# Crazing Studies of Polystyrene. II. Application of Fluctuation Theory

J. F. FELLERS and D. C. HUANG,* *Polymer Engineering, The University of Tennessee, Knoxville, Tennessee 37916*

## Synopsis

The present investigation deals with amorphous polystyrene crazing behavior at both the molecular and macroscopic levels. The nature of the amorphous state is considered from the perspective of statistical fluctuation theory, especially when a mechanical force field is acting on the polymer. Past crazing studies have rather fully described the phenomenological behavior. However, these studies did not generate a fundamental molecular explanation of crazing. We now suggest a molecular approach based on the density and density distribution of physical entanglements between polymer chains as a function of molecular weight. This approach permits the molecular entanglement concept and the phenomenological parameters such as stresses and temperatures associated with crazing to be related through the use of fluctuation theory. Two fundamental results are obtained and specifically demonstrated for polystyrene. First, an accurate theoretical prediction of the volume associated with microvoid formation is explicitly determined. Second, the dependence of the number of crazes on molecular weight is also shown.

## INTRODUCTION

The idea that a well-annealed, rigid amorphous polymer is a truly homogenous body capable of being treated solely with continuum concepts is discordant with known observations. Rigid amorphous polymers undergo crazing[1,2] and shear-banding[3] processes which are indeed manifestations of a nonuniform system subjected to one or more force fields. There is a fundamental question: at what size level does the system lose its homogeneous character?

Examination of the nature of the amorphous state of a polymer can be carried out in analogy to the treatment given to other systems displaying small fluctuations in their behavior. Outstandingly successful examples resulting from this treatment include the thermodynamic understanding of the polymer concentration dependence in light scattering,[4] transport of molecules by Brownian diffusion,[5,6] and the Maxwell velocity distribution of gas molecules.[7] To apply similar reasoning to amorphous polymers requires the simultaneous use of ideas of Newtonian mechanics and the physics of statistical fluctuation theory. Moreover, just as in the cases of the above-mentioned successful examples, such a treatment produces a greatly amplified understanding of the process when careful consideration is given to the molecular character of the system under observation.

The point of this paper is that when statistical fluctuation theory is applied to amorphous polymers, two fundamental expressions are obtained. The first one quantitatively relates the stress, temperature, and the volume associated with microvoid formation in the craze. The second one estimates the relation between the number of crazes generated and the molecular weight of the polymer.

* Present address: Chemplex Co., Rolling Meadows, Illinois 60008.

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Both developments are based on the physical entanglement of polymer chains, how entanglements are distributed, and how they depend on polymer molecular weight. To develop the above results, crazing is first briefly reviewed, followed by a model for amorphous entangled chains, and then the underlying ideas of statistical fluctuation theory are applied to give the above-mentioned results:

$$\omega_c = \left( \text{erf} \frac{\sigma_c}{[2kT_0(B/V)]^{1/2}} \right) = 1 \tag{1}$$

and

$$\omega_M = \frac{1}{2} \left[ 1 - \text{erf} \left( \frac{1 - 2M_e/\overline{M}_n}{\sqrt{2}\,(\overline{M}_w/\overline{M}_n - 1)} \right) \right] (\overline{N}_e^n)_M \tag{2}$$

The accuracy of these results is demonstrated by comparison to experimental results for polystyrene obtained in earlier studies by Fellers and Kee[8] and by LeGrand, Kambour, and Haaf.[9]

Symbols used throughout this paper are defined as follows:

$A$ = Helmholtz function
$B$ = bulk modulus
$C_1$ = probability normalizing constant
$k$ = Boltzmann constant
$M$ = molecular weight
$M_c$ = molecular weight between chemical crosslinks
$M_e$ = molecular weight between physical entanglements
$\overline{M}_n$ = number average molecular weight
$\overline{M}_w$ = weight-average molecular weight
$N_a$ = Avagadro's number
$\overline{N}_e$ = average number of physical entanglements per unit volume
$\overline{N}_e^n$ = average number of physical entanglements per unit volume counted only
     after the network is established
$p$ = pressure
$T$ = temperature
$T_0$ = equilibrium temperature
$U$ = internal energy
$V$ = volume
$V_0$ = equilibrium volume
$W$ = work
$\Delta^2$ = mean square value of the fluctuation around $\lambda$
$\lambda$ = arbitrary parameter used to characterize system fluctuations
$\rho$ = material density
$\sigma$ = stress
$\sigma_c$ = stress to initiate crazing
$\phi$ = distribution function
$\omega$ = probability
$\omega_c$ = crazing probability
$\omega_M$ = probability of crazing that depends on molecular weight

## CRAZING PHENOMENON

The extensive phenomenological information about crazing is roughly separated for the current purpose into two categories. Some observations speak more directly to craze initiation, others to a time later in the process such as craze propagation and an overall size. It will become clear that craze initiation is the more important category here.

Observations important to craze initiation include the fact that a minimum tensile stress component must be reached before crazing can start.[1,10] Furthermore, the magnitude of this stress depends on deformation rate[11-13] and temperature.[10,13] Another interesting observation is that above twice the entanglement molecular weight, the crazing stress is independent of molecular weight.[8] Below twice the entanglement molecular weight, crazes essentially do not form.[8,14] Another observation is that the number of crazes initiated increases as the molecular weight increases.[8,15] Lastly, a measurement of special significance to the arguments made here are the reports about the craze being a collection of spheroidal or irregularly shaped voids surrounded by polymeric material. The voids were reported for several polymers, including polystyrene, to be 80–100 Å in radius and correspond to a volume of about $2 \times 10^6$ Å$^3$.[9]

The view propounded here is that crazing traditionally has been characterized by macroscopic parameters such as temperature, strain rate, and stress; however, an additional set of molecular parameters should be used but have been largely overlooked. This view requires a molecular-level concept related to amorphous polymer behavior. The concept proposed here is that of physically entangled chains, the spatial distribution of entanglements, and how these depend on molecular weight.

It is vital to the concerns of this paper to explore the above concept in terms of a physical model for entanglements in an amorphous polymer. The considerations made here draw heavily on the reasoning used to discuss the chemical crosslink density[16] of elastomeric polymers. The analogy between $M_e$ and $M_c$ is of basic importance.

## PHYSICAL ENTANGLEMENTS IN A LINEAR AMORPHOUS POLYMER

All the reasoning used here is based on the physical reality of a chain entanglement. Figure 1 depicts several key features. The notions of interest include the molecular weight between entanglements, the part of the chain extending from the entanglement to a chain end, the number of chain entanglements per unit volume, and how this entanglement density varies with molecular weight and molecular weight distribution.

It is convenient to begin with the special case of infinite molecular weight. This simplifies the treatment in that the effects of chain ends and molecular weight distribution are eliminated. In this case the average entanglement density is given by

$$\overline{N}_e = \rho N_a / M_e \tag{3}$$

Now for finite molecular weight, the amount of chain between the chain end and an entanglement point lowers the entanglement density. Each chain end
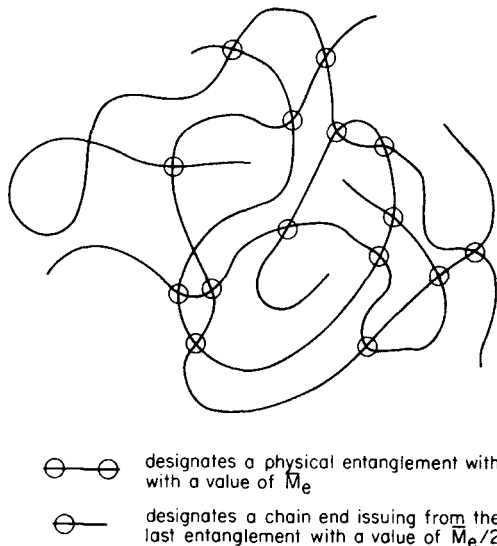
Fig. 1. Physical representation of a chain entangled network: physical entanglement with a value of $\overline{M}_e$ (⊖⊖); chain end issuing from the last entanglement with a value of $\overline{M}_e/2$ (⊖).

takes $M_e/2$ of a polymer chain and must be satisfied before an entanglement can form. Also, this must occur twice per chain for a linear polymer. Thus eq. (3) becomes

$$\overline{N}_e = \left(\frac{\rho N_a}{M_e}\right)\left(1 - \frac{M_e}{M}\right) \tag{4}$$

Now a consequence of some significance should be pointed out. Equation (4) gives the average number of entanglements per unit volume. This must be distinguished from the statistical network of entanglements, which is not established until $M = 2\,M_e$. Thus to count only those entanglements which enhance and tend to complete the basic network, we write

$$\overline{N}_e^n = \left(\frac{\rho N_a}{M_e}\right)\left(1 - \frac{2M_e}{M}\right) \tag{5}$$

Consideration can also be given to how molecular weight distribution effects the entanglement density. For this case

$$\overline{N}_e^n = \left(\frac{\rho N_a}{M_e}\right)\left(1 - \frac{2M_e}{M}\right)\phi\,dM \tag{6}$$

and

$$\int_0^\infty \phi\,dM = 1 \tag{7}$$

where $\phi$ is the distribution function. Now

$$\overline{M}_n = \left(\int_0^\infty \frac{1}{M}\phi\,dM\right)^{-1} \tag{8}$$

Thus

$$\overline{N}_e^n = \left(\frac{\rho N_a}{M_e}\right)\left(1 - \frac{2M_e}{\overline{M}_n}\right) \tag{9}$$

Figure 2 graphically depicts how $\overline{N}_e^n$ varies according to equation (9) when $M_e$ = 35,000 g/mol,[17] $\overline{M}w/\overline{M}n$ = 2, $N_a$ = 6.02 × 10²³ mol⁻¹, $\rho$ = 1.05 g/cm³,[18] and using a volume of 1.4 × 10⁶ Å³.

## A MACRO- TO MICRO-MODEL COMPARISON OF AMORPHOUS POLYMERS

The crazing microdeformation process speaks strongly to two notions. First, it sets a limit as to how completely the understanding of amorphous polymer deformation can be achieved solely from a continuum-based analysis. Second, it suggests a modified way of thinking about amorphous polymers. The generally used macroscopic material continuity view is still held here with the added modification that the total material volume be subdivided into a large number of contiguous microvolume elements (Fig. 3).

Such a model allows the material to still be treated with continuum concepts as long as the material response is consistent with the notion of whole-body homogeneity. When this criterion can no longer be met as is the case for crazing,
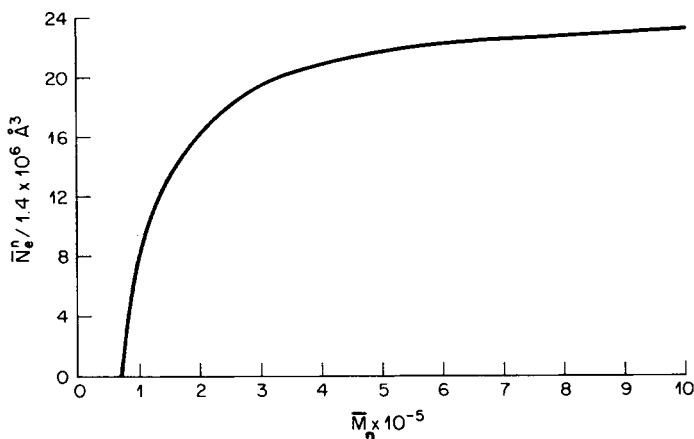
Fig. 2. Graphical presentation of eq. (9), the average number of entanglements in 1.4 × 10⁶ Å³ contributing to the perfection of network development as the molecular weight increases above $2M_e$ and $\overline{M}_w/\overline{M}_n$ = 2.
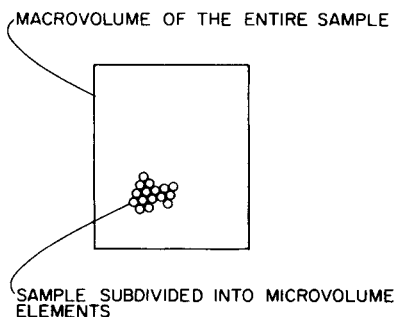
Fig. 3. Subdivision of macrovolume to microvolume elements, where the microvolume element is the volume necessary to guarantee the occurrence of a fluctuation that will lead to craze development.

this modified view allows the behavior to be analyzed on the basis of the characteristics of the microvolume elements. Furthermore, if these elements defy singular and uniform description, then statistical distribution representation may be used. This is especially pertinent when an imposed stress field can supply the energy to drive an entropy change within the microvolume element leading to a fluctuation of critical magnitude.

Two challenges confront the model proposed above. One of them is that it should be possible to relate the known physical parameters of amorphous polystyrene to the model. Two such parameters can be quickly dealt with. Since the craze microvoid volume is $2-4 \times 10^6$ Å$^3$ and it is the smallest dimensional entity uniquely associated with crazing, it can suggest the approximate volume of the elements in Figure 3. The other physical concept is the number of entanglements associated with this volume element. For polystyrene this is around 35 at a maximum. As this maximum would apply only to an infinite-molecular-weight polymer, any chain ends and packing imperfections would lower this number.

The second challenge the model faces is whether or not its validity is upheld and extended by existing fundamental theory. In the following section this is accomplished by the use of statistical fluctuation theory. This approach yields mathematical expressions which quantitatively relate the phenomenological parameters of crazing. Furthermore, the underlying significance of the molecular features of the amorphous state are clearly demonstrated and reconcile any previously held conflicting interpretation between continuum and statistical theories.

## FLUCTUATION THEORY APPLIED TO CRAZING

For the purpose of deriving a specific expression to describe crazing, equation (10) is assumed to be a general and valid probability expression for fluctuations occurring in a system depicted in figure 3. The foundation of this theoretical expression lies in the Boltzmann probability arguments and the Gaussian distribution function (a discussion of the general framework of this theory being available elsewhere[19]):

$$d\omega = C_1 \exp\left(-\frac{\Delta W(\lambda)}{kT_0}\right) d\lambda \qquad (10)$$

In the present case, $\Delta W(\lambda)$ is interpreted as the mechanical energy necessary to pay for an entropy fluctuation that opposes the direction expected on a spontaneous pathway.

One specific objective here is to express the work function $\Delta W(\lambda)$ for an amorphous polymer. One of the customary ways is to employ the internal energy function, so that

$$\Delta W(\lambda) = U(V) \, dV = dA + p \, dV_0 \qquad (11)$$

Since the fluctuation is now being considered around the equilibrium position of $V$, i.e., $V_0$, $\Delta U(V)$ can be expanded by a Taylor series around $V_0$:

$$\Delta U(V) = p \, dV + \left(\frac{\partial A}{\partial V}\right)_{V_0} (V - V_0) + \left(\frac{\partial^2 A}{\partial V^2}\right)_{V_0} \frac{(V - V_0)^2}{2} + \cdots \qquad (12)$$

The first two terms represent fluctuation about a symmetrical equilibrium position and cancel each other. Terms higher than second order are neglected, since they are small. Thus

$$\Delta W(\lambda) = U(V)\, dV = \left(\frac{\partial^2 A}{\partial V^2}\right)_{V_0} \frac{(V - V_0)^2}{2} \tag{13}$$

In this expression the term

$$\left(\frac{\partial^2 A}{\partial V^2}\right)_{V_0} = -\left(\frac{\partial p}{\partial V}\right)_{V_0} \tag{14}$$

Now the term $-(\partial p/\partial V)_{V_0}$ is of special interest in this case, where the application is to amorphous polymers. One sees that

$$\left(\frac{\partial p}{\partial V}\right)_{V_0} = -\frac{B}{V} \tag{15}$$

when it is realized that

$$\delta p = B \frac{\delta V}{V} \tag{16}$$

Here the mechanical concepts of modulus, stress, and strain are required, where $\delta p$ is the infinitesimal pressure or stress acting on a volume element, $\delta V/V$ is the infinitesimal strain of a volume element, and $B$ is the modulus of proportionality for the above stress-strain relationship.

Now the general form of the Boltzmann expression for probability involving fluctuations may also be written[19] as

$$d\omega = (2\pi\Delta^2)^{-1/2} \exp\left(-\frac{(\lambda - \lambda_0)^2}{2\Delta^2}\right) d\lambda \tag{17}$$

where $\Delta^2$ is the mean-square value of the fluctuation around $\lambda$ (in this case the volume $V$). Furthermore,

$$\Delta^2 = kT_0/U''(\lambda_0) \tag{18}$$

So in the present application,

$$\Delta^2 = \frac{kT_0}{U''(V)} = \frac{kT_0}{B/V} = \frac{kT_0 V}{B} \tag{19}$$

Substituting this for $\Delta^2$ in eq. (17) gives

$$d\omega = \left(\frac{2\pi kT_0 V}{B}\right)^{-1/2} \exp\left(-\frac{B(V - V_0)^2}{2kT_0 V}\right) dV \tag{20}$$

In the present application, concern with the mechanical situation is still the primary issue. Thus the notion of stress associated with volume fluctuation becomes important. From the $B$ and $V$ terms already introduced, one can write

$$d\sigma = B \frac{dV}{V} \tag{21}$$

or

$$\sigma = B \frac{\Delta V}{V} = \frac{B(V - V_0)}{V} \tag{22}$$

where $\sigma$ physically represents an energy density input to the system and drives the volume fluctuations.

The Boltzmann expression as given in eq. 20 can now be changed in form by making the substitution

$$dV = V\,d\sigma/B \tag{23}$$

so that

$$d\omega = \left(\frac{2\pi kT_0 V}{B}\right)^{-1/2} \exp\left(-\frac{B(V-V_0)^2}{2kT_0 V}\right)\frac{V\,d\sigma}{B} \tag{24}$$

and bringing the $V/B$ from the differential to the pre-exponental term gives

$$d\omega = \left(\frac{2\pi kT_0 B}{V}\right)^{-1/2} \exp\left(-\frac{B(V-V_0)^2}{2kT_0 V}\right)d\sigma \tag{25}$$

A substitution can also be made for the $(V - V_0)$ term on the basis of eq. (22) so that

$$(V-V_0)^2 = (V\sigma/B)^2 \tag{26}$$

and this gives for the case of crazing in a tensile stress field

$$d\omega_c = \left(\frac{2\pi kT_0 B}{V}\right)^{-1/2} \exp\left(-\frac{V\sigma^2}{2kT_0 B}\right)d\sigma \tag{27}$$

Integration over stress in such as way as to guarantee craze formation, that is, the probability equals 1, leads to

$$\omega_c = 1 = 2\int_0^{\sigma_c} \left(\frac{2\pi kT_0 B}{V}\right)^{-1/2} \exp\left(-\frac{V\sigma^2}{2kT_0 B}\right)d\sigma \tag{28}$$

$$\omega_c = 1 = \mathrm{erf}\left(\frac{\sigma_c}{(2kT_0 B/V)^{1/2}}\right) \tag{1}$$

Using standard mathematical tables for the error function yields

$$\frac{\sigma_c}{(2kT_0 B/V)^{1/2}} = 3.87 \tag{29}$$

All the above quantities except $V$ have been measured experimentally, so if one takes $\sigma_c = 3.1 \times 10^7$ N/m$^2$ (Ref. 8), $B = 2.8 \times 10^9$ N/m$^2$ (Ref. 20), $k = 1.38 \times 10^{-23}$ J/$^\circ K$, and $T_0 = 378^\circ K$ (i.e. the lowest temperature at which polystyrene could have been able to achieve equilibrium), we have, solving for $V$,

$$V = 4.5 \times 10^5 \text{ Å}^3$$

## THE MEANING OF V

The $V$ just calculated is the average size of the volume element which guarantees with a probability of 1 that a fluctuation associated with the crazing process will occur in it. *Note that its value lies under the $2 \times 10^6$ Å$^3$ experimentally reported for the volume of a microvoid in a crazed structure!*

This must mean that the stress acts in such a way as to open a void in this volume element. Furthermore, the void grows until it just gets beyond the dimensions of this element. Presumably, the large amount of strain (50–100%)

in the local craze region has resulted in a strain-hardened material that resists further expansion of the void.

There is yet one further possible application of fluctuation theory to the crazing process. This is developed in the next section.

## CRAZE FREQUENCY AND TEXTURE

A striking molecular-based feature of crazing observed only qualitatively so far was that the number of crazes formed in a given amount of polystyrene depended on its molecular weight.[8,15] As molecular weight increased, so did the number of crazes. Furthermore, these crazes changed from short, jagged ones at just above $2 M_e$ to rather long, fine-textured ones at higher molecular weights. This situation can also be treated with the principles of fluctuation theory to give further support and insight to the molecular model proposals given in the previous arguments.

Again by resorting to the model in Figure 3, a molecular view of craze initiation can be achieved. The microvoids that form in the crazing process can be imagined to start in a volume element containing no entanglements. It has been experimentally determined[9,21] that a craze is a series of microvoids surrounded by polymeric material. The molecular view used here is that while the origin of the microvoid is associated with a volume element containing no entanglements, crack growth does not occur from the microvoid because the immediately surrounding volume elements do contain entanglements. Hence the void development ceases in that region but occurs in other regions of similar character. Apparently, the regions most favorably disposed toward further microvoid formation are those positioned adjacent to an existing microvoid and projected normally to the applied stress direction. This would rationalize the fact that crazes always propagate perpendicularly to the tensile stress.

Since crazing of polystyrene essentially does not occur below $2 M_e$, it is reasonable to say that here cavitation is initiated with the growth of a hole to become a macrocrack. This is possible since no effective network of entanglements is present to impede microvoid to macrocrack development. In contradistinction then, crazing may be seen as a process of starting and stopping many holes.

To evaluate the situation of interest, it is necessary to determine the probability of finding a region in the amorphous polymer where a volume element with no entanglements exists but where the surrounding elements do contain entanglements, and they can be reasonably represented by the average entanglement density. Not only must this probability be evaluated, but it must be done for a system of specified molecular weight distribution. Furthermore, if this probability is to be applied to the case at hand, then it must be determined how this probability varies as the molecular weight of the sample increases.

This probability appears to be a product. Thus we seek a statement with the following form:

$\omega_M$ = probability of finding $V$ (no entanglements)

$$\text{surrounded by } xV \text{ (entanglements)} \quad (\overline{N_e^n})M$$

To get the form of the required statement, we imagine the $V$ (no entanglements) will be composed of polystyrene molecules with a molecular weight of less than $2 M_e$. Furthermore, we conceive of $xV$ (entanglements) to be the number of

nearest-neighbor volume elements containing a representative number of entanglements. These polystyrene molecules will eventually arrest the growth of the void and thus have their molecular weight above $2 M_e$. Schematically, we represent this in Figure 4, with $\overline{M}_w/\overline{M}_n = 2$ and where region I contains the polymer molecules incapable of significant entanglement network development. Region II then contains those polystyrene molecules which can and do develop an entanglement network that effectively stops the microvoid expansion.

To develop appropriate forms we begin with a statement of finding an element of no entanglements surrounded by entangled neighbors. Thus for a distributed molecular weight.

$$1 = \int_{-\infty}^{\infty} \phi \overline{M}_n \, dM \tag{30}$$

$$1 = \int_{-\infty}^{\infty} \frac{1}{\sqrt{2\pi} \, \Delta_m} \exp\left(-\frac{(M - \overline{M}_n)^2}{2\Delta_m^2}\right) dM \tag{31}$$

Now the extent to which a polystyrene sample has any of its molecular weight distribution overlap with the distribution function below $2 M_e$ can be expressed as

$$\text{Overlap} = \int_{-\infty}^{2M_e} \frac{1}{\sqrt{2\pi} \, \Delta_m} \exp\left(-\frac{(M - \overline{M}_n)^2}{2\Delta_m^2}\right) dM \tag{32}$$

$$= \int_{-\infty}^{(2M_e - \overline{M}_n)/2\Delta_m} \frac{1}{\sqrt{\pi}} \exp\left(-\frac{(M - \overline{M}_n)^2}{2\Delta_m^2}\right)\left(d \, \frac{M - \overline{M}_n}{\sqrt{2}\Delta_m}\right) \tag{33}$$

$$= \int_{(\overline{M}_n - 2M_e)/2\Delta_m}^{\infty} \frac{1}{\sqrt{\pi}} \exp\left(-\frac{(M - \overline{M}_n)^2}{2\Delta_m^2}\right)\left(d \, \frac{M - \overline{M}_n}{\sqrt{2}\Delta_m}\right) \tag{34}$$

$$= \frac{1}{2}\left(1 - \text{erf} \, \frac{\overline{M}_n - 2M_e}{\sqrt{2}\Delta_m}\right) \tag{35}$$

$$= \frac{1}{2}\left[1 - \text{erf}\left(\frac{1 - 2M_e/\overline{M}_n}{2(\overline{M}_w/\overline{M}_n - 1)}\right)\right] \tag{36}$$

The form of the overall probability expression we seek is then given by

$$\omega_M = \frac{1}{2}\left[1 - \text{erf}\left(\frac{1 - 2M_e/\overline{M}_n}{2(\overline{M}_w/\overline{M}_n - 1)}\right)\right] (N_e^n)_M \tag{2}$$
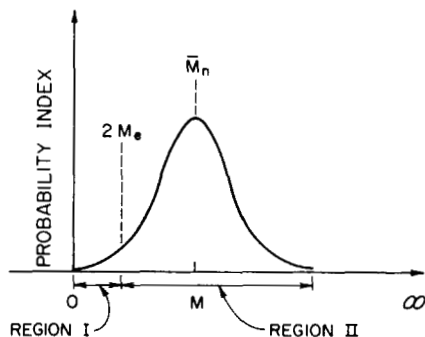


Fig. 4. Molecular weight distribution curve showing probabilities of finding whether a chain can participate in a network.

Figure 5 shows how this probability changes with molecular weight. In fact, the behavior is in accord with the qualitatively observed trend that the number of crazes increased between $\overline{M}_n$ of 70,000 and 150,000.[8] Also note that the theory predicts that for the higher molecular weights, the craze density should remain almost constant. This would be a further experimental point to investigate.

## CONCLUSIONS

The general concepts of the fluctuation theory was specifically applied to the crazing of amorphous polystyrene. In doing so, two equations of fundamental significance to crazing were derived. Equation (1),

$$\omega_c = \text{erf}\left(\frac{\sigma_c}{(2kT_0B/V)^{1/2}}\right) = 1$$

gives the volume necessary to ensure finding a site for microvoid formation to occur, cast in the energy-related parameters of stress and temperature, [eq. (2)],

$$\omega_M = \frac{1}{2}\left[1 - \text{erf}\left(\frac{1 - 2M_e/\overline{M}_n}{2(M_w/M_n - 1)}\right)\right](\overline{N}_e^n)_M$$

shows how the number of crazes formed per unit volume of the sample is controlled by the molecular weight. As is also the case for fluctuation theory applied to other phenomena, an enhanced understanding of crazing is gained by considering the molecular processes involved.

When the parameters of the above equations are combined with known molecular weight parameters, a model depicting the nature of the amorphous state is achieved. The model has statistical character and shows how variations of molecular weight and chain entanglements control the crazing phenomenon. If a network of entangled chains cannot be established, crazing essentially will not
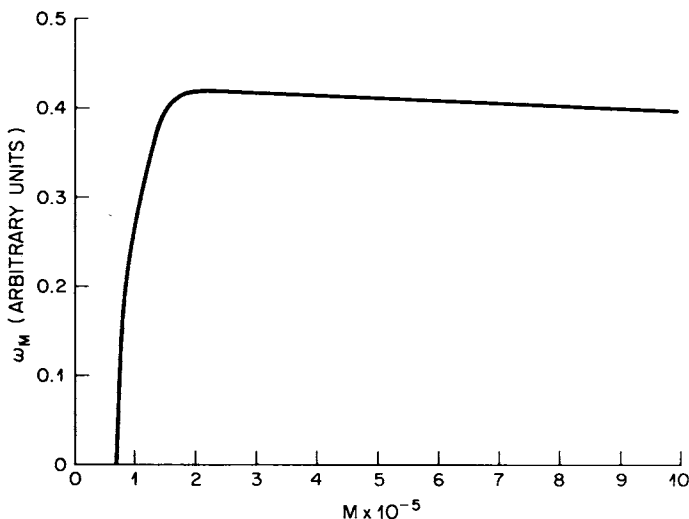


Fig. 5. Graphical presentation of eq. (2), the probability of craze formation as a function of molecular weight parameters.

occur. As a basic network is perfected by increasing the polymer molecular weight, crazing is actually promoted up to a limit.

There also is an interesting suggestion made by eq. (1). Since the crazing stress is a function of temperature,[10,13] a further view can be examined. It is known that $\sigma_c \to 0$ as $T_{\text{test}} \to T_g$. According to eq. (1), this is expected, since the volume element necessary to ensure finding a craze initiation site increases as the crazing stress decreases. Thus near the glass transition temperature crazes should not be observed, as indeed they are not. This suggests that the number of crazes formed per unit volume is then the inverse of the temperature at which stress is applied to form a craze. For those crazes that do form, however, the microvoid volume should increase as $\sigma_c$ decreases, as predicted by eq. (1). Thus a key experiment is to determine the number density of crazes formed at various stresses and to determine the associated microvoid volume. This key experiment would be another important step toward establishing the validity of both the applied theory and its associated model of the amorphous state. Indeed, in a related study of the crazing of rubber modified polystyrene just reported,[22] the results closely parallel the above predictions of this paper for homopolystyrene.

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