development up to the scale of about 100 Å. Development of a consistent statistical description of the phenomenon from the microscale to a macroscale is probably an unsolvable problem at the present time. The reasons for the difficulty are different interpretations of the observed phenomena, as well as the lack of technical means for studying the relations between stress and strain on submicron levels.

Nevertheless, it is possible to describe the macroscopic phenomenon of craze growth by using the idea of continuum and the general principles of thermodynamics, which are independent of micromechanisms of an observed phenomenon. It is worth mentioning that the laws of thermodynamics can be applied to rather large systems. In the case of crazing, there is a condition of statistical homogeneity of microheterogeneous craze structure that justifies the use of thermodynamic methods. Following the method of estimation of scale of statistical homogeneity [2], it was found that craze material can be considered homogeneous matter from the scales 1 to 10 μm. Characteristics of the real structure averaged over these scales serve as the thermodynamic parameters of that state.

Phenomenological approaches, which consider craze material as a homogeneous medium, have been developed in several papers [3–8]. The ideas of fracture mechanics have been used in these studies without analysis of the thermodynamic laws upon which mechanical models of the crack-cut are founded. However, other studies that deal with heat evolution during the growth of the crack with the craze ahead [9, 10] provide convincing evidence that craze growth cannot be regarded as a purely mechanical phenomenon. Moreover, the specific structure of polymer material and the specific change in morphology during craze formation should be reflected in a craze macromodel.

A craze in an amorphous polymer consists of an orientated polymer which differs from the initial isotropic material in structure and physical properties (e.g. the modulus of elasticity, the coefficients of thermal expansion, etc.) and is separated by a distinct boundary.

A part of a craze in polystyrene film is shown in Fig. 1, where the scale represents the craze material as a homogeneous continuum separated by a distinct boundary from the native material. By comparing the morphology and physical properties (averaged over the scales 1 to 10 μm) of the craze and the native material of a polymer, we can conclude that they are different phases of the material. Indeed, that part of a thermodynamic system that differs from other parts in its physical properties is by definition a new phase. In the present work, a thermodynamic model in which crazing is considered as a new phase development in the initially homogeneous material is proposed. Our study of phase growth under uniform extension of a specimen differs from conventional studies of the phenomena of phase transition. Craze growth is expected as a result of disturbance of global (and not local) equilibrium in the composite system. The growth of the new phase is specifically anisotropic in this case.

Thermodynamic investigation of new phase growth in an initially homogeneous material in relation to the problem of fracture in solids has already been conducted (Chudnovsky, *et al.*) [11, 12]. For the craze model, the results of that work are used, taking into consideration the features of craze material.

The growth of a craze in isothermic conditions will be considered. This assumption does not restrict the generality of the approach. In a quasi-equilibrium approach, different types of mechan-

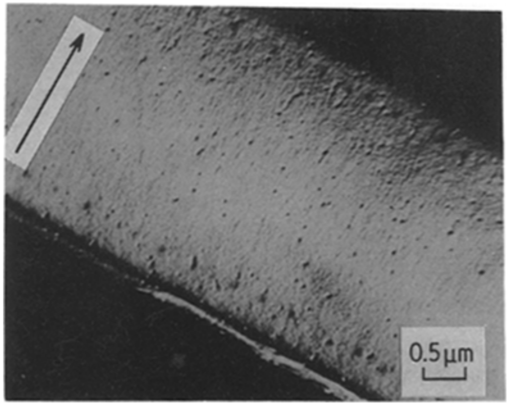

Figure 1 Micrograph of an area of a craze in a quenched PS film (2 μm thick). The craze is separated by a distinct boundary.

ical, heat (temperature), and phase (chemical) equilibria exist on the boundary which separates the two phases. The equation of phase equilibrium is the new element which is added to the existing mechanical models and the craze is considered as a new phase. Craze growth is a result of disturbance of phase equilibrium, not mechanical equilibrium.

When there is a disturbance of phase equilibrium, the difference in chemical potentials plays the role of a thermodynamic force that brings on the growth of a new phase. Such phenomena are characterized by special kinetic equations.

A new phase can result also from quasi-equilibrial growth. The phase equilibrium holds at any moment of time. The craze boundary displacement is controlled by bringing in or taking off the energy relevant to the hidden (latent) energy of the phase transition. In the present work, a model of quasi-equilibrial phase boundary movement is developed.

If heat is absorbed during phase transition, the energy condition is essential. If heat evolves during phase transition (this apparently takes place during development of a craze), the energy condition plays a secondary role. For an isothermal process, the condition is satisfied automatically. In this case, the equation for the evolution of the phase boundary follows directly from the condition of phase equilibrium.

Section 2 gives a short description of the general thermodynamic method of analysing a two-phase medium with a growing internal phase, and develops an equation of craze equilibrium in a thin film. Experimental data on craze morphology are used in the derivation of the equation. It is shown that the condition of constant stress along the active zone boundary (the part of the boundary where the phase transition takes place) follows from the condition of local phase equilibrium.

Section 3 develops a complete system of equations for the quasi-equilibrial craze growth. The length of the craze, the length of the active zone and the stresses along the inert zone (the part of the craze where there is no phase transition) are considered as the independent craze characteristics. The stress (or strain) along the specimen surface is the only external parameter controlling craze growth. The stress along the active zone boundary is a characteristic of the material. The complete system for these independent equations follows from the conditions of phase equilibrium, mechanical equilibrium and a kinematic condition. The analysis and the solution for the system are given in Section 4.

2. Equation of phase transition for a solid with a craze

The simplest model for the physical concept of craze growth described above is apparently, a two-phase perfectly elastic system (a craze-inclusion is an anisotropic elastic solid). The irreversibility of the whole process is due to the transformation of the native elastic material into the new anisotropic one, along a part of the craze boundary.

In accordance with the general principles of thermodynamics, we assume that a local equilibrium exists, so that the thermodynamic parameters of the state and the conventional relationships between these parameters hold at any point of continuum modelling the real body. As usual, the properties of a continuum point are determined as the average properties of a volume of the real material. The volume should be large enough to be comparable with the characteristic structural elements of the real material so that the thermodynamic limit will hold. On the other hand, the entire system should be small enough to be comparable with the dimensions of the specimen material in order to eliminate boundary effects. According to other studies [3–5], the morphology indicates that the characteristic size of the important structural elements (pores, craze nuclei and fibrils) is of the order of 200 to 500 Å. The structure becomes statistically uniform when the size of these elements is of the order of 10 μm. A rigorous definition of characteristic volume is given in [2].

Elastic stress tensor, σ, or elastic strain tensor, ϵ, and absolute temperature, T, can be assumed to be the parameters characterizing the elementary volume, $\{\sigma, T\}$ or $\{\epsilon, T\}$. According to the principle of local equilibrium, all the densities of thermodynamic state functions for an elastic medium are expressed by these parameters.

For simplicity, only the isothermic process will be considered. The densities of Helmholtz's free energy $f(\epsilon, T)$ and thermodynamic potential (Gibb's free energy) $g(\sigma, T)$ are expressed as follows:

$$f(\epsilon, T) = f_0(T) + \tfrac{1}{2}\epsilon : C : \epsilon \qquad (1)$$

$$g(\sigma, T) = f - \sigma : \epsilon = f_0(T) - \tfrac{1}{2}\sigma : C^{-1} : \sigma. \qquad (2)$$

Here the colon denotes the internal tensor multiplication operation (if $\sigma_{\alpha\beta}$ and $\epsilon_{\alpha\beta}$ are the matrices of tensor σ and ϵ components, then $\sigma : \epsilon \overset{\text{def}}{=} (\sigma_{\alpha\beta}\epsilon_{\alpha\beta})$,

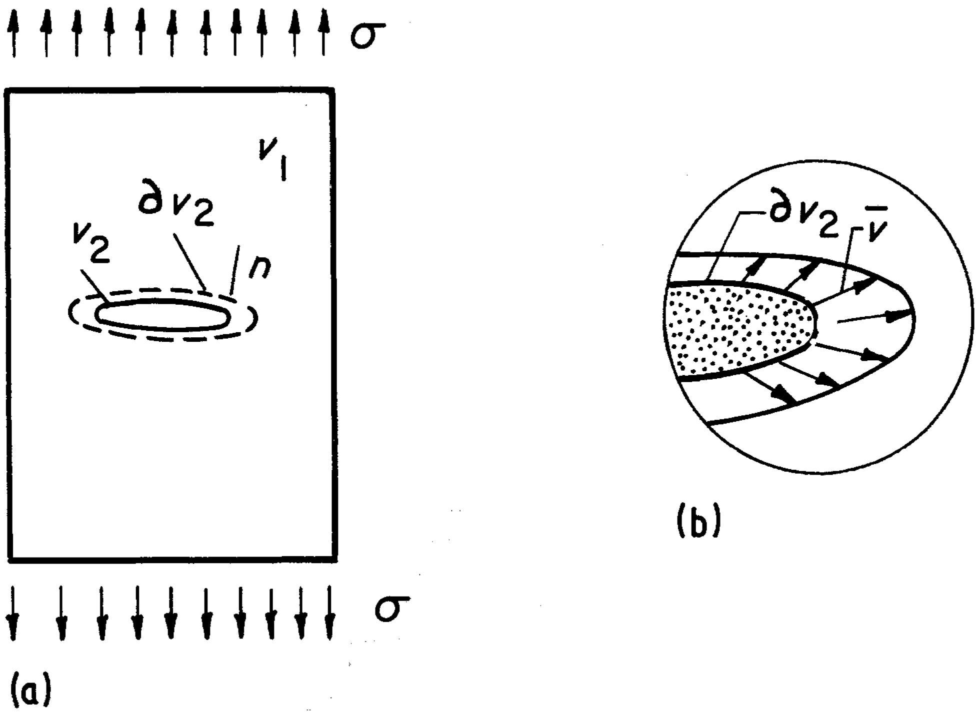

Figure 2 (a) Development of an inclusion of new phase in a plate under tension. (b) The rates of displacement along a part of the inclusion (craze).

C is the fourth rank tensor of the elastic moduli, and f_0 is the free energy density of the material in its natural state.

Normally, when there are no structural changes, f_0 is a constant and is not taken into consideration. However, this part of free energy becomes essential when structural changes are described.

The concept of global equilibrium implies that the time of phase transition along the phase boundary is negligible, so that the thermodynamic equilibrium of the two-phase system as a whole is fulfilled at any moment of time. Mathematically, thermodynamic equilibrium means the minimum of a thermodynamic potential, G, for the system as a whole, if external loads, P are given on the body surface, Σ, or the minimum of the Helmholtz free energy, F for the system as a whole if displacements, u are given on Σ. In mechanical experiments consideration was given mainly to these two cases.

Let V represent an area occupied by a solid body, V_1 represent the sub-area occupied by uncrazed material and V_2 represent the sub-area occupied by the new phase i.e. craze (see Fig. 2a). The characteristic function of craze area, χ, can also be introduced, such that

$$\chi(x) = \begin{cases} 1 \text{ if } x \in V_2 \\ 0 \text{ if } x \in V_1 \end{cases}, \tag{3}$$

and express F and G as follows

$$F = \int_v \{[1-\chi(x)]\,[f_{01}(T) + \tfrac{1}{2}\epsilon : C_1 : \epsilon] + \chi(x)[f_{02}(T) + \tfrac{1}{2}\epsilon : C_2 : \epsilon]\}\mathrm{d}V \tag{4}$$

$$G = \int_v \{[1-\chi(x)]\,[f_{01}(T) + \tfrac{1}{2}\sigma : C_1^{-1}\sigma] + \chi(x)[f_{02}(T) + \tfrac{1}{2}\sigma : C_2^{-1} : \sigma]\}\mathrm{d}V. \tag{5}$$

Here the subscripts 1 and 2 show the native and craze materials, respectively.

Usually, the equations of mechanical and thermal equilibrium follow from the principle of minimum F or G (depending on the problem). In this case, one more equation is necessary–the phase equilibrium equation:

$$\left.\frac{\delta F}{\delta \chi}\delta\chi\right|_{\substack{u = \text{constant} \\ T = \text{constant}}} = 0 \tag{6}$$

or

$$\left.\frac{\delta G}{\delta \chi}\delta\chi\right|_{\substack{P = \text{constant} \\ T = \text{constant}}} = 0. \tag{7}$$

Variation of the area (V_2) is naturally determined by a vector (v) of the displacement of the boundary (∂V_2) points. Therefore, a variation of the characteristic function χ can be expressed as

$$\delta\chi(x) = \mathrm{v}_\alpha \cdot \delta_\alpha(\partial V_2). \tag{8}$$

Here $\delta_\alpha(\partial V_2)$ is the vector δ-function localized on the boundary between V_1 and V_2 and is defined by the condition for any finite function ψ

$$\int_v \psi(x) \cdot \delta_\alpha(\partial V) \mathrm{d}V = \int_{\partial V} \psi(x) \cdot n_\alpha \, \mathrm{d}\Sigma. \tag{9}$$

Here n_α are the components of the vector of the external normal to ∂V, and $\mathrm{d}\Sigma$ is an element of the surface ∂V (an arch element for a two-dimensional problem). Variations of F and G are

$$\delta F = \int_v [(f_2 - f_1) v_\alpha \delta_\alpha(\partial V_2)] \, \mathrm{d}V \tag{10}$$

$$\delta G = \int_v [(g_2 - g_1) v_\alpha \delta_\alpha(\partial V_2)] \, \mathrm{d}V. \tag{11}$$

To make these expressions more concrete, we return to our observations of craze growth and emphasize the important evidence. Craze thickness remains small compared to the craze length for a reasonably well-developed craze. New native material transforms into craze material [16–19] along part of the boundary behind the craze tips. We will call this part of the craze an active zone. Therefore, the displacement vector, v (displacements are considered in the Lagrange coordinate system, "frozen" in the medium) differs from zero only along this part of the boundary. We account for transformation of the active zone of the craze growth as follows: isotropic extension and deformation, rotation with respect to the geometric centre, and shift of the position of geometric centre (centre translation). Then the displacement vector, v of point, ξ, of the active zone boundary presents itself as the linear combination of the displacements corresponding to the elements of transformation (Fig. 2b)

$$\begin{aligned} v_\alpha(\xi) = {} & v_\alpha(l_c) + \epsilon_{k\alpha\beta}\omega_k\xi_\beta + \lambda\xi_\alpha \\ & + e_{(\alpha\beta)}\xi_\beta + 0[(\xi)^2]. \end{aligned} \tag{12}$$

Here $\epsilon_{k\alpha\beta}$ is the alternating tensor; subscript $k \equiv 3$ corresponds to the out-of-plane axis (summation over the repeating subscripts is conventional); ξ is a radius vector of an arbitrary active zone boundary point in the coordinate system with the origin in l_c; $v_\alpha(l_c)$ are the components of the vector of translation of the centre of the active zone; ω_k is the rotation vector (the vector is normal to the plane of the film); λ is the expansion coefficient; $e_{(\alpha,\beta)}$ is the symmetrical tensor of second rank with the trace equal to zero and reflects the deformation of the active zone.

From Equations 10 and 11, taking into account Equations 9 and 12, we obtain

$$\begin{aligned} \delta F = {} & v_\alpha \int_\Sigma (f_2 - f_1) n_\alpha \mathrm{d}\Sigma + \epsilon_{k\alpha\beta}\omega_k \int_\Sigma (f_2 - f_1) \\ & \times \xi_\alpha n_\beta \mathrm{d}\Sigma + \lambda \int_\Sigma (f_2 - f_1)\xi_\alpha n_\alpha \mathrm{d}\Sigma \\ & + e_{\alpha\beta} \int_\Sigma (f_2 - f_1)\xi_\alpha n_\beta \mathrm{d}\Sigma \end{aligned} \tag{13}$$

$$\begin{aligned} \delta G = {} & v_\alpha \int_\Sigma (g_2 - g_1) n_\alpha \mathrm{d}\Sigma + \epsilon_{k\alpha\beta}\omega_\mathrm{k} \int_\Sigma (g_2 - g_1) \\ & \times \epsilon_\alpha n_\beta \mathrm{d}\Sigma + \lambda \int_\Sigma (g_2 - g_1)\xi_\alpha n_\alpha \mathrm{d}\Sigma \\ & + e_{\alpha\beta} \int_\Sigma (g_2 - g_1)\xi_\alpha n_\beta \mathrm{d}\Sigma. \end{aligned} \tag{14}$$

As it has been shown [12]

$$\begin{aligned} \int_\Sigma g_{(\mathrm{i})} n_\alpha \, \mathrm{d}\Sigma = {} & \int_\Sigma f_{(\mathrm{i})} n_\alpha \, \mathrm{d}\Sigma \\ & = \int_{\Gamma_{(\mathrm{i})}} (f_{(\mathrm{i})} n_\alpha - \sigma_{\gamma\beta} n_\beta u_{\gamma\beta}) \, \mathrm{d}\Gamma \equiv J_\alpha^{(\mathrm{i})} \end{aligned} \tag{15}$$

$$\begin{aligned} \epsilon_{k\alpha\beta} \int_\Sigma g_{(\mathrm{i})}\xi_\alpha n_\beta \, \mathrm{d}\Sigma = {} & \epsilon_{k\alpha\beta} \int_\Sigma f_{(\mathrm{i})}\xi_\alpha n_\beta \, \mathrm{d}\Sigma \\ = \epsilon_{k\alpha\beta} & \int_{\Gamma(\mathrm{i})} (\xi_\beta n_\alpha f_{(\mathrm{i})} - \sigma_\gamma \xi_\beta u_{\gamma,\alpha}) \, \mathrm{d}\Gamma \equiv L_k^{(\mathrm{i})} \end{aligned} \tag{16}$$

$$\begin{aligned} \int_\Sigma g_{(\mathrm{i})}\xi_\alpha n_\alpha \, \mathrm{d}\Sigma = {} & \int_\Sigma f_{(\mathrm{i})}\xi_\alpha n_\alpha \, \mathrm{d}\Sigma \\ = \int_{\Gamma_{(\mathrm{i})}} & (f_{(\mathrm{i})}\xi_\alpha n_\alpha - \xi_\alpha \sigma_{\beta\gamma} n_\gamma u_{\beta,\alpha}) \equiv M^{(\mathrm{i})} \end{aligned} \tag{17}$$

$$\begin{aligned} (1 - \delta_{\alpha\beta}) \int_\Sigma g_{(\mathrm{i})}\xi_\alpha n_\beta \, \mathrm{d}\Sigma = {} & (1 - \delta_{\alpha\beta}) \int_{\Gamma_{(\mathrm{i})}} f_\mathrm{i}\xi_\alpha n_\beta \, \mathrm{d}\Sigma \\ = (1 - \delta_{\alpha\beta}) \int_{\Gamma_{(\mathrm{i})}} & (f_{(\mathrm{i})}\xi_\alpha n_\beta - \xi_\alpha \sigma_{\delta\gamma} n_\gamma u_{\delta,\beta}) \equiv N_{\alpha\beta}^{(\mathrm{i})}. \end{aligned} \tag{18}$$

Subscripts (i) = 1,2 correspond to uncrazed and crazed material, respectively. Subscripts $\alpha,\beta,\gamma,\delta$ = 1,2.

The notations J, L, M correspond to accepted [20, 21] notation of known path independent integrals. The final form of Equations 10 and 11 is the same

$$\delta G = v_\alpha(l_c)(J_\alpha^{(1)} - J_\alpha^{(2)}) + \omega_3(L_3^{(1)} - L_3^{(2)}) + \lambda(M^{(1)} - M^{(2)}) + e_{\alpha\beta}(N_{\alpha\beta}^{(1)} - N_{\alpha\beta}^{(2)}) = 0. \tag{19}$$

The differences $(J^{(2)} - J^{(1)})$, $(L^{(2)} - L^{(1)})$, $(M^{(2)} - M^{(1)})$ and $(N^{(2)} - N^{(1)})$ play the role of generalized forces acting on heterogeneities in the elastic medium.

The generalized force $(N^{(2)} - N^{(1)})$ which corresponds to deformation, has in general no invariant presentation.

The equation of phase equilibrium is in addition to the equations of force and temperature equilibrium.

3. The equations of craze growth during simple extension of thin film

(a) It was concluded that the stresses are bounded and are constant along the phase transition boundary. This conclusion follows directly from the condition of local phase equilibrium at any points along the boundary

$$g_2(\sigma, T) = g_1(\sigma, T). \tag{20}$$

This equation gives the relationship between the stresses and the temperature of phase equilibrium. Imagine that we change the stress (σ) and the temperature (T), so that phase equilibrium holds. In other words, the increments of Gibb's potential density for phase equilibrium are

$$\mathrm{d}g_1 = \mathrm{d}g_2 \tag{21}$$

or

$$\frac{\partial g_2}{\partial \sigma}\mathrm{d}\sigma + \frac{\partial g_2}{\partial T}\mathrm{d}T = \frac{\partial g_1}{\partial T}\mathrm{d}\sigma + \frac{\partial g}{\partial T}\mathrm{d}T. \tag{22}$$

Note that

$$\frac{\partial g}{\partial \sigma} = -\epsilon \qquad \text{and} \qquad \frac{\partial g}{\partial T} = -S. \tag{23}$$

By substituting Equation 23 into Equation 22 and taking into account that the jump of deformation phase transition is expressed by the jump of the elastic moduli

$$\epsilon_{\alpha\beta}^{2} - \epsilon_{\alpha\beta}^{1} = [C_{\alpha\beta\gamma\delta}^{-1}\sigma_{\gamma\sigma}] \tag{24}$$

we obtain (ignoring the jump of the stress)

$$[C_{\alpha\beta\gamma\delta}^{-1}]\sigma_{\gamma\delta}\,\mathrm{d}\sigma_{\alpha\beta} = -(S_2 - S_1)\,\mathrm{d}T. \tag{25}$$

If we assume that the jump of the elastic moduli is constant, and the jump of the entropy does not depend on stress, then Equation 25 can be integrated as follows

$$\frac{1}{2}\sigma:[C^{-1}]:\sigma = c_0 - \int_0^T [S]\,\mathrm{d}T. \tag{26}$$

Here c_0 is the value of a quadratic form of the stress at $T = 0$.

This equation indicates the existance of a critical stress. This critical stress is a necessary but insufficient condition of phase transition. A condition of energy balance must be introduced for endothermal or exothermal phase transition.

The assumption that the entropy jump is independent of phase transition conditions has reasonable experimental foundation (Richardson rule, Trutton rule) [22]. The assumption that the jump of elastic moduli is independent of temperature is provisional. Equation 26 is also provisional. However, the conclusion that the critical stress of transition $\sigma = \sigma_y$ exists is justified. The stress σ_y is a constant for an isothermal process.

(b) Craze body (inert zone)–the whole craze area behind the active zone–is an anisotropic elastic material under stress $\sigma(x) < \sigma_y$. Spasmodic elongation of native material during the phase transition leads at a certain moment of craze evolution to unloading of a zone beyond the craze tip zone.

(c) The craze was considered as an inclusion of a new phase in the native elastic material (Fig. 2a). The stress field in a solid body with an inclusion is discussed elsewhere. Since for craze, δ/l is very small we make use of the asymptotic representation of stress field at $\delta/l \to 0$ to characterize the stress field in the native material. Asymptotic stress field in the crack vicinity has in general the singularity $1/\sqrt{r}$, where r is the distance from the crack tip. Conditions to obtain bounded stress are investigated in the Dugdale model [23]. The asymptotic stress field is expressed as $\sigma = (K/\sqrt{r})\phi(\theta)$, where ϕ is a function of a polar angle θ, and K is the stress intensity factor.

$$K = \int_{-l}^{l} p(x)\sqrt{\left(\frac{l+x}{l-x}\right)}\,\mathrm{d}x. \tag{27}$$

Here $p(x)$ is the distributed load along the boundary (Fig. 3), and the condition for stress to be bounded is

$$K = 0. \tag{28}$$

This equation gives one relationship for the follow-

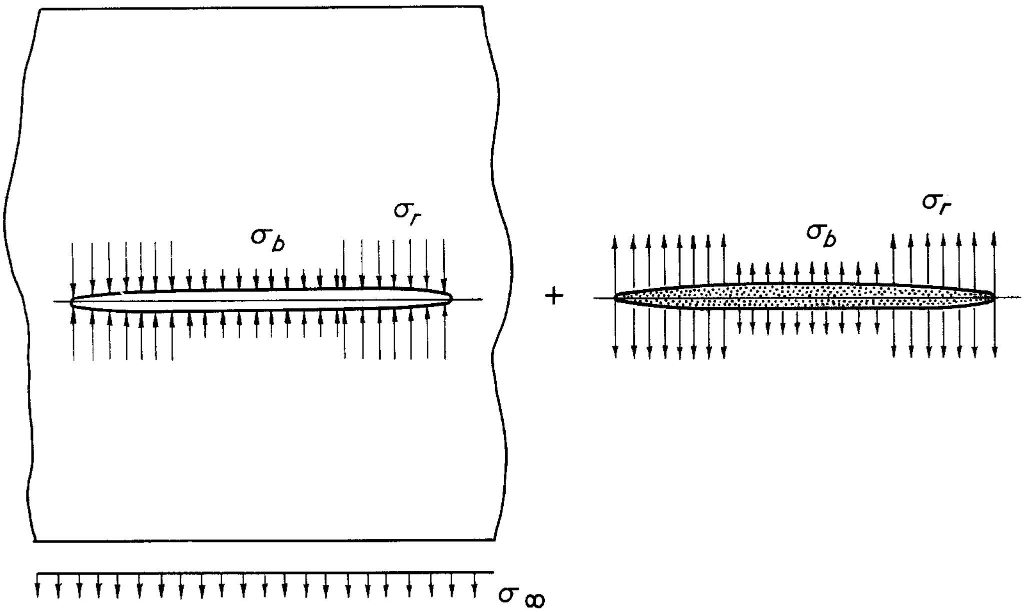

Figure 3 The stress along the craze boundary models the interaction between uncrazed and crazed materials.

ing variables: craze length $2l$; the length of the active zone $2b$; stress in the inert zone σ_b; σ_y and σ_∞. Since the last two variables are known, we obtain one equation bounding the three unknown functions l, b, and σ_b.

(d) In the asymptotic representation, craze is a line with a jump of elastic moduli localized on it and with two active zones behind the tips. We assume that craze growth consists of (a) translation of the centre (l_c) and (b) similar expansion (λ) of the active zones along the axis χ. This assumption implies that we should put $\omega = 0$, $e_{\alpha\beta} = 0$, $v_1 = \delta l_c$, $v_2 = 0$, and $\lambda = \delta b/b$ in the phase transition Equation 13 for the general case, as follows

$$\delta l_c(J_1^{(2)} - J_1^{(1)}) + \lambda(M^{(2)} - M^{(1)}) = 0 \quad (29)$$

(e) The third equation can be obtained in various ways. It can be the equation of continuity of displacement along the phase boundary. We cannot, however, obtain a reasonable equation of continuity in our model because only the first asymptotic of the elastic solution and representation of the craze as a cut has been implemented.

However, a kinematic condition that reflects the features of a growing craze can be used to formulate the missing equation. As has been shown earlier, the phase transition ceases on the boundary between the active and inert zones. The thickness of the layer that is transformed into the craze stays constant from this moment. The stresses along the active zone are determined by the condition of local phase equilibrium and are constant. Therefore, the transversal dimension of the craze on the boundary between the active and the inert zones is constant during the entire process.

The kinematic condition can be written as follows

$$\delta^*(l_c, b, \sigma_y, \sigma_b(x)) = \delta_0^* = \text{constant}. \quad (30)$$

Here $\sigma_b(x)$ is the stress acting along the boundary of the inert zone.

At this point, we make additional assumptions. Because the crazed material is highly oriented and loosely connected in the transversal direction, we assume that the stress exists only in the direction of loading. We assume also that the stress is the same along the boundary of the inert zone: $\sigma_b = \text{constant}$. This assumption looks reasonable, since the length of the inert zone is large compared with the thickness of the craze.

We are substituting the resisting action of the craze material for the forces distributed along the boundary (Fig. 3). The craze opening on the boundary of the active and inert zones can be represented as follows (see also Appendix 1, Equation A4)

$$\delta^* = \frac{8}{\pi} \frac{\sigma_y - \sigma_b}{E_1} (l_c - b) \ln\left(\frac{l_c + b}{l_c - b}\right). \quad (31)$$

Substituting Equation 31 into Equation 30 confines the system of equations for quasi-equilibrial craze growth.

4. Solution of the system of equations for quasi-equilibrial craze growth

Equations 28, 29 and 30 make up a complete system. They can be rewritten as in Appendices 1 and 2. (See Equations A3, A7 and A4 respectively).

Finally, we have

$$\begin{cases} \left(\dfrac{l_c - b}{l_c + b}\right) = \cos\dfrac{\pi}{2}\left(\dfrac{\sigma_\infty - \sigma_b}{\sigma_y - \sigma_b}\right) & (32) \\ (a_0 f_2 - \sigma_y \delta_0^*)\, \mathrm{d}l_c - [a_0 f_2 + \alpha)\sigma_y \delta_0^*]\ \mathrm{d}b = 0 & (33) \\ \dfrac{8(\sigma_y - \sigma_b)}{\pi E_1}(l_c - b)\ln\left(\dfrac{l_c + b}{l_c - b}\right) = \delta_0^*. & (34) \end{cases}$$

Let $l = l_c + b$ stand for one-half of the craze length. The system (Equations 32 to 34) characterizes the craze growth starting from the l_0 at which the inert zone appears. At this moment, we assume $\sigma_b = 0$.

The system has a simple solution (for $l \geqslant l_0$):

$$\frac{l}{l^*} = \frac{E}{\sigma_y - \sigma_\infty} \qquad (35)$$

$$\frac{2b}{l^*} = \left(\frac{1 - \cos A}{\sigma_y - \sigma_\infty}\right) \qquad (36)$$

$$\sigma_b = \frac{\pi}{2}\left(\frac{\sigma_\infty - \sigma_\infty^0}{\operatorname{arc\,sec} A}\right) \qquad (37)$$

where l^* is a certain characteristic length

$$l^* = \delta_0^*\left(\frac{\pi - 2\operatorname{arc\,sec} A}{8A \ln A}\right) \qquad (38)$$

The parameter A

$$A = \left(\frac{f_2}{\sigma_y \lambda_*} + \alpha\right) \Big/ (1 + \alpha) \qquad (39)$$

depends on (besides the σ_y) the density of free energy of the crazed material (f_2), the value of its extension $\lambda_* = \sigma_0^*/a_0$ and the shape of the active zone (coefficient α); σ_∞^0 is the value of external stress at the moment the inert zone appears.

The model considered above is essentially based on the asymptotic elastic solution for a plane with a cut. The asymptotic solution can be used for characterizing the growth of a developed craze if $\delta/l \ll 1$; therefore, the craze growth from its initiation until the moment of inert zone appearance is not discussed by this model. At that moment, however, in accordance with the experimental data, the ratio $\delta/l < 0.01$. This evidence justifies the model.

The proposed model of new phase growth also permits a model to be set up for the initial stages of craze growth. The transversal dimension of a craze should be taken into account in this case. However, the model of the unidimensional cut can still be used. For this purpose, not only the first asymptotic (with the singularity $1/r$ for the energy), but also the next (with the singularity $1/r^2$) should be taken into consideration.

The law of quasi-equilibrial craze growth makes possible the solution of problems on the effective elastic properties of a material with crazes. It can be shown that the nonlinear experimental stress–strain diagram is described by the effective elastic properties of a two-phase system. The same result can be obtained for a single craze in a strip. This problem differs only in some details from that considered above. The problem of the effective properties of a specimen with multiple crazes is somewhat more difficult; however, the difficulties are only mathematical.

We assume that the model of orientated phase transition developed above allows the plastic behaviour of polymer to be characterized in a wide range of conditions; in particular, in the case of shear bands and also in the case of time-dependent craze growth.

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Appendix 1

The stress state in a plane with the unidimensional inclusion under simple extension (Fig. 3) can be represented as a superposition of (1) the homogeneous stress state σ_∞ in the plane without the inclusion and (2) the stress state in the plane with the cut, substituting the inclusion. The boundary loads to be applied to the cut boundaries are

$$p(x) = \begin{cases} \sigma_y - \sigma_\infty & |x| > l_c - b \\ \sigma_\infty - \sigma_b & |x| < l_c - b. \end{cases} \qquad (A1)$$

Note that $(\sigma_y - \sigma_\infty) \equiv (\sigma_y - \sigma_b) - (\sigma_\infty - \sigma_b)$, and the problem on the stress state in the material outside the inclusion is reduced to Dugdale's problem [23] if we substitute σ_∞ for $(\sigma_\infty - \sigma_b)$ and σ_y for $(\sigma_y - \sigma_b)$.

The substitution of $p(x)$ Equation A1 into Equations 27 and 28 gives

$$\frac{1}{\sqrt{(\pi l)}}\int_{-l_c-b}^{l_c+b}(\sigma_\infty-\sigma_b)\sqrt{\left(\frac{1+\xi}{1-\xi}\right)}\,\mathrm{d}\xi$$

$$+\frac{1}{\sqrt{(\pi l)}}\int_{-l_c-b}^{-l_c+b}(\sigma_y-\sigma_b)\sqrt{\left(\frac{1+\xi}{1-\xi}\right)}\,\mathrm{d}\xi$$

$$+\frac{1}{\sqrt{(\pi l)}}\int_{l_c-b}^{l_c+b}(\sigma_y-\sigma_b)\sqrt{\left(\frac{1+\xi}{1-\xi}\right)}\,\mathrm{d}\xi = 0. \tag{A2}$$

By integrating Equation A2, the following relationship between l_c, b and σ_b is obtained

$$\left(\frac{l_c-b}{l_c+b}\right) = \mathrm{Cos}\,\frac{\pi}{2}\left(\frac{\sigma_\infty-\sigma_b}{\sigma_y-\sigma_b}\right). \tag{A3}$$

This conformation gives the craze opening displacement on the boundary of the active and inert zones directly from the Dugdale solution [23] as follows

$$\delta^* \equiv \delta|_{x=l_c-b} = \frac{8}{\pi E_1}(\sigma_y-\sigma_b)$$

$$\times\,(l_c-b)\ln\left(\frac{l_c+b}{l_c-b}\right). \tag{A4}$$

Appendix 2

To calculate the components of the thermodynamic forces $J_1^{(2)}, J_1^{(1)}, M^{(2)}$ and $M^{(1)}$ in Equation 29, we use the invariant representations [20] of J and M for the native and craze material.

The contour Γ_1 (Fig. 4) running just along the top and the bottom of the active zone was chosen and a circumference Γ_1' that goes around the tip (singularity) was picked out as a contour. The projection of n_1 of a normal n on the axis x_1 is equal to zero everywhere on Γ_1 except on Γ_1'. Normal stress on Γ_1 everywhere on Γ' is $\sigma_{\alpha\beta}n_\beta = \sigma_{22}+\sigma_{12}=\sigma_{22}=\sigma_y$, due to the boundary condition (the condition of local phase equilibrium).

The translation along x_1 was considered. Then

$$J_1^{(1)} = 2\int_{-b}^{b}\sigma_y\cdot\partial_{x_1}^{u_2}\,\mathrm{d}x + \int_{\Gamma'}(f_1 n_k - \sigma_{\alpha\beta}n_\beta u_{\alpha,k})\,\mathrm{d}\Gamma'. \tag{A5}$$

The second integral is calculated by using the stress and strain asymptotic and is well known

$$\int_{\Gamma'}(f_1 n_k - \sigma_{\alpha\beta}n_\beta u_{\alpha,k})\,\mathrm{d}\Gamma' = \frac{K_1^2}{2E_1} \tag{A6}$$

where K_1 is the stress intensity factor. The first integral is

$$2\int_{-b}^{b}\sigma_y\partial_{x_1}u_2\,\mathrm{d}x = 2\sigma_y\left[u_2(x)|_{x=b}-u_2(x)|_{x=-b}\right]$$

$$=\sigma_y\delta^* \tag{A7}$$

where δ^* is the craze opening displacement at the point of separation of the active and inert zones,

$$J_1^{(1)} = \sigma_y\delta^* + \frac{K_1^2}{E_1}. \tag{A8}$$

The first method described cannot be applied to the calculation of $J_1^{(2)}$ (the integral inside the area occupied by craze material) because the current field of displacements is not the displacement field of an elastic transformation, but a superposition of displacements due to phase transformation and the following elastic deformation. This is the reason we will pick out the contour Γ_2 that is parallel to the axis x_2 (Fig. 5) for $J_1^{(2)}$ calculation. A normal (n) to the contour Γ_2 has only one nonzero component n_1. The stress normal to this contour is $\sigma_n = \sigma_{\alpha\beta}n_\beta = 0$, since we have assumed (Section 2) that the stress tensor $\sigma_{\alpha\beta}$ for craze material has only one nonzero component σ_{22}. Thus

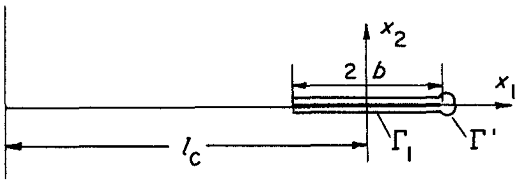

Figure 4 The contour for calculation of the invariant integrals in the external area V.

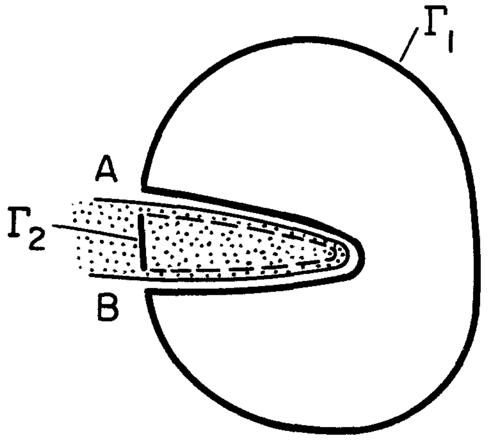

Figure 5 Contour for calculation of the invariant integrals in the internal area V_2.

$$J_1^{(2)} = \int_{\Gamma_2} (f_2 n_k - \sigma_{\alpha\beta} n_\beta u_{\alpha,\mathrm{k}})\, \mathrm{d}\Gamma_2 = \int_{\frac{a_0}{2}}^{\frac{a_0}{2}} f_2\, \mathrm{d}x_2 = a_0 f_2. \qquad \text{(A9)}$$

The thermodynamic force $(M^{(2)} - M^{(1)})$ corresponding to the transformation of similar expansion can be calculated in a similar manner

$$M^{(1)} = [f_1 x_1 n_1 - x_1 \sigma_{\alpha\beta} n_\beta u_{\alpha,1}]\, \mathrm{d}\Gamma$$

$$= 2\int_{-b}^{b} -x_1 \sigma_y \frac{\partial u_2}{\partial x_1}\, \mathrm{d}x_1$$

$$+\int_{\Gamma'} [f_1 x_1 n_1 - x_1 \sigma_{\alpha\beta} n_\beta u_{\alpha,1}]\, \mathrm{d}\Gamma' = \Big|_{x_1 = b}$$

$$= \sigma_y b \delta^* + 2\sigma_y \int_{-b}^{b} u_2\, \mathrm{d}x_1 + b\frac{K_1^2}{E_1}. \qquad \text{(A10)}$$

The last term is obtained by substituting the asymptotic stress and displacement fields in the integral along Γ' and Γ' tends to the point. The expression $2\int_{-b}^{b} u_2\, \mathrm{d}x_1$ is the area of the active zone and can be represented as $b\delta^*\alpha$ where α is a coefficient that depends on the shape of the active zone ($\alpha = \frac{1}{2}$ for a triangular shaped zone).

Finally,

$$M^{(1)} = (1+\alpha)\sigma_y b \delta^* + b\frac{K_1^2}{E_1}. \qquad \text{(A11)}$$

Calculation of the integral $M^{(2)}$ along the contour Γ_2 gives

$$M^{(2)} = f_2(-b)\,\mathrm{d}x^2 = \int_{\frac{a_0}{2}}^{\frac{a_0}{2}} f_2(-b)\, \mathrm{d}x_2 = -f_2 b a_0. \qquad \text{(A12)}$$

Therefore, Equation 29 can be represented as follows

$$\left(a_0 f_2 - \sigma_y \delta^* - \frac{K_1^2}{E_1}\right)\mathrm{d}l_c - \left(a_0 f_2 + (1+\alpha) \times \sigma_y \delta^* + \frac{K_1^2}{E_1}\right)\mathrm{d}b = 0. \qquad \text{(A13)}$$

References

1. H. H. KAUSH, "Polymer Fracture", (Springer-Verlag, Berlin, 1978).
2. A. CHUDNOVSKY and YU SHRAIBER, "Issledovanija po Uprugosti i Plastichnosti", Vol. 11, (Leningrad State University, 1976).
3. E. M. ANDREWS and L. BEVAN, "Physical Basis for Yield and Fracture", (Institute of Physics, London, 1966) p. 209.
4. G. P. MARSHALL, L. E. CULVER and J. G. WILLIAMS, *Proc. Roy. Soc.* A319 (1970) 165.
5. E. H. ANDREWS and L. BEVAN, *Polymer* **13** (1972) 337.
6. J. G. WILLIAMS and G. P. MARSHALL, *Proc. Roy. Soc.* A342 (1975) 55.
7. J. G. WILLIAMS, *J. Mater. Sci.* **12** (1977) 2525.
8. N. VERHEULPEN-HEYMANS and J. C. BAUWENS, *ibid.* **11** (1976) 7.
9. K. N. G. FULLER, P. G. FOX and J. E. FIELD, *Proc. Roy. Soc.* A34 (1975) 5347.
10. R. WEICHART and K. SCHONERT, *Mech. Phys. Solids* **26** (1978) 151.
11. A. CHUDNOVSKY, V. A. DUNAEFSKY and V. A. KHANDOGIN, *Archives of Mechanics,* **30** (1978 Warshawa) 165.
12. A. CHUDNOVSKY and V. A. KHANDOGIN, "Dynamics and Strength of Aircraft Constructions", (1978, Novosibirsk).
13. R. P. KAMBOUR, *J. Polymer Sci. D.* **7** (1973) 1.
14. B. RABINOWITZ and P. BEARDMORE, *CRC Crit. Rev.* **1** (1973) 1.
15. S. T. WELLINGHOFF and E. BAER, *J. Macromol. Sci. Phys.* **11** (1975) 367.
16. R. P. KAMBOUR and R. W. KOPP, *J. Polymer Sci.* **7** (1969) 183.
17. P. BEAHAN, M. BEVIS and D. HULL, *J. Mater. Sci.* **8** (1973) 162.
18. G. W. WEIDMANN and J. G. WILLIAMS, *Polymer* **16** (1975) 921.
19. J. S. TRENT, I. PALLEY and E. BAER, Technical report No. 9, (1979, CWRU).
20. J. K. KNOWLES and E. STERNBERG, *Arch. Rational Mech. Anal.* **44** (1972) 187.
21. B. BUDIANSKY and J. R. RIC, *J. Appl. Mech.* **40** (1973) 201.
22. SWALIN, "Thermodynamics of Solids", (J. Wiley, New York, 1972).
23. D. S. DUGDALE, *J. Mech. Phys. Solids* **8** (1960) 100.

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