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A Proposed Approach to the Application of Nonlinear Irreversible Thermodynamics to Fracture in Composite Materials

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A PROPOSED APPROACH TO THE APPLICATION OF NONLINEAR IRREVERSIBLE THERMODYNAMICS TO FRACTURE IN COMPOSITE MATERIALS

by Paul H. Lindenmeyer

SUMMARY

We have shown that the fracture criteria upon which most fracture mechanics is based (i.e. some modification of Griffith crack theory) are not appropriate criteria for the fracture of viscoelastic materials such as polymer matrix composites. Griffith crack theory is an equilibrium thermodynamic theory based upon an energy balance in which time plays no role. A viscoelastic material is by definition time dependant and consequently requires a nonequilibrium theory based upon a power balance. We have proposed such a criterion based upon a reformulation of the second law of thermodynamics. We have defined two experimentally measureable functions, the uncompensated dissipation of energy, ξ, and its time rate of change, $\dot{\xi}$. Measurement of these functions does not require a knowledge of crack length or orientation and can account for strain hardening due to molecular orientation or dislocation pile-up as well as strain softening due to the formation and propagation of cracks. Our fracture criterion is a critical value of the change in excess energy, $\Delta\mathcal{E}$, given by the definite integral of ξ over time and volume. This critical value, $\Delta\mathcal{E}_c$, occurs when the first variation, $\delta\mathcal{E}$ equals zero and the second variation, $\delta^2\mathcal{E}$, is negative. Thus our failure criterion involves integration over both the time required to fracture and the volume involved in irreversible deformation. We have proposed methods for experimentally measuring and calculating these parameters. The integral of $\dot{\xi}$ over time and the thickness of the specimen may be shown to be equivalent to Rice's J integral if the only irreversible change involves the propagation of a single crack completely through the thickness. In a similar manner, it reduces to the Irwin strain energy release rate if the sample is assumed to be completely elastic.

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INTRODUCTION

This report represents the final summary of a nineteen month study on the application of nonlinear irreversible thermodynamics (NIT) to composite materials. The general objective of this study was to explore the application of some recently discovered thermodynamic principles (1) to the characterization and testing of composite materials. More specifically our immediate objective was to use these principles in an attempt to develop screening tests for the measurement of toughness in viscoelastic matrix materials for use in high modulus graphite fiber composites.

This project represents only a part of a program much larger in scope in which the principles of NIT are applied to a wide variety of measurements, accelerated aging and control of the effect of various environments on the properties of materials and systems of materials (see Appendix A). In brief this more general program involves a reformulation of the second law of thermodynamics in which the concept of entropy is replaced by the concept of excess energy. The principal advantage of this reformulation is that while entropy can only be calculated indirectly from static measurements made on systems presumed to be at equilibrium, excess energy can be directly obtained from dynamic measurements on systems that are not necessarily at equilibrium. In effect this reformulation has shifted the burden of accounting for the time evolution of thermodynamic systems from the increase in entropy of isolated systems - which can only be approximated in real life - to the change in excess energy of real systems that may be open or closed with respect to the exchange of energy and matter. Thus we suggest that "it is the minimization of the uncompensated dissipation energy of the system of interest - not the increase in entropy of the universe - that represents the practical embodiment of the second law." The uncompensated dissipation of energy is defined as the change in the internal energy minus the change in excess energy. The excess energy is in turn defined as the total Legendre transform of energy with respect to all extensive properties.

This reformulation of the second law has made possible an experimental approach to NIT using dynamic measurements and real time data processing that has only become feasible with the advent of microprocessor control of experimentation and computer processing of data in real time.

ASSESSMENT OF THE PROBLEM

Modern graphite fiber-organic matrix composites offer great potential for use in the aerospace industry since the strength to weight and modulus to weight ratios of these materials can substantially exceed those of the metals now in use. The design of reliable structures using such materials has not been able to make use of much of this potential as a consequence of the fact that the failure modes of composites are substantially different from the metals they might replace. In particular the impact failure and the compressive failure of composites occur by substantially different mechanisms than the corresponding failures in metals. Since these failure modes are not well understood, designers must rely on ultimate properties rather than modulus or fracture toughness in order to design reliable structures. This tends to wipe out much of the apparent advantage of composite materials.

Two approaches are available for improving this situation. First, one can attempt to chemically (or physically) modify the properties of both the fiber and the matrix to increase the ultimate strength and elongation without sacrificing the modulus. Alternately, one can attempt to measure the fracture toughness by modifications of conventional fracture mechanics techniques. It has been shown by I. Wolock and his colleagues [2] that such measurements, while possible, are quite complex and cannot be reduced to a single number probably due to the high anisotropy of local regions and the multiple cracking which frequently exists even in a macroscopically isotropic structure.

Clearly new measurement techniques are called for since even in the first approach one requires some measure of toughness to use in screening the various possible chemical and/or physical modifications that one might make. Since this contract was funded by a group having responsibility for the first approach, our primary effect was devoted to obtaining such a qualitative screening test. However, since fracture toughness has proven so successful in designing with some materials it is important that the relationship between any qualitative screening test and the conventional fracture toughness parameters be established as well as possible.

Two conditions were accepted by all concerned at the beginning of this project. First, it was agreed that any screening test must be made on a composite laminate

rather than the neat resin since there is considerable evidence both theoretical and experimental that the morphology and consequently the properties of the matrix might be substantially modified by the presence of a large fraction of high modulus fibers. The second condition was that any test must take into account the inherent viscoelastic nature of polymeric material. Thus the newly discovered principles of NIT (1) were a logical starting point.

FRACTURE CRITERIA

The fracture criteria used in fracture mechanics are all either modifications of Griffith crack theory or can be directly related to it. Thus these criteria are all dependant upon some sort of energy balance and are based upon an equilibrium thermodynamics in which time plays no role. The original Griffith theory was applied to brittle ceramic or glassy materials in which the energy required to propagate a crack was balanced by the energy required to create the new surfaces. Thus failure was presumed to occur whenever G, the strain energy release rate per unit crack length and thickness, equaled or exceeded twice the surface energy

$$(G - 2\gamma) \geq 0 \qquad (1)$$

The critical value, G_c, where the above expression equals zero would thus appear to be a material parameter which need be determined only once for each material. While this might be approximately the case for the very brittle materials which Griffith considered, application of these ideas to metallic systems soon showed that additional energy was required and that this additional requirement could be attributed to the energy necessary to plastically deform the material at the tip of the propagating crack. A number of ways have been suggested to theoretically derive or experimentally measure the critical strain energy release rate, G_c, or its conjugate parameter the stress concentration factor, K_c. We shall not discuss these methods which can be found in standard textbooks on fracture mechanics.(3) Rather we only point out that they all involve some assumption or experimental measurement of the length and orientation of the propagating crack. Furthermore, these methods all assume that the difference between plastic and elastic deformation is obvious and requires no definition. Thus, plastic deformation is permanent and irreversible, whereas elastic deformation is reversible and returns to its initial state when the stress is removed. The fracture toughness of a material as measured by G_c or K_c is

thus the total amount of irreversible work that may be done on the material before catastrophic failure occurs.

We shall retain this definition of toughness and its relationship to the usual parameters G_c and K_c and explore other means of measuring the amount of irreversible work that can be done on a material prior to catastrophic failure. In particular we need measurement techniques which are applicable to polymer matrix composites. Except in very unusual cases (e.g., delamination), the fracture of such composites does not occur by the propagation of a single crack in a given direction. Rather one observes multiple cracks in different directions over a volume of the material. Consequently, a parameter suitable for measuring the fracture toughness of a composite should involve an energy per unit volume rather than the energy per unit area.

We must emphasize two fundamental differences between polymeric composites and the metals they may hope to replace. These differences are critical in understanding fracture phenomena. The first of these is the fact that such composites exhibit a very high degree of local anisotropy. As far as crack propagation is concerned, this anisotropy is not removed by the symmetry of the lay-up. Thus, even the simplest unidirectional composite has tetragonal symmetry requiring six elastic constants for its complete description at the local or crack-tip level and typical composite lay-ups may require up to the full 81 constants of triclinic symmetry. The extreme complexity of such a situation serves to emphasize the difficulty and the approximate nature of any application of the traditional fracture mechanics parameters such as G_c or K_c.

The second and even more important difference is the fact that this multiplicity of elastic "constants" are not at all constant but are functions of both time and temperature, changing by as much as two to three orders of magnitude over the range of times and temperatures encountered in practice. For example, Figures 1 and 2 display the elastic and the loss moduli of a typical composite laminate deformed in a bending mode. These measurements were made by the Dynastat Viscoelastometer operating in the very low amplitude region (~25 microns) where linear viscoelastity clearly applies. These figures are by the courtesy of Professor S. Sternstein. Thus, polymer composites are clearly viscoelastic and any reasonable fracture criterion must

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involve the time over which fracture occurs as well as the volume over which the specimen undergoes irreversible deformation.

NONEQUILIBRIUM FRACTURE CRITERIA

The idea of applying a nonequilibrium thermodynamics to fracture criteria is not new since it is obvious that fracture is a nonequilibrium process. Rice[4] has proposed that the Griffith fracture criterion, equation (1), should be modified by multiplying by the velocity of crack propagation.

$$(G - 2\gamma)\frac{da}{dt} \geq 0 \tag{2}$$

He bases his further development upon crack propagation via a "quasi-static" mechanism which makes his approach compatible with both of the two principle schools of thought on nonequilibrium thermodynamics.[5] However, this restricts his reasoning to the region very close to equilibrium where one can only apply linear nonequilibrium thermodynamics and it is quite generally agreed that instability phenomena such as fracture require nonlinear conditions.

We have proposed a novel approach to a nonlinear irreversible thermodynamics (see Appendix A) which introduces the excess energy functional, $\mathcal{E}$,

$$\mathcal{E} = \iint \dot{\xi}\, dV dt \tag{3}$$

where $\dot{\xi}$ represents the Eulerian time derivative of the specific Lagrangian (i.e. the difference between the kinetic and the potential energy per unit volume and unit time).

We now suggest that fracture occurs when this excess energy changes by some critical amount. This critical value occurs when the change in excess energy over a definite volume and a definite interval of time reaches a positive maximum. According to the calculus of variations, such a maximum will occur when the first variation of the excess energy, $\delta\mathcal{E}$, vanishes and its second variation, $\delta^2\mathcal{E}$, is negative-definite for all possible changes in the nature of the extremizing function ξ.

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Before showing how one can experimentally measure this extremizing function and its time derivative, we first show that the excess energy functional can be reduced to the Rice J-intergral under special conditions.

The change in excess energy is a functional dependant upon time, t, measured in units of the observers time scale and the position vector, r, measured over a volume determined by the observers distance scales (see Appendix A) so that equation (3) becomes

$$\mathcal{E} = \iint \dot{\xi}\, dV dt = \iint \left(\frac{\partial \xi}{\partial t} + \nabla \xi \frac{dr}{dt} \right) dV dt \tag{4}$$

But ξ has been defined (see Appendix A) as follows:

$$\xi(r,t) = \hat{X}(t) - \bar{X}(r) \tag{5}$$

so that,

$$\begin{aligned} \mathcal{E} &= \iint \left[\frac{d\hat{X}}{dt} - \nabla \bar{X} \cdot \frac{dr}{dt} \right] dV dt \\ &= \int \left[\int \frac{d\hat{X}}{dt} dV - \int \nabla \bar{X} \cdot \frac{dr}{dt} dV \right] dt \end{aligned} \tag{6}$$

Now by Green's theorem we can convert the second integral from a volume to a surface integral so that

$$\mathcal{E}(r,t) = \int_t \left[\int_V \frac{d\hat{X}}{dt} dV - \int_A n\bar{X} \cdot \frac{dr}{dt} dA \right] dt \tag{7}$$

where n is the vector normal to a simple convex surface, A, surrounding the volume, V.

We now assume the special case where the system is elastic-plastic rather than viscoelastic. That is to say, we assume that the time scale of the observer is such that creep and stress relaxation are negligible small. We then remove the time dependency and write the volume as a triple integral over the cartesian coordinates, x, y, z.

$$\mathcal{E}(x,y,z) = \iiint \hat{X}\, dx\,dy\,dz - \int n\bar{X} \cdot dr\, dA \qquad (8)$$

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If the only contribution to the excess energy is a single crack of length, a, in the x direction extending through a plate of constant thickness, b, in the z direction, we can carry out the integration over y and z, divide by b and differentiate with respect to a. The result is an expression for the excess energy change as a surface energy change per crack length and per unit thickness

$$\begin{aligned} \mathcal{E}(a) &= \int \hat{X}\, dy - \int_s n\bar{X} \cdot \frac{\partial r}{\partial a}\, ds \\ &= \int_\Gamma \hat{X}\, dy - n\bar{X} \cdot \frac{\partial u}{\partial a}\, ds \end{aligned} \qquad (9)$$

where integration is now over an arbitrary curve Γ in the x, y plane surrounding the crack tip and dr, becomes du, the displacement normal to the curve. If we now identify $\hat{X}$ with the strain energy function, W and $n\bar{X}$ with the traction vector, T, our excess energy per unit surface with a crack of length, a, becomes

$$\mathcal{E}(a) = \int_\Gamma W\, dy - T \cdot \frac{\partial u}{\partial a}\, ds \equiv J \qquad (10)$$

which we recognize as the Rice J-integral. It is well known (3) that if the additional assumption of linear elastic behavior is made, the J-integral becomes equivalent to the Irwin strain energy release rate, G.

Thus we have shown that our excess energy functional is a more general formulation, applicable to viscoelastic materials with multiple cracks, that reduces to J for elastic-plastic materials with a single crack and to G for linearly elastic materials. The fracture criterion, $\Delta\mathcal{E}_c$, is the maximum value of the excess energy functional and represents the total amount of irreversible work which can be done on a system with a definite volume over a definite period of time. It covers any irreversible process including strain hardening caused by molecular orientation or dislocation pile-up as well as the usual strain softening due to the formation and propagation of cracks.

INSTABILITY CRITERIA

The fracture criterion suggested in the previous section is a more general measure of fracture toughness that includes the usual fracture toughness parameters as special cases. Fracture is in turn a special case of a thermodynamic system driven to the point of instability by the flow of energy and/or matter to or from its environment. By considering the more general thermodynamic instability criteria we can include all environment influence on the system of interest, not just the mechanical field.

The thermodynamic instability criteria proposed by Glansdorff and Prigogine[6] are expressed in terms of the second variation of entropy $\delta^2 S$ and its time rate of change. These criteria have been criticized by several authors[5,7,8] primarily because the first variation of entropy represents a force holding the system from equilibrium and consequently cannot vanish. We do not wish to take either side in this polemic. Instead we have reformulated the second law of thermodynamics by taking the total Legendre transform. A Legendre transform may be understood as the transformation that changes a function from a set of moving coordinates to a set of fixed coordinates or vise versa. In our case, it changes the independant variables from the extensive properties (i.e., moving or Lagrangian coordinates) to the intensive properties (fixed or Eulerian coordinates). The total Legendre transform of energy is called an excess energy and vanishes at equilibrium.

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By taking the total Legendre transform we have shifted the burden of accounting for the time evolution of thermodynamic systems from an increase in the entropy of an isolated system - that can only be approximated in real life - to the change in the excess energy of real systems which may be either open or closed. Since energy is a conservative quantity, it is easier to think of it as moving from one point in space to another, as well as increasing and decreasing in various parts of the system. Thus, we have avoided the use of the concept of entropy production and entropy flow. Entropy will only be considered as a property of the total system of interest when it has reached a state of equilibrium where it can be rigorously defined. If the system is not at equilibrium, any entropy associated with it will be considered as a virtual entropy. That is to say, the virtual entropy of a nonequilibrium system at any instant of time will be the entropy that the system would have if it were isolated at that instant of time and allowed sufficient time (infinite if necessary) to come to equilibrium. In order to deal with such a virtual entropy we need to define its conjugate variable (i.e., temperature) as the instantaneous space average temperature $\hat{T}$ (read T hat). Actually, we need to define a space average for all intensive quantities that are environmental variables (see Appendix A).

However, by far the most important consequence of this reformulation is experimental rather than theoretical. Entropy can only be calculated indirectly from static measurements made on the surface of systems that are at equilibrium. With the help of modern microprocessor technology and the computer analysis of data, we can not only directly measure the change in excess energy, $\Delta\mathcal{E}$, but we can experimentally obtain an approximation to its variation, $\delta\mathcal{E}$, by dynamically fluctuating one or more intensive properties and measuring the response of the systems extensive properties. Thus we have the means to convert irreversible thermodynamics from an esoteric theoretical science to an experimental science that offers many practical possibilities.

THE EXTREMIZING FUNCTION,

Recall our definition of fracture toughness as the total amount of irreversible work that can be done on a material by a given mode of deformation prior to failure. If this deformation is applied by means of a dynamic force, each complete cycle will carry the material through a thermodynamic cycle back to the same apparent state. Any irreversible work done upon the material will manifest itself as a change in the

internal energy of the system. We propose to measure this change in internal energy by measuring the response (i.e. displacement) of the system to the dynamic force and separating the work (i.e. force times displacement) into an in-phase and an out-of-phase portion. The in-phase or conservative portion is the reversible work and the out-of-phase portion is the dissipative or irreversible work. This separation is arbitrarily dependant upon the time scale of the observer as determined by the frequency of the dynamic force.

During the first half of such a cycle the environment does work on the material, energy flows from the environment to the system. Some of this energy (i.e., elastic strain energy) is stored by the system. But since energy has flowed, some part of it must also have to be dissipated in the form of heat which flows back to the environment. During the second half of the cycle, the elastic strain energy stored in the system during the first half cycle flows back to the environment as the system does work on the environment. But this flow of energy also dissipates energy in the form of heat that flows back to the environment. At the end of a complete cycle, the net amount of work done on the system by the environment may be equal to, greater than, or less than the amount necessary to compensate for the dissipation of energy. If it is exactly equal, the system may be said to have been driven through a reversible thermodynamic cycle by the environment. All the energy dissipated during the cycle has been compensated by work done on the system by the environment and the system is unchanged by the fact that it has been driven through a reversible cycle. There is no uncompensated dissipation of energy.

On the other hand if the work done on the system is either greater or less than the amount of energy dissipated, the internal energy of the system is changed. If the work done is less than the energy dissipated, the internal energy is decreased, and we have, for example, the release of frozen strains. If the work done is greater than the energy dissipated, the internal energy is increased, and we have, for example, strain softening or the creation and propagation of cracks.

MEASUREMENT OF THE EXTREMIZING FUNCTION

The extremizing function, ξ , is important theoretically since it provides a specifically defined function of time and space that can be differentiated with respect

to both time and location within the system subject to the time and distance scales of the observer (see Appendix A). However, its most significant property is the fact that both it and its derivative with respect to time can be experimentally measured using dynamic techniques. A general description of this procedure is as follows:

(1) Drive the load in a sinuscidial manner with controlled amplitude and frequency.

(2) Measure the displacement of the system in response to this load.

(3) Calculate the in-phase or conservative power (load times displacement per unit time) and integrate over a complete cycle.

(4) Calculate the out-of-phase or dissipative power (displacement times load per unit time) and integrate over a complete cycle.

(5) Add the change in the conservative energy per cycle to the change in the dissipative energy per cycle. The result is an experimental measurement of the extremizing function, ξ (i.e., the uncompensated dissipation of energy) for the particular time and distances scales as well as the level of dynamic power used. As long as the amplitude of the fluctuating load is small enough for the linear approximation to be valid within experimental measurement precision, the result will be zero.

(6) If there is no measurable value for the extremizing function, it will be necessary to increase the amplitude until a finite or measurable value is obtained. The minimum power level at which a measurable value for the extremizing function may be obtained is the onset of measurable irreversibility (see next section). The change in the measured value of extremizing function from one cycle to the next is a measure of the time derivative of the extremizing function, (i.e., $\dot{\xi}$).

It may be desirable to carry out the integrations in steps (3) and (4) over successive half cycles and calculate their sum over half cycles as well as full cycles. This information is useful in determining the onset of asymmetry, to be discussed in a latter section.

THE ONSET OF IRREVERSIBILITY

When the amplitude of our dynamic fluctuation is small enough so that the displacement can be approximated as a linear function of the load, the conservative energy change in the first half cycle will be equal and of opposite sign to the conservative energy change in the second half cycle so that the conservative energy per cycle vanishes. On the other hand, the change in dissipative energy is equal and opposite in sign to that of the conservative energy so that in the linear approximation the sum of the conservative and the dissipative energy changes per half cycle vanish and there can be no uncompensated dissipation of energy in the linear approximation.

However, as the amplitude of the fluctuating load is increased, a point will be reached where the linear approximation fails and it becomes possible to measure an uncompensated dissipation of energy. This is the onset of measurable irreversibility. We suggest that this represents an important measurable parameter that can be used to compare materials systems. We recognize that such a parameter will be dependant upon the time and distances scales as well as the measurement precision of the observer, never the less, it will provide a relative number that can be used to rank materials according to their response to various kinds of load.

Once one has a measurable value for the extremizing function, one can proceed in various ways. For example, one can change the frequency (i.e., the time scale) of the fluctuating load and observe the effect on the uncompensated dissipation of energy. By this means, one can obtain the maximum change in the system's response either by finding the "resonance" frequency if it lies within the experimentally available range or by using the maximum or minimum available frequency.

THE ONSET OF ASYMMETRY

After one has a measurable onset of irreversibility and perhaps has adjusted the frequency to obtain the most sensative detection of uncompensated dissipation of energy, the next step is to explore the information that one can deduce from this measurement. First of all the sign of ξ is significant.

If the system is initially in equilibrium with its environment, a sinusoidal fluctuation of the load will tend to drive the system away from equilibrium. That is to say, the uncompensated dissipation of energy will be positive, the dissipative energy per cycle exceeds the conservative energy and the excess energy of the system increases. For example, this might correspond to a release in elastic strain energy due to crack propagation.

On the other hand, if the system is not a true equilibrium structure, for example, a polymeric glass or a metal with frozen-in strain energy, then fluctuating the load may cause the system to approach equilibrium. In this case, the extremizing function is negative and the excess energy of the system decreases.

Finally, we recall that no uncompensated dissipation of energy is measurable as long as the system obeys the linear approximation within the measurement precision. However, the departure from linearity can occur in a number of different ways. In particular, our proposed measurements will permit us to distinguish between a measurable nonlinearity in the dissipative energy and one in the conservative energy. Recall that in the linear case the dissipative energy averages to zero for each half cycle whereas the conservative energy vanishes when averaged over one cycle. Consequently, a nonlinearity in the dissipative energy which yields a measurable value for ξ, will be symmetric. That is to say, equal amounts of uncompensated dissipation of energy will occur in the positive and negative halves of the cycle. However, if the nonlinearity causing the uncompensated dissipation occurs in the conservative energy, it must be asymmetric so that more uncompensated dissipation of energy occurs in one half cycle than in the other.

The difference between a symmetric and an asymmetric extremizing function is very significant. A symmetric function does not necessarily result in any permanant change in the excess energy of the system. The extremizing function may remain constant from one cycle to the next so that $\dot{\xi} = 0$. However, a nonlinearity in the conservative energy that results in a measurable asymmetric extremizing function produces a measurable change in excess energy for each cycle.

Thus, the onset of measurable asymmetric represents the second parameter which we may use to characterize our system. Fluctuating the load at an amplitude sufficient to show asymmetry will accelerate the approach to equilibrium or the deviation from equilibrium depending upon sign of the uncompensated dissipation of energy. This kind of accelerated change is particularly useful since it occurs without any change in the average environmental properties since they are varied sinusoidially about their average value.

THE ONSET OF INSTABILITY

As we have indicated earlier, the stability of a nonequilibrium thermodynamic system has been the subject of a long standing polemic in the literature. We do not propose to take either side in this argument. Rather, we suggest that our dynamic methods provide an experimental approach to actually driving the system farther and farther from equilibrium until instability can be experimentally observed. We believe that once the experimental measurement of instability has provided a sufficient number of examples, it may be possible to resolve the differences between the various proposed criteria.

Based on very limited measurements from mechanically stressed systems, we have suggested that the instability resulting in fracture may be characterised by a critical value of the change in excess energy, $\Delta\mathcal{E}_c$. This critical value occurs when the variation in excess energy vanishes and the second variation become negative. See Appendix A for an explanation of how an approximation to the first and second variations of a functional may be obtained experimentally.

SUMMARY

We have derived a nonequilibrium fracture criterion based upon a reformulation of the second law of thermodynamics. This criterion is particularly applicable to polymeric composites or other viscoelastic materials where conventional fracture criteria are most seriously in error. Our fracture criterion is the critical value of the excess energy functional that occurs when the excess energy, which involves an integral over both time and the volume of the material, reaches a maximum. We have shown that in the special case of a single crack propagating in a nonlinear plastic-elastic material, our excess energy functional reduces to the Rice J-integral. Thus our fracture criterion is clearly a more general criterion, applicable to viscoelastic materials and which contains all of the conventional criteria as special cases.

However, the most important accomplishment was the definition of an experimentally measurable function and its time derivative which should make it possible to measure experimentally the excess energy functional and its variations. These experimental measurements do not require a knowledge of the length or orientation of the crack or cracks involved in the failure mechanism. Furthermore, important parameters related to this fracture criterion can be measured without fracturing the specimen. One therefore has the possibility of making successive measurements on the identical specimen after subjecting it to various treatments that may effect its performance.

RECOMMENDATIONS

In order for these measurements to result in useful criteria for the design of composite structures it will be necessary to build up a data base of experience. This will involve computer programs to measure these functions, reduce the data in real time, and feed backthe results to the measuring device in order to control the frequency and amplitude of the dynamic fluctuations which make possible this novel dynamic approach to a truly dynamic thermodynamics.

Clearly the next step to be taken involves programming these calculations into a computer controlled MTS testing machine so that these measurements can be made in real time. This will make it possible to independently control the frequency, the amplitude and the average load while observing the effect on the measured values of ξ and its time rate of change.

We are convinced that this approach to dynamic testing of materials may represent an important breakthrough in predicting and improving the long term performance of materials since it offers a means of predicting failure without actually failing the specimen. One therefore has the possibility of making successive measurements on the identical specimen after subjecting it to various treatments which may effect its performance.

REFERENCES

1. P. H. Lindenmeyer, "Principles of Nonlinear Irreversible Thermodynamics Applied to The Testing of Materials," Boeing Document D18025582-1 (1980).

2. I. Wallick, et. al, ACS Meeting, August 1981. See also "Fracture Criteria for Composites," by P. M. Mast et al in "High Performance Composites and Adhesives for VSTOL Aircraft," ed by L. B. Lockhart Jr. NRL Report 4005, May 1979.

3. J. F. Knott, "Fundamental of Fracture Mechanics," Butterworths, London (1973).

4. J. R. Rice, "Thermodynamics of the Quasi-Static Growth of Griffith Cracks," J. Mech. Phys. Solids, 26, 61, (1978).

5. B. H. Lavenda, "Thermodynamics of Irreversible Processes," Halsted-Wiley, N.Y. (1978).

6. P. Glansdorff and I. Prigogine, "Thermodynamic Theory of Structure, Stability and Fluctuations," Wiley, N.Y. (1971).

7. J. Keizer and R. F. Fox, "Qualms Regarding the Range of Validity of Glansdorff-Prigogine Criterion for Stability of Nonequilibrium States," Proc. Nat. Acad. Sci. USA, 71, 192(1974).

8. R. Landauer, "Inadequacy of Entropy and Entropy Derivatives in Characterizing the Steady State," Phys. Rev., A12, 636(1975).

APPENDIX A

A Novel Approach Toward a Truly Dynamic Thermodynamics

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"Two Roads diverged in a Wood, and I
I took the one less traveled by
And that has made all the difference"

Robert Frost

INTRODUCTION

It has long been recognized that the usual equilibrium thermodynamics should more appropriately be called thermostatics, since the only dynamic processes it can describe are the so-called "quasi-static" processes, which proceed so slowly that each point on the path between states can also be considered an equilibrium state. Our objective is to develop a truly dynamic thermodynamics that will permit the treatment of the overall kinetics of a complex process in a manner analogous to the way the usual thermodynamic potentials treat the overall energetic averages. This dynamic thermodynamics will encompass the kinetics of the overall chemical and structural changes occurring within the system and will reduce to the usual equilibrium thermodynamics and the nonequilibrium thermodynamics of linear processes as special cases.

The usual approach to the development of a nonequilibrium thermodynamics involves either the assumption of local equilibrium[1,2,3] or the use of the Clausius-Duhem inequality as a constraint upon the constitutive equations of a continuum mechanics.[4] For an excellent, up-to-date review of these different approaches, see Lavenda.[5] All of these approaches involve an entropy balance equation that introduces time and space dependence into the concept of entropy by means of an entropy production and an entropy flow. Without in any way questioning the validity of these approaches, we only point out that this marks the "divergence in the road," and we shall have no occasion to use an entropy production or an entropy flow. Our motivation for this is a very practical one—it is not possible to directly measure entropy. We suggest that the concept of entropy is difficult enough for most people to understand without introducing the temporal and spatial derivatives of this nonconservative concept.

EQUILIBRIUM AND NONEQUILIBRIUM THERMODYNAMICS

A rigorous experimentally based thermodynamics permits one to use the thermodynamic properties obtained from static measurements made on the surface of two systems at equilibrium to predict the thermodynamic properties of the combined system once it has again attained equilibrium. In practice one of the two equilibrium systems, called the environment, is presumed to be very large so that its thermodynamic properties do not change by a measurable amount. Note, however, that the environment must be a uniform equilibrium system in order that a rigorous equilibrium thermodynamics may be applied.

In an exactly analogous manner we shall propose a way to make dynamic measurements on systems that are not at equilibrium and to predict the dynamic thermodynamic properties of the combined systems as a function of time. This dynamic thermodynamics encompasses the kinetics of the overall chemical and structural changes within the system and reduces to the usual linear/nonequilibrium thermodynamics as the amplitude of our dynamic measurements are reduced and to equilibrium thermodynamics as the amplitude becomes zero.

The basic difference between equilibrium and nonequilibrium thermodynamics, as we perceive it, is that in the former, energy (and, in some cases, matter) can flow only in one direction as the system approaches equilibrium. In contrast, nonequilibrium thermodynamics permits the flow of energy (or matter) both into and out of (i.e., through) the system. That is to say it can flow either from the system to the environment or from the environment to the system but never both ways. This flow can occur either continuously, in at one point in space and out at another or alternately in at one time and out at another, depending upon the nature of the environment in contact with the system of interest.

The rate of energy flow plays no role in determining the state of the system in equilibrium thermodynamics. On the other hand, if the environment is nonuniform either in space or time, so that energy can flow through the system, then the rate of flow (i.e., power) plays a determining role. It may determine not only the state, but also the path by which it moves toward this state. Thus power, rather than energy, is the sine qua non of nonequilibrium thermodynamics.

TIME AND DISTANCES SCALES

Having thus distinguished between equilibrium and nonequilibrium thermodynamics, our next major point is the assertion that this distinction is arbitrarily dependent upon the time and distance scales adopted by the observer. All thermodynamic quantities represent averages over a very large number of complex processes occurring within the system of interest. An average can be taken only over a definite interval of time or space (distance). As a practical minimum, thermodynamic quantities must be considered as being averaged over the time required to make a measurement and the space occupied by the measuring device. The practical upper bound to these time and distance scales is given by the size of the system and the time it is under observation. If the system is at equilibrium, these time and distance scales may appear to be of no importance, since an equilibrium system is both homogeneous (or at most composed of a limited number of homogeneous phases) and time independent. But a little thought will allow one to realize that the definitions of both homogeneity and time independence are also arbitrarily dependent upon the time and distance scales adopted by the observer.

The ability of the observer to arbitrarily define the time and distance scales has suggested a whole new series of dynamic measurements that have only become experimentally feasible with the advent of modern microprocessor technology. These measurements involve driving the system through a series of closed thermodynamic cycles by causing the environmental variables to fluctuate in a sinusoidal manner. The frequency of these dynamic measurements fixes the time scale; the size of the system or the distance between measuring devices determines the distances scales and the amplitude of the fluctuations controls the power that passes through the system with each cycle.

THE GIBBS ASSUMPTION AND LEGENDRE TRANSFORMS

Since most other approaches to nonequilibrium thermodynamics employ some sort of a generalized Gibbs equation, it is instructive to review this most valuable contribution to thermodynamics. Gibbsian thermodynamics is based upon the assumption that the energy of a system can be expressed as a linear homogeneous function of its extensive variables. This is equivalent to the additivity postulate or the assumption that all contributions to energy scale linearly with size. This assumption is always valid when the system is sufficiently macroscopic and at equilibrium. When it is also isolated, the

approach of such a system to equilibrium is determined by the maximization of the entropy function. If, instead of being isolated, the system is able to exchange energy (or matter) of a given kind with a uniform environment, the extensive variable appropriate to this kind of energy becomes dependent upon its conjugate intensive variable, which is controlled by the environment. The systems approach to equilibrium then is determined by the minimization of the appropriate partial Legendre transform with respect to the extensive variable. A Legendre transform may be thought of as a coordinate transformation from a set of moving (Lagrangian) coordinates to a set of fixed (Eulerian) coordinates, or vice versa. In this respect, extensive thermodynamic variables are analogous to Lagrangian and intensive ones to Eulerian coordinates. Thus, in an isothermal system, temperature becomes an independent variable controlled by the environment and the partial Legendre transform with respect to entropy—better known as the Helmholtz free energy—becomes the function that must be minimized as the system approaches equilibrium. Similarly, the Gibbs free energy, which is the partial Legendre transform with respect to entropy and volume, is the function that must be minimized as an isothermal-isobaric system approaches equilibrium.

If the Gibbs assumption is valid, the total Legendre transform with respect to all the extensive properties vanishes, yielding the Gibbs-Duhem relationship. This relationship can be solved for one of the extensive properties, usually volume or mass. This may be used as a scale factor to convert the other extensive properties into densities or specific quantities. Only when one has such a scale factor is it possible to express energy or entropy as a density or a specific quantity and to speak of their derivatives with respect to time and/or space. That is to say, only when the time and distance scales adopted by the observer (who defines the system and determines the measurement precision) are such that the Gibbsian assumption can be made is it possible to convert extensive properties to intensive properties and express them as functions of time and space. This is probably why most authors have chosen to generalize the Gibbs equation and the Gibbs-Duhem relationship as a means of introducing time and space into equilibrium thermodynamics.

We shall not make the Gibbs assumption, but rather we follow the example of Hill,[6] who showed that when the system becomes small there are a number of contributions to the energy that do not scale linearly with size and hence cannot be neglected. As a consequence, energy cannot be expressed as a linear homogeneous function of the extensive variables, the total Legendre transform does not vanish, and there is no

Gibbs-Duhem relationship to provide a scale factor. Instead, we shall assume that, in general, every thermodynamic system may have a nonlinear term or excess energy given by the total Legendre transform of energy, and we shall attribute all variation in time and space to this excess energy. Following Hill, we use the symbol $\mathcal{E}$ for this excess energy. However, we do not restrict our system only to equilibrium states, as did Hill. Thus, in addition to the small systems effects, which may become negligible as the system increases in size, our excess energy includes all possible contributions to the nonlinear or heterogeneous nature of the system. For example, it includes gradients in the intensive properties, which may be introduced or maintained by nonuniform environments or by pseudothermodynamic fields (i.e., mechanical, electrical, or magnetic). In addition, this excess energy may include gradients in intensive properties that are no longer maintained by a nonuniform environment or an external force, but have not yet dissipated. That is to say, they appear to be frozen into the nonequilibrium structure as a consequence of the time scale of the observer. In effect, the total variation of energy with time and space is contained in this excess energy, so that the evolution of the system with time is shifted from the concept of entropy to that of excess energy. As we shall see, this gets around the most difficult problem in nonequilibrium thermodynamics—namely, how to define entropy when the system is not in equilibrium.

REFORMULATION OF THE SECOND LAW OF THERMODYNAMICS

The essential feature of our approach to a nonlinear irreversible thermodynamics is a reformulation of the second law in which the concept of entropy is replaced by the concept of an excess energy. Thus we propose that "It is the minimization of the uncompensated dissipation of energy within the system of interest - not the increase in entropy of the universe - that represents the practical embodiment of the second law". The uncompensated dissipation of energy is defined as the change in the internal energy of the system minus change in the excess energy of the system. The excess energy is in turn defined as the total Legendre transform of energy with respect to all of its extensive properties. Note that if the system of interest is isolated, the dissipation of energy and the increase in entropy become synonymous and the excess energy vanishes as the system approaches equilibrium.

The principle advantage of this reformulation is that while entropy can only be calculated indirectly from static measurements made on systems presumed to be at equilibrium, the change in excess energy can be directly obtained from dynamic

measurements made on systems that are not necessarily at equilibrium. In effect this reformulation has shifted the burden of accounting for the time evolution of thermodynamic systems from the increase in entropy of isolated systems - that can only be approximated in real life - to the change in the excess energy of real systems that may be open or closed with respect to the interchange of energy and/or matter with their environments.

In contrast to entropy, energy is a conservative quantity that can easily be visualised as moving from one point in space to another. Thus we shall completely avoid the use of the concept of entropy production and entropy flow. Entropy will only be considered as a property of the system of interest when it has reached a state of equilibrium. Under these conditions entropy has been rigorously defined in terms of static measurements. If the system is not at equilibrium any entropy which we associate with it will be considered to be a virtual entropy. That is to say, the virtual entropy of a nonequilibrium system at any instant in time will be the entropy that the system would have if it were isolated at that time and allowed a sufficient time (infinite, if necessary) to come to equilibrium. In order to deal with such a virtual entropy, we need to define its conjugate variable (i.e. temperature) as the instantaneous space averaged temperature, $\hat{T}$ (read T hat) at the same instant for which the virtual entropy is desired. Actually we will need both space averages, $\hat{X}$ and time averages $\bar{X}$ (read X bar) for all intensive thermodynamic properties.

Since equilibrium thermodynamic systems are by definition homogeneous and time independant, the basic problem in developing a formalism for a nonequilibrium thermodynamics is how to introduce time and space coordinates into the thermodynamic quantities. We shall always express all extensive thermodynamic properties as their instantaneous value for the total system of interest. Thus the total instantaneous energy of a nonequilibrium system is given by

$$E(t) = \hat{X}_i(t)\, a_i(t) + \mathcal{E}(t, t_0)$$

where we have relegated all influence of past history, as well as all unhomogeneities, gradients etc., to the excess energy which we express as a functional.

THE EXCESS ENERGY FUNCTIONAL

Recall that we have defined the excess energy as the total Legendre transform of the energy of the system of interest with respect to all its extensive properties. The

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excess energy may vary with both time and location in space within the system. That is to say, the excess energy of a nonequilibrium system is manifest as gradients in the intensive properties of the system. In order to find the total excess energy of a system we must integrate over the volume of the system as well as over a definite interval of time. The integral over time covers the complete history of the system from the time it was last in a state of equilibrium, t_0, until the time of observation, t. Thus excess energy is not just a thermodynamic function of time and space but it is actually a functional involving a definite integral over both the volume of the system and the time since it was last at equilibrium.

In the most general terms we can write the excess energy functional as

$$\mathcal{E} = \iint \mathcal{L}\left[r, t, \xi_t, \nabla \xi\right] dt\, dV$$

where r is a position vector with respect to a set of fixed spacial coordinates, $\mathcal{L}$ is the Lagrangian specific power density function, ξ is the extremizing function and $\nabla\xi$ and ξ_t its spacial and temporial derivatives.

Now according to our reformulation of the second law, this functional will always assume a minimum value subject to the constraint that there must always be a balance of power between the system and its environment. The calculus of variations tells us that a necessary condition for a functional to assume a minimum value is that its first variation $\delta\mathcal{E}$ must vanish

$$\delta \mathcal{E} = \delta \iint \mathcal{L}\, dV\, dt = 0$$

and a necessary and sufficient condition that the first variation of a functional shall vanish is given by the Euler-Lagrange equation

$$\left(\frac{\partial \mathcal{L}}{\partial \xi}\right) - \sum_{\alpha} \frac{\partial}{\partial \alpha}\left(\frac{\partial \mathcal{L}}{\partial \xi_\alpha}\right) = 0 \qquad \alpha = r, t$$

Two possibilities exist, either $\mathcal{E}$ attains a stationary state in the time interval $t-t_0$ and over the volume V or it does not. If it does the first variation vanishes and we have a variational problem with fixed limits. If it does not then our problem becomes one of predicting the time t when the functional will reach a steady-state, that is to say we have a variational problem with an undetermined upper limit. Both of those situations can be approached via the calculus of variations. Whether or not solutions exist will depend upon the nature of the Lagrangian specific power density function, $\mathcal{L}$ and the

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constraints placed upon it by the necessity that there must be a balance of power between the system and its environment at any stationary state.

The technique for introducing a constraint into a variational problem by means of a Lagrangian undetermined multiplies is well known provided one has a suitable equation for describing the constraint. To put it briefly one simply defines a new Lagrangian as

$$\mathcal{L}^* = \mathcal{L} + \lambda(\text{Power Balance Equation})$$

where λ is the undetermined multiplyer. Since the power balance equation is equal to zero, this additional term will not influence the value of the functional but it will influence its variation and λ must be determined in a manner that causes the variation to vanish.

The necessary and sufficient requirement that the Euler-Lagrauge equation shall have a unique solution is that all terms in the Lagrangian must be the drivative of some function. If the specific Lagrangian power density function, $\mathcal{L}$, is a linear function of $\dot{\xi}$, the equations have a unique solution, independent of the choice of ξ. That is to say the excess energy depends only upon the integration limits. Under these conditions the system will evolve to a stationary state via the by now well established linear nonequilibrium thermodynamics, where Onsager's reciprocal relations apply, the dissipative forces may be drived from a potential, and Prigogines principle of minimum entropy production remains valid.

However, in the more general case, where the power balance constraint cannot be expressed as the derivative of some potential function the Euler-Lagrange equation cannot be integrated and the excess energy functional is not stationary but continues to evolve with time. It is in this most general case that our experimental approach becomes most unique. Instead of attempting to devise vector or local potentials or some other means that will yield an analytic solution to the Euler-Lagrauge equations, we propose an experimental approach in which the extremizing function, ξ is defined as the uncompensated dissipation of energy. That is to say ξ represents the difference between the intensive variables averaged over an experimentally determined volume at a given time and the same variables averaged over an experimentally determined interval of time at a given point within the system. With this definition of the extremizing function the constrained Lagrangian specific power density function, $\mathcal{L}^*$ becomes the Eulerian time derivative of the extremizing

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function, $d\xi/dt = \dot{\xi}$ where both ξ and $\dot{\xi}$ may be measured experimentally for a variety of time scales (determined by the frequency of dynamic measurements) and distance scales (determined by the distance between measuring devices) or sample sizes.

THE EXTREMIZING FUNCTION

We begin by defining an n-dimensional vector X whose components include all of the intensive thermodynamic variables, as well as the components of any pseudothermodynamic fields, a reaction parameter for each possible reaction, and the necessary order parameters for any structural transitions. Each of these components is assumed to be a function of time and space, so that $X = X(\mathbf{r},t)$ where $\mathbf{r}$ is the position vector in a fixed coordinate system. Although X is a function of time and space, it cannot be differentiated, since its components must be averaged over either time or space before taking an infinitesimal limit. To get around this difficulty, we define two different kinds of averages:

a space or "hat" average

$$\hat{X}(t) = \frac{1}{\mathring{V}} \int^{\mathring{V}} X(\mathbf{r},t)\,dV$$

and a time or "bar" average

$$\bar{X}(\mathbf{r}) = \frac{\omega}{2\pi} \int_{-\pi/\omega}^{\pi/\omega} X(\mathbf{r},t)\,dt$$

and we further define their differences as

$$\xi(\mathbf{r},t) = \hat{X}(t) - \bar{X}(\mathbf{r}) \qquad (5)$$

In contrast with X, ξ is a continuous function with continuous derivatives with respect to both time and distance. It is an all-inclusive representation of the heterogeneities in the system. Note that the value of this function depends upon the time scale $t^{\circ} = \frac{2\pi}{\omega}$, and the distance (or volume) scale as well as the precision of measurement; all of which may be controlled by the observer. Thus $\xi(\mathbf{r},t)$ becomes operationally equal to zero when the time and distance scales of the observer causes the difference between the hat and the bar averages to become less than the measurement precision. We submit that <u>any</u> thermodynamic quantity depends upon the time and distance scales as well as the measurement precision of the observer. We have simply made these explicit instead of following the usual Gibbsian assumption which implicitly assumes that the time and distance scales are large enough so that the measurement precision

has no influence on the results. Since ξ explicitly involves time and distance scales, it can be used to operationally define the various states of a thermodynamic system, as illustrated in Figure 1.

OPERATIONALLY DEFINED THERMODYNAMIC STATES

If the observed change in ξ with both time and distance is less than the measurement precision, the system is operationally in equilibrium. If the change with time is less than the measurement precision, but its change with distance is not, the system is operationally in a steady state. Similarly, if the change with distance is less than the measurement precision, but the change with time is not, the system is operationally in a homogeneous but unequilibrated state. However, the most interesting and unusual case occurs when the hat and bar averages are both changing, but their difference (i.e., ξ) remains a nonzero constant. This is an oscillating state and represents the true dissipative structure a la Prigogine. Such a structure is formed, stabilized, and controlled by the interaction between the flow of energy and the motion of matter. From this point of view, one can recognize a steady state as a time-degenerate dissipative structure. An inhomogeneous "steady-state" structure may exist even after the isolation of the system has removed the external forces that caused it to form if the time scale of the observer is too short to allow measurement of changes in the hat averages. It is in this sense that we have proposed[7] that all morphology in polymeric solids can be considered as frozen or time-degenerate dissipative structures a la Prigogine.

This ξ function plays the central role in our approach to nonequilibrium thermodynamics. The astute reader will already have noticed the similarity in our definition of ξ and the "error in the ergodic hypothesis." Many other analogies exist. Since this function must vanish or become negligibly small as the system approaches equilibrium, we may also think of it as representing a quantitative measurement of the deviation of the system from equilibrium. Thus, we are assured that our nonequilibrium thermodynamics merges smoothly into equilibrium thermodynamics as the system approaches equilibrium.

Still more insight can be gained on how the measurement precision and the time and distance scales of the observer can influence his preception of the thermodynamic states by considering the Lagrangian specific power density function. This specific power density function, $\dot{\xi}(r,t)$, represents the rate at which the system is changing at a

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point in both space and time (where time and space are measured in units of the observers time and distance scale). It corresponds to an "infinitesimal phenomenological equation." If integrated over the volume of the system, it represents an instantaneous rate of energy flow (power) throught the system, and if, in addition, it is integrated over some period of time, it represents the total change in energy of the system during that time; thus:

$$\mathcal{E} = \iint \dot{\xi}(r,t)\, dV\, dt \tag{6}$$

Here $\mathcal{E}$ represents the total Legendre transform or excess energy that the system has because either (1) it is constrained from equilibrium by contact with a nonuniform environment or a pseudothermodynamic field, or (2) it contains heterogeneities of time and space that do not scale linearly with the time and distance scales of the observer.

The integrand of equation (6) can be expanded in terms of the partial derivatives of time and space as

$$\dot{\xi} = \frac{\partial \xi}{\partial t} + \nabla \xi \cdot \frac{dr}{dt} = \frac{\partial \bar{X}}{\partial t} - \nabla \bar{X} \cdot \nu \tag{7}$$

where ν is the baryocentric velocity, dr/dt. We now see that there are four different ways in which equation (7) can vanish. If all three components become less than the measurement precision, and ξ also vanishes, the system is operationally at equilibrium.

When the first term becomes less than the measurement precision, we have an operational steady state when either the gradient, $\nabla \bar{X}$ or the velocity, ν becomes less than the measurement precision. Thus, in principle the steady-state may exist in two extremes, in the first there are measurable gradients in the intensive properties but no measurable flow and in the second there is measurable flow but no measurable gradients. Finally, we have the possibility of measurable values for all three components but with the derivative of the space average always being equal to the product of the gradient of the time average times the velocity so that ξ is a nonzero constant but $\dot{\xi}$ vanishes. These conditions are summarized in Table I.

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THE PRINCIPLE OF MINIMUM DISSIPATION OF ENERGY

The principle of minimum dissipation of energy has been known for many years. In fact in the form that we shall use it, this principle can be considered as simply another form of Hamilton's principle of varying action which states that the integral over time of the Lagrangian has a stationary value provided the forces can be drived from a potential. In which case the variation of the action integral vanishes, so that

$$\delta \mathcal{A} = \delta \int L \, dt = 0$$

where the Lagrangian, L, is the difference between the kinetic and the potential energy of the system. Since we have defined the dissipation of energy as the change in the excess energy, the principle of minimum dissipation of energy can be expressed as

$$\delta \mathcal{E} = \delta \iint \mathcal{L} \, dV \, dt = 0$$

whereupon we can identify the excess energy, $\mathcal{E}$, with the Eulerian time derivative of the Hamiltonian action, $\mathcal{A}$ and Lagrangian specific power density function, $\mathcal{L}$, with the Eulerian time derivative of the Lagrangian, L expressed as a specific energy density.

Thus the principle of minimum dissipation of energy, as we have formulated it, states that the difference between the change in specific kinetic energy density and the change in specific potential energy density will evolve to a stationary state when integrated over a definite volume and a definite interval of ime, always provided that all constraints on the system may be derived from potentials.

The condition that all forces on the system be derivable from potentials or the exactness conditions of integrability on all differentials represents a limit on the validity of the theory (see Lavenda (5)). It is the existance of this limit which has restricted the practical applicability of nonequilibrium thermodynamics to situations sufficiently close to equilibrium where Onsager's reciprocial relations are valid.

But we have defined a constrained Lagrangian specific power density function as

$$\mathcal{L} = \dot{\xi} = d\hat{X}/dt - \nabla \bar{X} \cdot v$$

which is experimentally measurable regardless of the nature of the constraints. However, it does depend upon the time and distance scales of the observer as well as his measurement precision. We are therefore able to adjust the time and distance scales to operationally define the state of the system.

Of still more importance we can adjust the rate at which energy is caused to flow through the system. We do this in two different ways (1) by contacting the system with an environment that is nonuniform in space so that energy flows in at one point and out at another or (2) by an environment that is nonuniform in time so that energy flow undergoes dynamic fluctuations. The two ways are analogous to the direct current and alternating current flow of electrical energy.

By controlling the level of power flowing through the system we have a means of both measuring the dynamic changes occuring within the system and to some extent actually controlling what these changes will be.

VARIATIONS OF THE EXCESS ENERGY FUNCTIONAL

We carefully distinguish between the change in the value of the excess energy functional and its variation in the mathmatical sense as used in the calculus of variations. In the latter sense the variation of a functional is a virtual change corresponding to a change in the nature of the extremizing function in all possible directions. In the calculus of variations we are interested in this virtual variation only as a criterion for determining the stationary state of the functional. The first term in a Taylor expansion of the functional about such a stationary state is called the first variation, δ , and the second term is called the second variation δ^2.

A necessary and sufficient condition for a functional to have a stationary state is that its first variation shall vanish. However this is not a sufficient condition for the functional to have a minimum value since the first variation will also vanish for a maximum and even for the equivalent of a "horizontal tangent" or "saddle point". A second necessary condition for a functional to have a minimum is that its second variation shall be positive semidifinite. The corresponding condition for a maximum is that the second variation be negative semidefinite. These criteria are still not sufficient in a rigorous mathmatical sense but they will suffice for our purposes.

We also must point out that from a practical point of view a functional may have a value that does not correspond to a stationary state where the first variation does not vanish because it is restricted by the boundary criteria on the independant variables. Consequently the excess energy functional, integrated between definite limits of time and space, will either be at a stationary state, in which case its first variation vanishes or its value will be determined by the limits on the integrals and the total variation will determine whether this represents an apparent maximum or minimum.

Regardless of whether or not the first variation vanishes, the sign of the total variation is an important criterion in determining the state of a nonequilibrium system. Thus it would be very desirable to have an experimental procedure for approximating at least the sign of the total variation in excess energy.

DYNAMIC MEASUREMENT OF THE VARIATION IN EXCESS ENERGY

We propose that one can measure the sign of the total variation in excess energy in a manner directly analogous to the way one would measure the sign of the differential of an ordinary function. One changes the value of the independant variable by an amount sufficient to cause a measurable change in the function. Now the variation of a functional is caused by the change in the extremizing function rather than a change in the variables since their influence on the functional is fixed by the limits as the integral. Furthermore, the variation of the extremizing function must be in *all* possible directions (unlike the differential which corresponds to a change in the variables in a definite direction). We propose to simulate the variation in the extremizing function by driving the independant variable in a cyclic fashion. By changing the variables through a complete cycle, we will have caused the extremizing function to have varied in all possible directions without changing its average value and we can measure the effect of this variation on the excess energy functional. Just as in experimentally determining the sign of a differential of an ordinary function where it was necessary to change the variable by an amount sufficient to cause a measurable change in the function, the amplitude of the cyclic change must be sufficient to cause a measurable change in the excess energy functional. Now since we cannot cause an instantaneous cyclic change in the variables, the variation will be experimentally determined over a period of time, determined by the cyclic frequency. Likewise the results or change in the excess energy must be measured over some distance, determined by the separation of the measuring devices. Thus our experimentally determined variation of the excess energy functional will be for a

given time and distance scale as well as at an amplitude sufficient to exceed the measurement precision.

In order to describe these dynamic measurements we shall collectively designate the independant or controlled intensive variables as the "load" and the measured or dependant extensive properties as the "displacement" as would be the actual case if one only considered the pseudo thermodynamic mechanical force field. Now energy is given by the product of the load times the displacement but the instantaneous power is composed of two terms: (1) the load times the derivative of the displacement with respect to time and (2) the displacement times the derivative of the load with respect to time. The first of these power terms represents the negative of the change in the potential energy and is functionally dependant upon position whereas the second term is the change in kinetic energy and is functionally dependant upon time. Thus the Lagrangian power density function is given by the sum of these two power terms.

Now if the cyclic load is sinusoidial the two power terms can be readily separated since the time derivative of the load is always 90 degree out of phase so that the change in potential energy or conservative power represents the in-phase power whereas the change in kinetic energy or dissipative power is 90 degrees out-of-phase with respect to the applied load. Integrating these two powers over a complete cycle and taking their sum provides an experimental measurement of the specific Lagrangian energy density which can also be interpreted as the variation in excess energy per cycle and for the unit volume defined by the separation of the measuring devices.

Note that in the linear approximation (i.e., when the dissipative forces are a linear function of the velocity and the conservative forces are linear functions of the displacement and the acceleration) the sum of the two power terms integrated over a complete cycle vanish. Thus only when the amplitude of the cyclic load is sufficient to produce nonlinear responses will it be possible to measure even the sign of the variation in excess energy.

We shall designate this experimentally measurable variation by the symbol Δ_δ in direct anology to the use of Δ for a finite value of the differential. Thus, just as $\Delta \rightarrow d$ in the limit of infinitesinal changes in variables so $\Delta_\delta \rightarrow \delta$ as the amplitude of our cyclic fluctuating varibles is decreased.

But we have defined ξ as the extremizing function of the constrained Lagrangian, $\mathcal{L}^*$, and by our cyclic fluctuation of the independant variables we have imposed an additional constraint on the system. The experimentally measurable approximation to the variation of the origionally constrained extremizing function, $\Delta_\delta \xi$ is identical to the extremizing function of the Lagrangian which has the added constraints determined by the additional alternation power applied to the system. Thus $\Delta_\delta \xi \equiv \xi(\overset{\circ}{V}, \overset{\circ}{t}, A)$ where A is the amplitude of the fluctuation.

These additional fluctuating constraints not only permit us to determine the sign of the variation in excess energy but by adjusting the level of this alternating power (i.e., by changing its frequency and amplitude) we can accelerate the rate it is changing. Of even more impotance by adjusting the frequency and amplitude to increase the power, the system may become unstable and one obtains the dissipative structures to be described in the next section. Application of alternating thermodynamic and pseudo thermodynamic forces at the resonance frequency of various thermodynamic systems represents an important new practical application of this nonequilibrium thermodynamics and will not be discussed further due to pending patent action.

DISSIPATIVE STRUCTURES AND STABILITY CRITERIA

Prigogine [2] coined the word "dissipative structure" in order to distinguish the structure of systems that have formed in the region far from equilibrium where the environmental conditions are such as to drive the system of interest to the point of instability. His stability criteria [1] which are formulated in terms of the second variation of entropy production and its time rate of change have been the subject of criticism.[5] We shall not comment further on this controversy since our experimental approach effectively side-steps the issue rather than contributing to one side or the other. Regardless of the resolution of this polemic, we believe that Prigogine and his colleagues have made a substantial contribution to science in simply calling attention to the fundamental difference between an equilibium structure and a dissipative structure.

A dissipative structure will form whenever the environmental conditions surrounding a system are such that the relationship between the flow of energy and the motion of matter is sufficiently nonlinear so that some sort of rotary motion can decrease the dissipation of energy within the system. Since a rotational motion is involved there will be at least one characteristic distance and one characteristic time.

Our interest in these dissipative structures [7] origionated from the realization that if such structures occured during the solidification process, the rotational motion would be frozen. That is to say the characteristic time becomes infinite in the time scale of the observer but characteristic size(s) would remain as a permenant feature of the solid. Thus we suggest that the theoretical basis for understanding and controlling the morphological structure of most solid materials in general and polymeric solids in particular is much more nearly related to these frozen dissipative structures than to equilibrium (i.e., crystal) structures. The nonequilibrium thermodynamic theory of dissipative structures therefore represent the key to a theoretical understanding of solid state morphology.

In the usual approach to nonequilibrium thermodynamics the entropy of a nonequilibrium system is not defined and only its change with time is expressed as the sum of the entropy that flows into or out of the system and the entropy produced within the system. In contrast to this approach we have defined the instantaneous entropy of a nonequilibrium system as the sum of its virtual entropy and an entropy deficiency defined as the negative of the excess energy divided by the space averaged temperature, $\hat{T}$.

The thermal energy of any system at time, t is an invarient given by

$$\hat{T}S\{t\} = \hat{T}\overset{o}{S}\{t,t_0\} - \mathscr{E}\{t,t_0\}$$

but since the virtual entropy is an equilibrium entropy by definition, its first variation must vanish and its second variation must be negative semi-definite by the second law (i.e., the entropy of an isolated system at equilibrium is a maximum). Since the instantaneous thermal energy is invarient, the variation of the excess energy must be the negative of the variation of the virtual entropy times the space averaged temperature. It follows that since the virtual or equilibrium thermal energy is always a maximum, the excess energy can never become a maximum. Thus the stability criterion for any thermodynamic system is that its excess energy (i.e., its total Legendre transform with respect to all extensive properties) shall have a non-negative second variation. That is to say the first variation of the excess energy always tends to zero and if the second variation becomes negative the excess energy has reached a maximum and must decrease. If the second variation of the excess energy becomes negative definite the decrease is catastrophic (i.e., the system is unstable).

In contrast to theoretically derived stability criteria, the experimentally measured values of the extremizing function and its rate of change per cycle permits an unequivocal determination of operational stability criteria. For example, if the measurable extremizing function is positive and does not change by a measurable amount from one cycle to the next then the system is operationally at a stable minimum. If the measurable extremizing function is positive and decreases from one cycle to the next the system is asymptotically approaching a stable minimum, that is to say the excess energy is positive but is becoming less positive under the total constraints on the system. These stability criteria are summarized in Table II. Although the excess energy can be positive or negative, examples of negative excess energy are rarely encountered in nature, but they may exist (e.g., super heated crystal or one with less than the equilibrium concentration of defects). If one has an asymptotically unstable maximum it will ultimately become unstable with the formation of a dissipative structure. The length of time required for this to occur then becomes a problem in variational calculus with an undetermined upper limit.

SUMMARY AND CONCLUSIONS

By taking the total Legendre transform of energy with respect to all the extensive variables we have reformulated the second law of thermodynamic so that the burden of accounting for the time evolution for a thermodynamic system is shifted from the concept of entropy, which can only be rigorously defined for an isolated system at or near equilibrium, to the concept of an excess energy functional that is applicable to open or closed systems as well. We proposed that "It is the minimization of the uncompensated dissipation of energy within the system of interest — not the increase in entropy of the universe — that represents the practical embodiment of the second law." By defining the uncompensated disipation of energy, as the change in the internal energy of the system minus the change in excess energy we can equate the second law to the variational principle of minimium dissipation of energy. This principle can, in turn, be shown to be the Eulerian time derivative of Hamilton's principle of varying action. The difficulty in applying this principle to a system that can exchange energy or matter with its environment, comes in applying the necessary constraint that at a stationary state there must be a balance of power between the system and its environment. If the nature of the environment is such that this constraint can be expressed as the derivative of some function, the excess energy evolves to a stationary state by the usual linear nonequilibrium thermodynamics where Onsager's reciprocal relations apply and all forces can be derived from a potential. In

the more general case, the Euler-Lagange equations cannot be integrated, the excess energy functional is not stationary but will continue to evolve with time.

We have approached this more general case by taking advantage of the fact that the time and distance scales of the observer as well as his measurement precision, may be combined to determine the state of the system from an operational point of view. By defining the extremizing function as the difference between the intensive variables averaged over an experimentally determined volume at a given time and the same variables averaged over an experimentally determined interval of time at a given position within the system, we obtain a function that is both differentiable and experimentally measurable.

Using this function and its Eulerian time derivative we can approximate the variation of the excess energy functional in a manner exactly analogous to the way one can experimentally approximate the differential of an ordinary function. The procedure involves driving one or more of the intensive environmental variables in a cyclic manner and measuring the response of the systems extensive properties. The frequency and amplitude of this cyclic fluctuation provides an additional constraint on the system so that these dynamic fluctuations not only yield an estimate of the state of the system and how it is changing because of the initial constraints but by increasing the amplitude and varying the frequency it is possible to accelerate these changes or influence the state to which the system is changing.

This treatment allows for the possibility of actually driving the system to an instability or a maximum in the excess energy (a concept that does not occur in the entropy production and entropy flow treatments). In addition, by controlling the frequency of the fluctuation we can effect some control over the particular nonequilibrium state to which the system evolves when driven beyond instability.

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TABLE I

OPERATIONALLY DEFINED THERMODYNAMIC STATES

	$\frac{d\hat{X}}{dt}$	$\nabla \bar{X}$	$\nu = \frac{d\bar{r}}{dt}$	ξ	$\dot{\xi}$
Equilibrium State	0	0	0	0	0
Steady-State	$\left\{ \begin{matrix} 0 \\ 0 \end{matrix} \right.$	$\begin{matrix} \neq 0 \\ 0 \end{matrix}$	$\begin{matrix} 0 \\ \neq 0 \end{matrix}$	$\begin{matrix} \neq 0 \\ \neq 0 \end{matrix}$	$\left. \begin{matrix} 0 \\ 0 \end{matrix} \right\}$
Uequilibrated-State	$\neq 0$	0	$\neq 0$	$\neq 0$	$\neq 0$
Oscillating-State	$\left[\frac{d\hat{X}}{dt} = \nabla \bar{X} \cdot \nu \right]$			$\neq 0$	0
Unsteady-State	$\neq 0$	$\neq 0$	$\neq 0$	$\neq 0$	$\neq 0$

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TABLE II

EXPERIMENTALLY DETERMINED STABILITY CRITERIA

IF $\xi > 0$ and $\dot{\xi} = 0$ then $\mathscr{E} > 0$, $\delta\mathscr{E} = 0$, $\delta^2\mathscr{E} > 0$

and we have an operationally stable minimum

IF $\xi > 0$ and $\dot{\xi} < 0$ then $\mathscr{E} > 0$, $\delta\mathscr{E} + \delta^2\mathscr{E} < 0$

and we have an asymptotically stable minimum

IF $\xi > 0$ and $\dot{\xi} > 0$ then $\mathscr{E} > 0$, $\delta\mathscr{E} + \delta^2\mathscr{E} > 0$

and we have a asymptotically unstable maximum

REFERENCES

1. P. Glansdorff and I. Prigogine, "Thermodynamic Theory of Structure, Stability, and Fluctuations, Wiley-Interscience," New York (1971).
2. I. Prigogine, "Introduction to Thermodynamics of Irreversible Processes," 3rd ed., Wiley-Interscience, New York (1967).
3. I. Gyarmati, "Non-equilibrium Thermodynamics," Springer-Verlag, Berlin (1970).
4. C. Truesdell "Rational Thermodynamics," McGraw Hill, New York (1969).
5. B. H. Lavenda, "Thermodynamics of Irreversible Processes," Wiley, New York (1978).
6. T. L. Hill, "Thermodynamics of Small Systems," Benjamin, New York, Part I 1963, Part II 1964.
7. P. H. Lindenmeyer, Polymer J., 11, 677 (1979); J. Polymer Sci.-Phys., 17, 1965 (1979).

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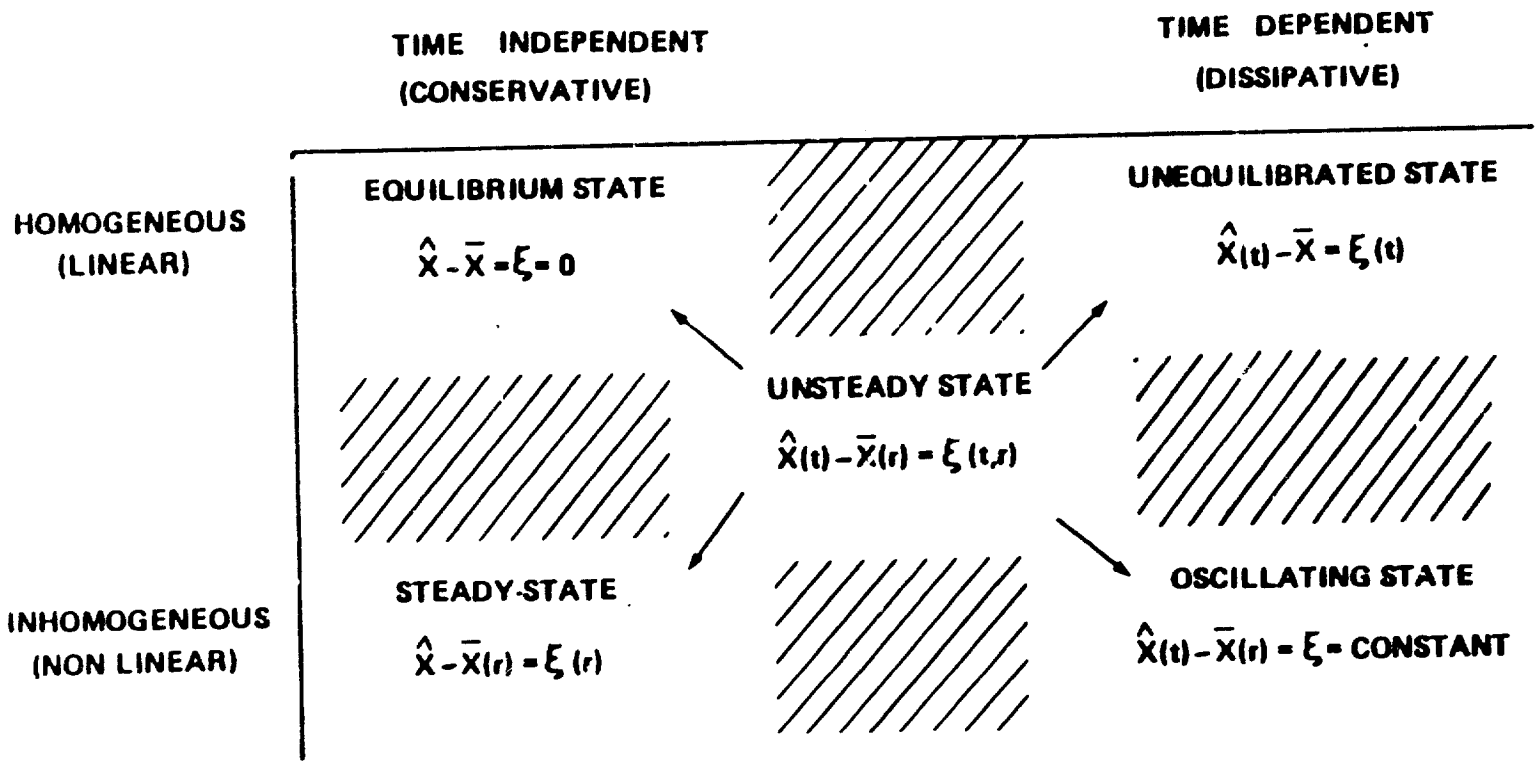

Figure 1

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