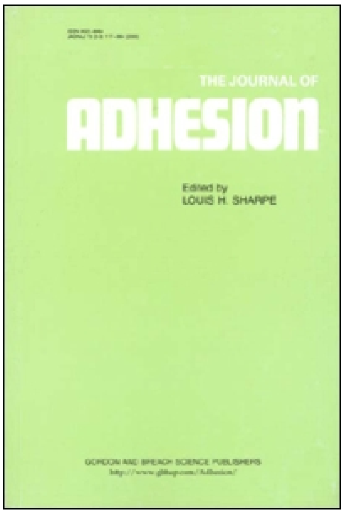

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The Interphase in Adhesion: Bridging the Gap*

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This paper addresses the origin, structure and properties of the interphase in adhesion. By interphase is meant that interfacial region between bulk adhesive and bulk adherend over which the local density displays a spatial gradient. In such a region all the local thermodynamic properties, including the mechanical properties, will be a function of distance from the surface. The question of how large these variations may be both in terms of magnitude and range is clearly a matter of some import in adhesive technology. The term "local" is a key consideration because meaningful discussion of the interphase can hardly be contemplated without explicit recognition that matter in the interphase should be regarded properly as existing in a thermodynamically metastable small system of low dimensionality. The results of a number of our numerical and theoretical studies, namely molecular dynamics simulation of realistic interfaces and nonlinear dynamical analysis, have been used to investigate the nature of materials close to surfaces. It has been found that the form and range of the density profile are indeed sensitive to the chemical nature of the surface but it has not been possible to rationalize the existence of the macroscopic long-range interphase on the basis of the usual type of spatial correlation. Recognizing that many adhesive bonds are formed using a reactive resin system we have investigated the effects of nonlinearities in the reaction kinetics on the structure and morphology of the interphase. When these factors are taken into account, a theoretical description of the interphase is possible in which the coupling between the various distance scales arises in a very natural fashion.

KEY WORDS Adhesion; interphase; chaos; surface; molecular dynamics; kinetics; theory; interface simulation; nonlinear dynamical analysis; scaling.

1.0 INTRODUCTION AND BACKGROUND

The development of a proper understanding of the behavior of the interphase is of importance in an exceedingly wide range of technologies. For example, during the fabrication of electronic devices with very high densification (nanosystems), it is necessary to manufacture interphases which may be just a few atoms thick and some tens of atoms wide.[1] The preparation of thin films and interphases with well known and predictable properties is clearly of central importance in such fields as adhesion and tribology as well as in the areas of polymeric and biological membranes.[2] The science of interfaces is a highly interdisciplinary subject spanning a range of academic disciplines from quantum mechanics to mechanical engineering. At the quantum mechanical level, it is clearly of importance to have a basis for understanding the electronic rearrangements

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which result in strong and stable chemical bonds at interfaces when an atom or molecule is brought close to the surface. The rearrangement of molecular and electronic structure to form new equilibrium geometries and chemisorbed species near the surface is an effect which will be of importance at a distance of about 1 to 3 Å from the surface. The quantum mechanical approach[3], including application of the density functional theory,[4,5] provides a theoretically sound basis for some of the semi-empirical methods which have been found to be remarkably useful in treating the short-range phenomena. These approaches, with particular reference to adhesion, have been reviewed recently by Lee.[6]

At the phenomenological level most of the focus has been on short-range interactions. For example, the recent text edited by Mittal and Anderson provides a useful and timely review of the state of the art in terms of generalized acid-base interactions.[7] In this view, the work of adhesion, W_A, between two phases is held to arise from a nonspecific Lifshitz-van der Waals contribution, W^{LW}, and any specific chemical interactions which are termed acid-base interactions in the generalized sense of a Lewis acid, so that

$$W_A = W^{LW} + W^{AB} \tag{1}$$

where W^{AB} is the Lewis acid-base contribution. Further, one may assume in analogy with the well-known Lorentz-Berthelot combining rules[8] which are common in liquid-state theory that the dispersion contribution is given by a geometric mean rule. Fowkes[9] put forward the idea that the acid-base contribution to the intensive reversible work of separating the adhesive-adherent interface could be written:

$$W^{AB} = fN(\Delta H) \tag{2}$$

where the intensive property ΔH refers to the molar enthalpy change, N is the number of moles of accessible functional groups per unit area on the solid surface and f is a factor which converts the enthalpy term to a free energy leading to the expression,

$$W_A = 2(\sigma_s^{LW}\sigma_a^{LW})^{1/2} + fN(-\Delta H) \tag{3}$$

where σ_s^{LW} and σ_a^{LW} are the Lifshitz-van der Waals contributions to the surface free energies of the adherend (solid) and adhesive, respectively. The first term in Equation (3) may not be quantitatively correct but should predict the correct trend and, in analogy with liquid mixture theory,[8] be good to perhaps something of order 10%.

In regard to the second term, it should be noted that one cannot turn an enthalpy into a free energy by multiplying by a factor. The entropy changes, ΔS, can in general be positive or negative and only in the case where $\Delta S = 0$ will $f = 1$. Urbanac and Berg[10] have tested Equation (3) and found f to be substantially less than unity (~ 0.2 to 0.6) and to exhibit a positive temperature coefficient. Clearly, the entropic term is important and the heuristic approach embodied in Equation (3) should be treated with caution.

Indeed, as we shall see there is clear evidence that surface-induced ordering is a quite common phenomenon and this provides a strong hint that the approximation $\Delta S = 0$ may not be a good approximation in general. While there are a large number of systems for which a treatment based on Equation (3) appears satisfactory, there are many instances where the inadequacy of this approach is clearly evident. Moreover, this type of phenomenological approach is not capable of providing even a qualitative picture of interphase formation and it is not possible to extend the treatment in a systematic fashion.

In terms of these chemical interactions, it is also important to bear in mind that chemical bonding will only occur over a distance scale of, say, 1–3 Å of the surface. Practical bondline thicknesses are typically of order 500 μm or 5×10^6 Å so that the actual distance scales over which these bondlines fail are millions of times greater than the distance scale over which the chemical surface interactions might be expected to be important. Failure often occurs both along the surface and into the bulk of the adhesive so that intermolecular forces, entanglement density, etc., should all be important factors. Add to this the uncertainties in surface morphology, the effects of surface defects, and the presence of voids and inhomogeneities in the adhesive and it is no wonder that fundamental progress in this area has been notably slow.

The Interphase

Notwithstanding the above comments it should be pointed out that the application of recent advances in the area of inhomogeneous fluids, polymers, and particularly in the dynamical theory of non-linear systems may provide the basis for the development of a theory of adhesion in which the chemical and mechanical aspects may be treated in a unified fashion. Each of these disciplines represents a substantial specialty and it is at first sight not particularly clear, for example, what relevance, if any, the area of liquid state theory or quantum mechanics has with regard to the structure, morphology or mechanical response of an adhesive film. The primary objective of the present paper is to demonstrate how new methods can be used to probe the microscopic structure of the interphase and to illustrate, using a simple model, how the incorporation of a fluctuation term in a non-linear analysis provides a plausible mechanism for the creation of a macroscopically thick interphase. The physics of the problem requires, of necessity, that a number of distance scales be discussed in terms of the underlying phenomena. In adopting this approach it should be recognized clearly that even though a fairly wide range of phenomena are addressed we are not attempting even a cursory review of the extensive literature but are endeavoring, rather, to highlight how a small number of new approaches provide insights which may form the basis for the development of a unified quantitative theory.

In this paper the focus is entirely on the physico-chemical aspects of the interphase though it should be mentioned that the same basic methodology can be applied to the mechanical aspects of adhesive science. For example, in a recent letter to *Nature*, Yuse and Sano[11] have reported a particularly insightful study of crack propagation and (often fractal) morphology. The scaling behavior of an appropriately defined relaxation time suggested that the transition between the various morphologies is a Hopf bifurcation "like those seen in a variety of other nonlinear systems". Also, there has been considerable recent interest in atomistic computer simulation of mechanical phenomena such as avalanche in adhesion,[12] shear-mediated instabilities,[13] and the mechanical response of solids.[14] In particular, Hoover *et al.*,[15] have conducted a careful study of indentation using both molecular dynamics and continuum Lagrangian mechanics and have remarked that "it is particularly interesting that the initial mirror symmetry of the atomistic indentation problem can be completely destroyed by thermal fluctuations. The underlying chaotic atomistic dynamics can have macroscopic consequences."

The surface region between the bulk adhesive and the adherend plays an important role in the strength and durability of a joint.[16] This region, which is now commonly referred to as the "interphase", is thought to extend from several to perhaps hundreds of nanometers from the surface. The interphase is characterized by differences in secondary and tertiary structure, composition, density and molecular weight distribution from the bulk adhesive. The surface effectively modifies thermodynamic and mechanical properties of the adhesive which in turn affects the strength and durability of a bond. However, it is not obvious how or why relatively thick interphases should form in adhesive systems.

The phenomena which govern the formation of the interphase are not well understood and in addition to the Lifshitz-van der Waals physical interactions, there are also strong chemical interactions. Previous work has indicated clearly that the chemical reaction mechanisms of reactive chemical species coming close to the surface are influenced by the presence of the surface itself.[17] The normal reaction pathways for, say, a curing epoxy resin, involve the nucleophilic attack of the amine group on the epoxide moiety with subsequent ring opening. It would seem plausible, for example, that one may have attack by oxygenated species on the surface on the epoxy moiety.

What has not been clear is how this sort of essentially short-range surface concentration fluctuation might couple to chemical kinetics and diffusional processes. In this paper, we address these physio-chemical issues from the standpoint of attempting to provide a somewhat more unified perspective. The paper is organized as follows. Section 2.0 introduces short-range phenomena and discusses, briefly, the current status in relation to quantum mechanical approaches. Section 3.0 discusses medium-scale phenomena both from the standpoint of analytic theory and presents our molecular dynamics numerical computer simulation results for reactive surfaces. Section 4.0 introduces nonlinear dynamics and illustrates how long-range structure and morphology may arise through coupling diffusion with reaction. A key element in this is the recognition that it is the very tiny statistical fluctuations in the local concentration or number density, that, under suitable circumstances, are amplified and may give rise to a particular sort of surface-induced morphology. Without preempting the results in Section 4.0, it might be mentioned here that such nonlinear effects may also be responsible for the ubiquitous formation of distinct macroscopic polymer morphology from what are originally homogeneous polymer melts. Polymer morphology and the interphase are intimately connected and the development of a quantitative theory connecting kinetics and morphology, both in the bulk and near surfaces, may help bridge a gap in our current understanding.

2.0 SMALL-SCALE PHENOMENA

The schematic shown in Figure 1 illustrates the distance scales involved. At distances of order 1.0 Å (1 nm = 10 Å) we are concerned with essentially short-range interactions which may be either physical or chemical. Surface chemistry is a dominant factor at these distance scales and many species will undergo electronic rearrangement and form

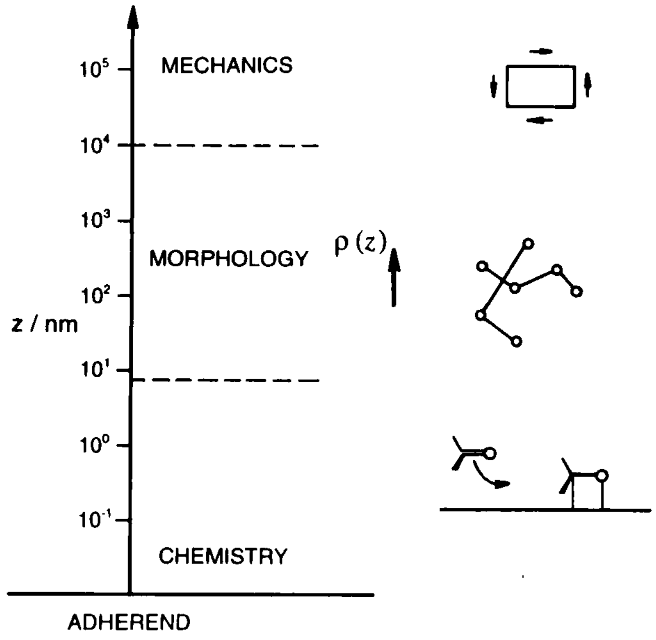


FIGURE 1 Distance scales of relevance in interphase and adhesion.

long-lived entities on the surface which may be capable of unique chemistry which gives rise to strong surface coupling. Indeed, it is precisely the presence of specific chemical acid-base type surface interactions which has given rise to the extensive literature and numerous useful empirical correlations of data. Over distance scales of perhaps 10 Å to 10,000 Å we are concerned with a distance scale where it is not the individual bonds between atoms which are of importance but rather how microscopic matter arranges its tertiary structure or morphology. Notice here that we still have no really satisfactory theory of polymer morphology over macroscopic (100 Å) distance scales. The longest distance scale in which we shall be interested is the region of about 10^6 Å by which point the usual bulk macroscopic descriptions apply. It is natural to attack the problem of the interphase from an eassentially reductionist view. For example, the time-dependent Schrödinger equation,

$$i\frac{\partial}{\partial t}|\Psi\rangle = H|\Psi\rangle \tag{4}$$

with

$$H = -\frac{\nabla^2}{2M} + v(r) \tag{5}$$

provides, in principle, an exact solution to the problem.

The most straightforward and certainly the most naive approach to a solution of the dynamical problem of adsorption of a large collection of molecules or other reactive moieties on a given surface is to attempt a solution of the time-dependent Schrödinger equation for the coupled system of solid plus molecule treated essentially as a "super molecule." This involves expansion of the total wavefunction for the coupled system into a complete orthonormal basis set and solving the secular determinant at discrete times. Since the basis set must be unusually large for an adsorption problem, and since the time to diagonalize the Hamiltonian goes as the cube of the number of terms in the basis set, such a "head on" approach is at present truly prohibitive in terms of computer time and is likely to remain so for the foreseeable future.

Given the well-known challenges associated with the direct approach, recent interest has focused on two related areas. The first is the solution of the time-dependent Schrödinger equation using the initial value approach. In this scenario, the time-dependent Schrödinger equation is viewed analogously to the classical Fickian diffusion equation (with the electronic probability density playing the role of a generalized concentration) and solved on a finite spatial mesh subject to some initial conditions for the wave packet. There are a number of ways in which this can be done and a number of efficient algorithms have been reported.[18,19] For example, the spatial derivative of the Laplacian $\nabla^2\Psi(r,t)$ in Equations (4) and (5) transforms in momentum space to $-|iq|^2\Psi(q,t)$, where q is the wavevector, so that the operation of taking a second derivative in real space is simplified to a multiplication. Fast Fourier transform routines are readily available so that the method has a number of advantages. There are a number of caveats, however, in that the transform of the pseudopotential terms may give rise to artifacts, including spurious periodicities, and some practitioners prefer a real space approach. This is of more than academic interest because, as we shall see later, it is precisely these very small-scale fluctuations which may be of central importance in determining the structure of the macroscopic interphase.

3.0 MEDIUM-SCALE PHENOMENA

When a polymer or any group of atoms comes close to a solid interface, the presence of the interface induces changes in the tertiary structure of the polymer. The theory of polymer surfaces and interfaces has been admirably captured in the recent monograph by Sanchez.[20] For non-linear systems the combination of molecular dynamics and scanning tunnelling microscopy provides unequivocal evidence for the formation of ordered structures near surfaces. Using the same computational methods detailed in Reference 21 we have investigated the conformational changes in relatively long (100 methylene units) polyethylene oligomers as they are brought close to a graphite surface. Figure 2a shows the conformation in the gas phase. The important point for our purposes is that the presence of the surface causes a perturbation in the local density close to the surface. This small-scale perturbation may provide the "nucleus" from which a macroscopically observable "skin" may grow. On approaching the surface (Figure 2b) the polymer adheres to the surface and for about sixteen methylene units remains commensurate with the underlying graphite lattice. At this point, the lattice mismatch induces a change in direction of the adsorption leading to an overall folding of the polymer on the surface. Also, as noted previously,[21] the presence of a surface causes physisorbed oligomeric fragments to straighten and stiffen. Experimentally it is

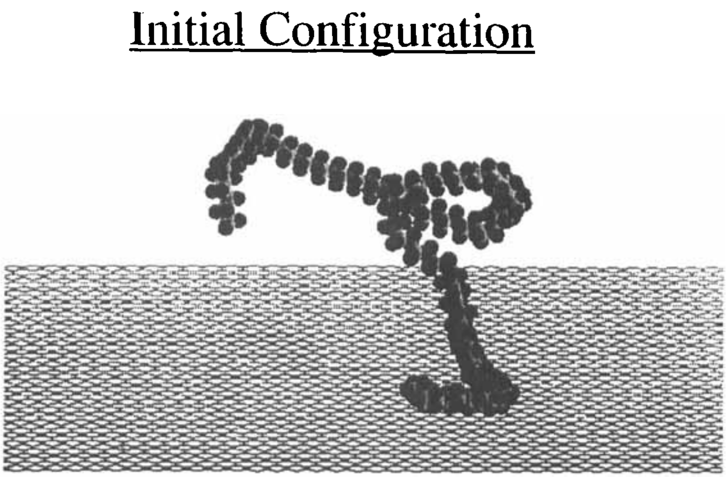


FIGURE 2a. Conformation of a polyethylene oligomer of 100 methylene units in the gas phase.

also found that surfaces induce order. Figure 3 shows an STM image of *n*-hexadecane on the surface of highly-ordered pyrolytic graphite. The alkane molecules adopt a rank and file structure which is very different from the bulk.

Molecular Dynamics Simulation

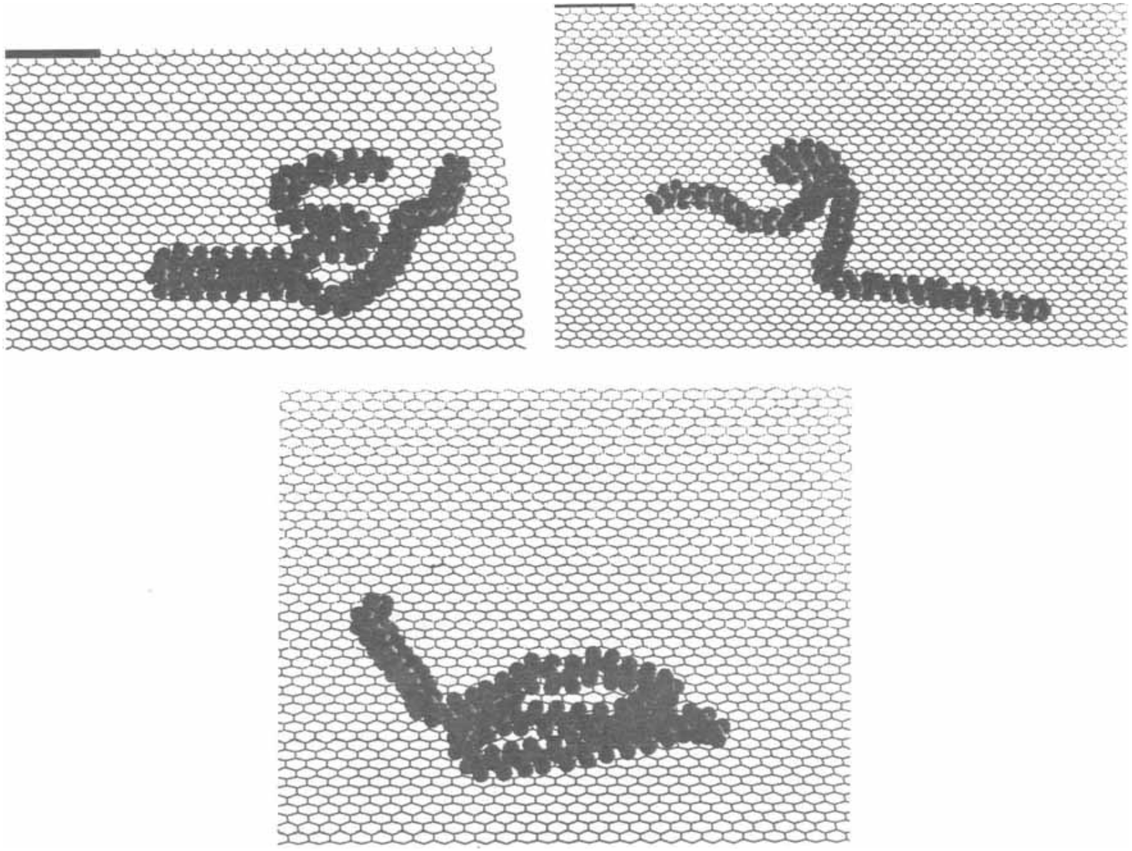
Molecular dynamics simulation is now a well-established method of investigating the macroscopic properties of N-body systems. The application of the technique to polymer-solid interfaces has recently been reviewed by Theodorou.[22] In this approach the interaction potential is assumed to be known and the N-body problem is solved numerically, subject to suitable initial and boundary conditions. While this technique is not in general very useful in the area of chemical reaction kinetics, where changes in chemical bonding occur, it can provide useful insights into the effects of various chemical structures and even strong specific interactions such as hydrogen bonds on the surface.

For example, van der Waals interactions may be represented through the Lennard-Jones potential

$$u(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{6}$$

where ε is the depth of the minimum in the potential energy well and σ is the collision diameter of the atom pair. A strong "chemical" interaction has large ε while a "weak" "physical" interaction has a small ε. The resultant force on each atom is obtained as a function of time from the vector sum,

$$\bar{F}_i = -\sum_j \nabla u(r_{ij}) \tag{7}$$



Configurations from Different Runs (50 ps)

FIGURE 2b Same oligomer adsorbed on a graphite surface. The final configurations from three runs are shown.

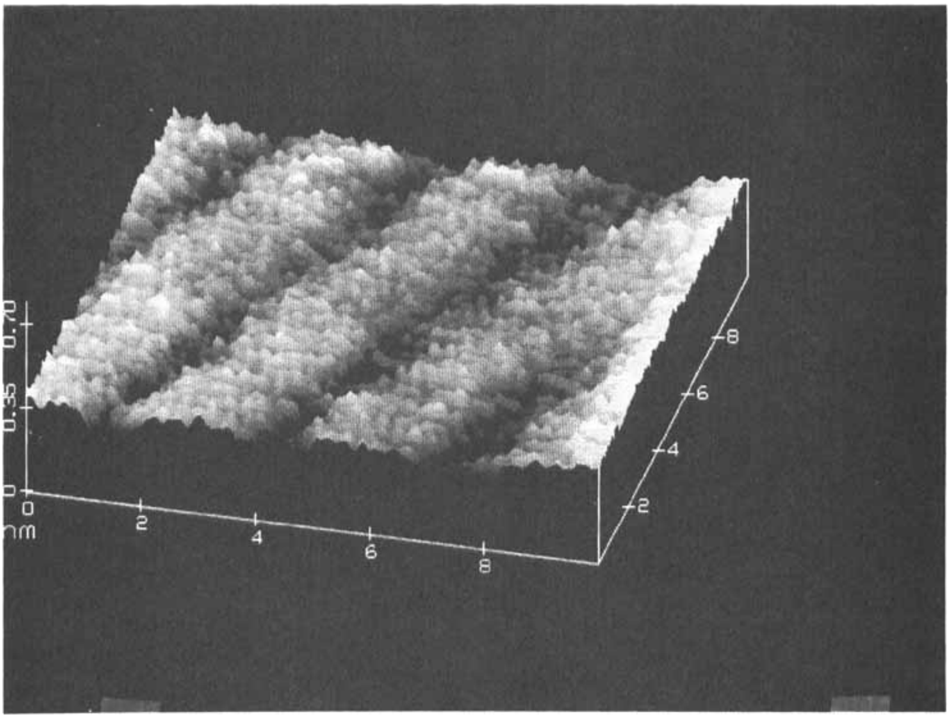


FIGURE 3 A scanning tunnelling microscope image of n-hexadecane on the surface of highly-ordered pyrolytic graphite.

Let us first consider the influence of a surface on the structure of a crosslinked epoxy network. The network was constructed solely from 54 monomers of the diglycydyl ether of bisphenol A (DGEBA) on an alumina surface. Though somewhat idealized it might be hoped that such a model will give a fair representation of the manner in which the structure of a network is altered by a surface. Since we are focusing on qualitative aspects of the structure modification the hydrogen atoms were removed in order to decrease computation time. The network was placed a few angstroms from the surface and a molecular dynamics simulation was performed for a duration of 12 ps at a temperature of 300 K.

A three-dimensional rendering of the network and the surface is shown in Figure 4. In Figure 5 the distribution of atoms in the network normal to the interface is shown. The distribution function is calculated by accumulating atoms in finite bins for each configuration and then dividing the number in each bin by the number of configurations. Therefore, the normalization factor for the distribution is the number of atoms in the network. The density profile may be obtained from the distribution by dividing by the volume of an individual bin. Such a distribution illustrates clearly the perturbations in the structure due to the surface. Notice that the density profile oscillates at several spatial frequencies. The distribution, which includes only the aromatic carbons, indicates that these atoms are responsible for the three peaks nearest the surface. This

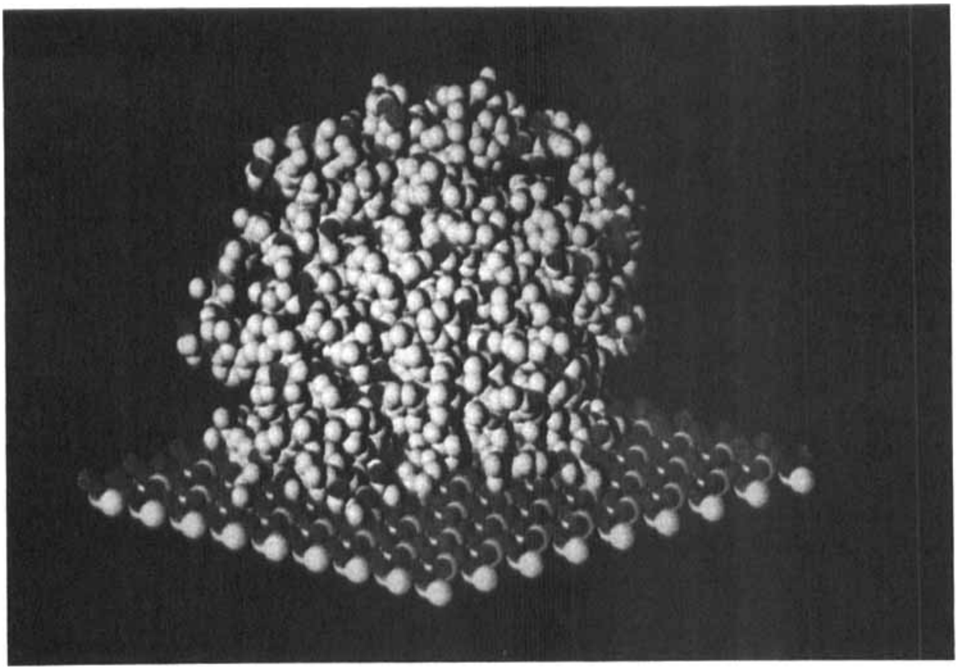


FIGURE 4 DGEBA monomers adsorbed on the alumina surface. In this figure, aluminum atoms are purple, oxygen atoms are red, and carbon atoms are grey.

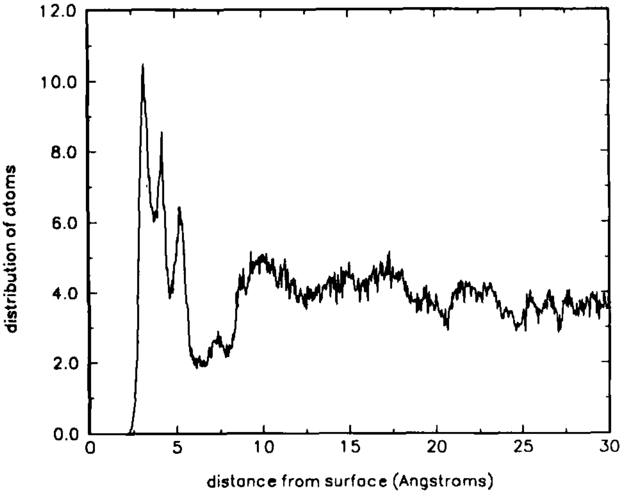


FIGURE 5 Total atomic distribution function calculated normal to the surface for the system depicted in Figure 4.

suggests that the aromatic rings have a preferred orientation that is parallel to the surface. The oscillations appear to decay to a bulk value at approximately 20 Angstroms from the surface. This behavior is qualitatively very similar to that which has been reported for simple model fluids (hard spheres) in contact with a wall.[23]

We now turn to the influence of specific interactions on the molecular structure of monomers at the alumina interface. In particular, the influence of hydrogen bonding on the internal molecular structure of DGEBA and diaminodiphenyl sulphone (DDS) monomers was investigated. We performed two sets of calculations involving systems consisting of eight DGEBA and eight DDS monomers adsorbing on alumina. In one case the alumina is hydrated by bonding one hydrogen atom to each oxygen on the surface. The duration of the simulations in each case was 12 ps and the temperature was set at 300 K. Figure 6 shows an illustration of the material adsorbed on the alumina.

In Figure 7 the atom distributions near each surface are compared. Overall the profiles for each surface are similar. The influence of the specific interactions is illustrated by the atomic distributions. Figure 8 compares the distributions of the epoxide oxygen for each surface. While the epoxide oxygen appears to have no strong preference for the nonhydrated surface, its distribution is sharply peaked very close to the hydrated alumina surface. This strong preference is due to strong hydrogen bonding interactions between the epoxide oxygen and the hydrogen on the surface. The sulfur distribution for each surface is shown in Figure 9. Again we see a large peak close to the surface in the distribution for the hydrated alumina. Note also that the amine is

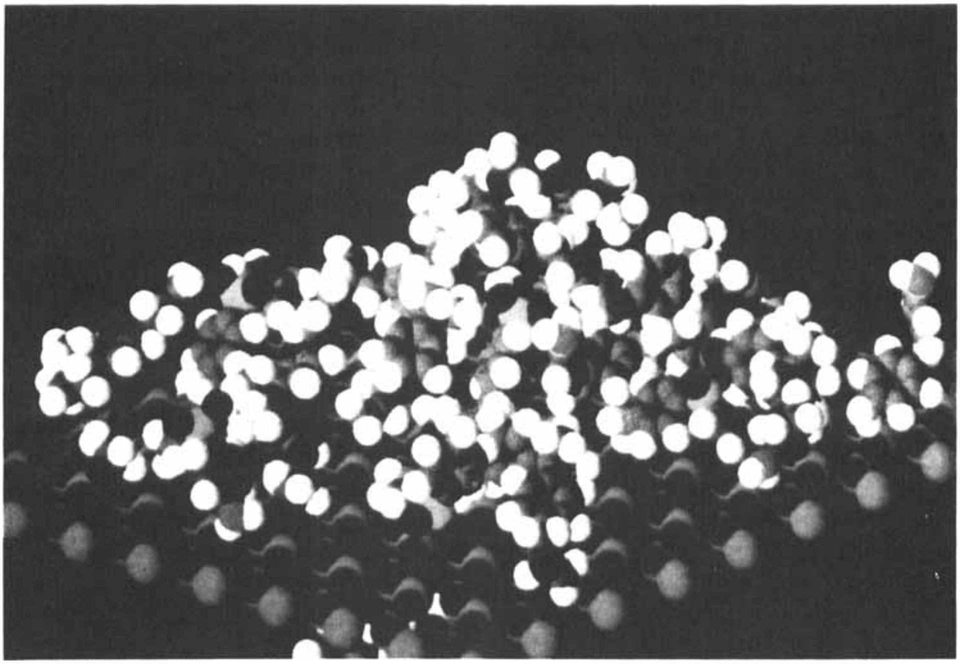


FIGURE 6 Eight DGEBA and eight DDS monomers adsorbed on the alumina surface. In this figure, hydrogen atoms are white, sulphur is yellow and nitrogen is blue.

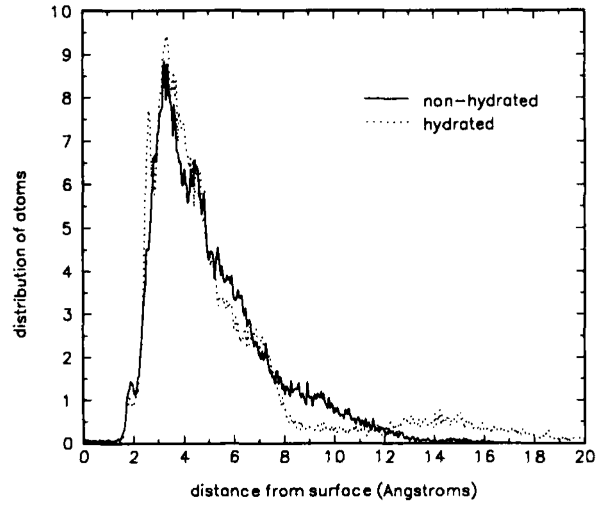


FIGURE 7 Total atom distributions as a function of distance from the surface for both hydrated and nonhydrated alumina surfaces.

preferentially adsorbed on both surfaces since the profile indicates no DDS molecules migrated beyond 9 Å .

There are three points to be made. First, for the surface with nonspecific chemical interactions (in this case no hydrogen bonding) the atomic site density profile shows clearly a number of characteristic oscillations. The presence of the surface induces these oscillations which have a form and range which is very reminiscent of the surface density profile for a simple fluid. This finding is in agreement with the results of Mansfield and Theodorou[24] who have reported a similar calculation for glassy atactic

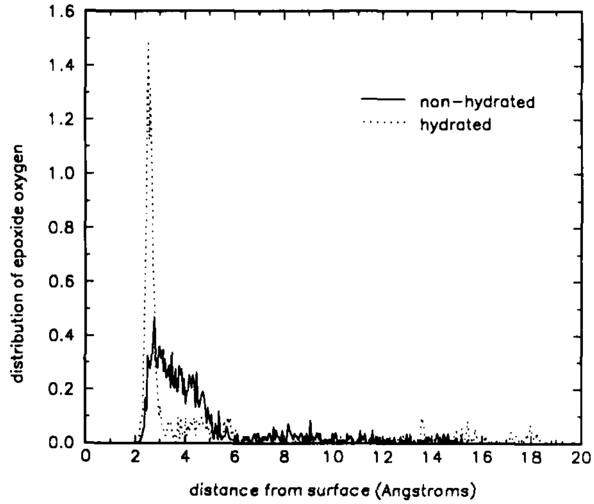


FIGURE 8 Distribution of epoxide oxygen for hydrated and nonhydrated alumina surfaces.

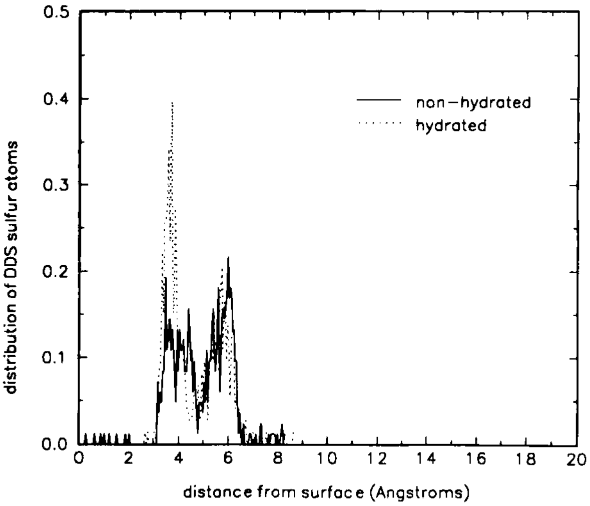


FIGURE 9 Distribution of sulfur atoms in DDS as a function of distance from the surface for hydrated and nonhydrated surfaces.

polypropylene on the basal plane of graphite. Notice, however, that the distance scale of these density fluctuations is small (less than about 20 Å). Experimentally it is difficult to find evidence for density variations over these distance scales. For example, in a series of careful experiments using neutron reflectivity Wu[25] has investigated the density profile of a deuterated film of highly monodisperse poly(methylmethacrylate) (PMMA) on a silicon single crystal wafer. While the technique showed clearly the differences in surface density profile as a function of temperature, the technique did not show evidence of fine structure in the density profile over these short distance scales. Secondly, when specific chemical interactions such as hydrogen bonding play a role the surface density function is modified, sometimes considerably. The third and most important aspect of this molecular dynamics work on "medium-scale" distances in relation to the interphase is that there remains a fundamental difficulty. This pertains to the nature and range of the interphasal region. Our simulation results and those of others[22] have shown quite unambiguously that the surface induces spatial density patterns in the neighborhood of the surface. These have a range of order 25–30 Å which is clearly much longer than the length of a chemical bond (1–2 Å) so we have a rationale as to why the interphase region is significantly longer than the length of chemical interactions.

However, the most important point relates to the pressing question of the width and macroscopic morphology of the macroscopic interphase region. A recent compilation[26] of papers from a meeting entitled, "Controlled Interphases in Composite Materials" contains over eighty papers devoted to this topic. While there is a huge body of experimental study, there is no theory which can treat some of the diverse observations within a unified framework. For example, powerful techniques such as X-ray absorption fine structure have been applied to composite interfaces and spatial correlations of order 10 Å have been discerned experimentally.[27] Graphitic/polymer interfaces have been probed using infrared mapping and interphase thicknesses of order 10 μm have been observed.[28] Similarly, microscopic observation of the growth of the transcrystalline regime in thermoplastic systems on the order of 25 μm and the formation of nuclei in the bulk polymer suggest rather strongly that the underlying fundamental mechanisms may be similar. It might be added that even a cursory inspection of the shapes of the transcrystalline front[26] and bulk nuclei strongly suggest a fractal nature to the process and the prospect of underlying non-linear dynamics of the sort outlined in this paper. Note that our profiles are uniform beyond 20 Å and it is not likely that molecular dynamics, or current theory based on inhomogeneous fluids approaches, could be useful in probing such thick interphases. For this reason, we have examined the possible role of nonlinear dynamical aspects of interphase formation. When these phenomena are included, it turns out that not only can we provide plausible rationale for many aspects of interphase formation but also touch on the more general question of the relationship between polymer processing and polymer morphology.

4.0 MACROSCOPIC

In this section, we present a simple model for interphase formation which is based essentially on the ideas developed in the area of nonlinear systems. The model is of a very general nature and may be applicable to a broad range of systems. In the present work we illustrate the general features.

Nonlinear Chemical Kinetics

Many adhesives are applied as liquids (or applied as films and melted) and undergo a polymerization reaction while being held in intimate contact with the surfaces of the adherend. The formation of an adhesive bond, therefore, involves consideration of a complex system which is not in chemical equilibrium. In this section we shall consider under what circumstances such a system could exhibit density or concentration fluctuations in both space and time. For concreteness, we shall apply the analysis to polyimides.

For a large class of polymeric resins, it has been found that the solution of the fully-coupled kinetic model can be summarized in a simple parametric form,[29]

$$\frac{d\alpha}{dt} = k\alpha^m (1-\alpha)^n \tag{8}$$

where k is a rate constant and m and n are constants. Equation (8) has a particularly suggestive form in that for $m = n = 1$, it reduces to the logistic equation of classical ecology. The latter is prototypical in the study of deterministic chaos[30] in nonlinear systems and it is this aspect which we wish to explore in relation to the interphase. For $m = 1$ and $n = 0$ we have the usual exponential growth. It has been found experimentally that $m = 0$, $n = 3$ describes the cure of PMR-15 polyimide very well.[29] With these values for m and n the integral of Equation (8) is,

$$\alpha(t) = 1 - \left(\frac{1}{2kt+1}\right)^{1/2} \tag{9}$$

The rate constant k may be approximated by the Arrhenius expression,

$$k = Ae^{\frac{-\Delta\varepsilon}{\beta T}} \tag{10}$$

where A is the so-called pre-exponential factor, β is Boltzmann's constant, T is the absolute temperature, and $\Delta\varepsilon$ is the activation energy. Substituting Equation (10) into Equation (9) provides the traditional, if somewhat naive, prescription for "predicting" the dependence of the degree of cure, α, on temperature and time, i.e.,

$$\alpha(t, T) = 1 - \left(2tAe^{-\frac{\Delta\varepsilon}{\beta T}}\right)^{-1/2} \tag{11}$$

This is the usual analytic from of the models of adhesive cure for polyimides. The essential points to note for present purposes are (a) the degree of cure appears deterministic at the start of the cure, $t = 0$, $\alpha = 0$, and in the limit, $t \to \infty$, $\alpha \to 1$, with a rate which accelerates with temperature, and (b) Equation (8) is totally symmetric in that the degree of cure in any volume element of the adhesive is supposedly given by Equation (11), i.e., there is nothing in the kinetic description which breaks the spatial symmetry of the system and would allow α to become a function of distance from the surface as well as temperature and time.

It is essential to recognize that under some circumstances, indeed, under most if not all circumstances, this kind of treatment may be totally inadequate to describe what is actually happening, not only in the bulk adhesive but especially close to a surface.

At this point it is useful to introduce some terminology from the area of nonlinear systems. Defining $f(\alpha) = d\alpha/dt$ and representing the n^{th} iterate (not the n^{th} power) of $f(\alpha)$ as $f^n(\alpha)$, we may map Equation (8) as shown in Figure 10. What we mean by $f^n(\alpha)$

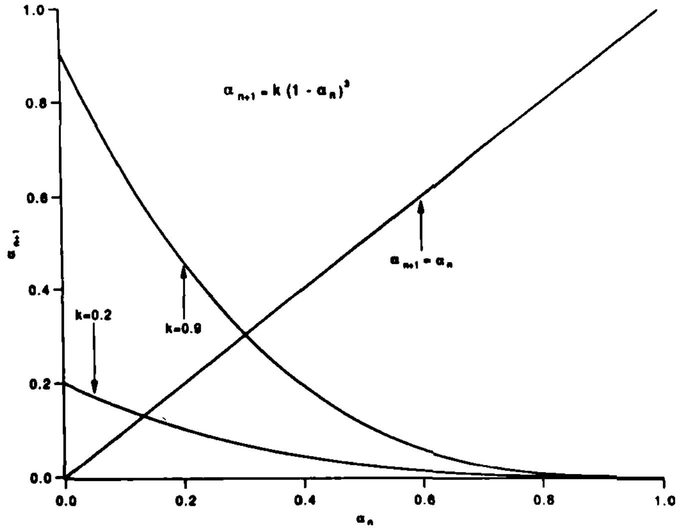


FIGURE 10 The logistics map of Equation (8) for values of the rate constant $k = 0.2$ and $k = 0.9$. In this figure, α at the n interval of time is plotted on the abscissa and α at the $n + 1$ interval is plotted on the ordinate.

is that the $n+1$ value of α should be determined from the n^{th} value. For example, if $f(x) = x^2$, $f^2(x) = [x^2]^2$, $f^3(x) = \{[x^2]^2\}^2$, etc. A convenient way to map the cure function for the polyimide is to plot α_{n+1} vs α_n and draw the diagonal $\alpha_{n+1} = \alpha_n$. In Figure 10 we have plotted the logistics maps of Equation (8) using the representation which has been developed in the area of nonlinear systems. In this figure, the degree of cure, α_{n+1}, on the ordinate is that expected at a short time after the degree of cure, α_n, plotted on the abscissa, i.e., the plot is the right-hand side of Equation (8). Using literature values for A and $\Delta\varepsilon$ in the equation, then we obtain the series of curves shown in the figure. These curves represent the rate of cure as a function of temperature. The particular values of A and $\Delta\varepsilon$ for the cure of PMR-15 are 2.023×10^{11}/sec and 104.01 kJm/mole, respectively.[29] Figure 11 shows the iteration map for the low vlue of $k (= 0.2)$ which corresponds to a temperature of 453 K. Starting on the abscissa at any convenient (low) level of $\alpha (= 0.05)$ one goes vertically to the curve to determine the new $(n+1)$ value of α. This is the value of α which should be used as the next "initial" value so that now we go horizontally to the diagonal line $(\alpha_{n+1} = \alpha_n)$ as the starting point and read the next value from the cure curve. The interesting point to note is that when $k < 0.6$ (i.e., the temperature is below 470 K), the function is stable and the function has a fixed point. However, as the value of k is increased above 0.6, corresponding to raising the temperature above 470 K, the cure kinetics become unstable. At high values of k the situation is quite different as shown in Figure 12. It is clear from this figure that the system has bifurcated with final α values grouping around high values of ~ 0.89 and low values of ~ 0.001. The kinetics are quite unstable at high value of the rate constant. In Figure 13, we have summarized the situation in which the final degree of cure is plotted, not as a function of temperature or time, but rather as a function of k and the bifurcation point at 0.59 is clearly evident. Notice, in particular, the unstable branch and the quite different behavior from that predicted by the conventional model. If we

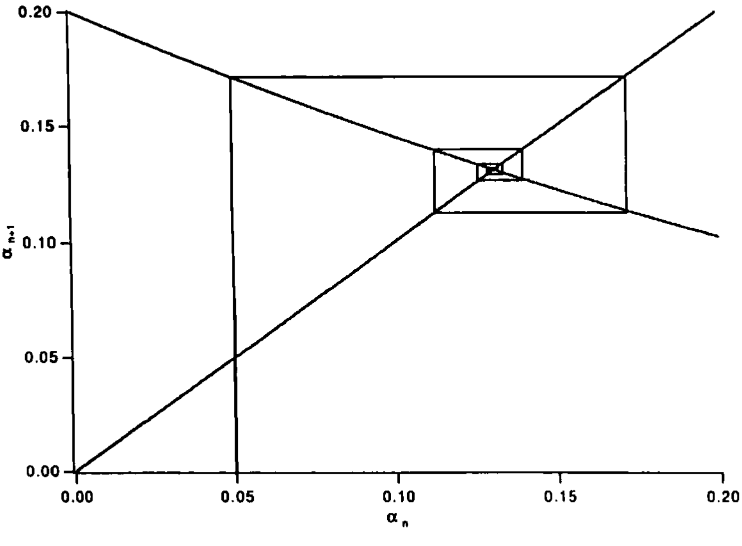


FIGURE 11 Iteration map of Equation (8). Notice that when the slope of $\alpha_{n+1} = \alpha_n < 1$ the function converges to a fixed point.

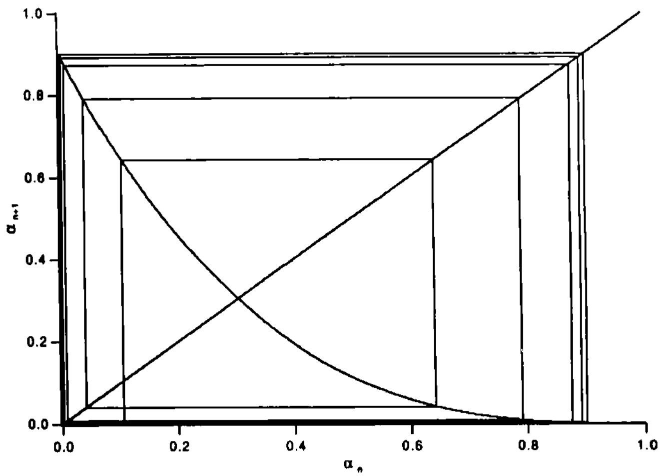


FIGURE 12 Final values of alpha = 0.001 and 0.89 are obtained from an initially low value for α ($\alpha_0 = 0.1$).

envisage α as a generalized concentration, one may write

$$\frac{d\alpha}{dt} = \nabla D \nabla \alpha + \frac{d\alpha'}{dt} \tag{12}$$

where $d\alpha'/dt$ is a source term given by Equation (8) and the $\nabla D \nabla \alpha$ term is the usual Fickian diffusion term.

By virtue of the fact that Equation (8) is nonlinear and, as demonstrated above, exhibits essentially temporal instability, so too is Equation (12) also nonlinear and may

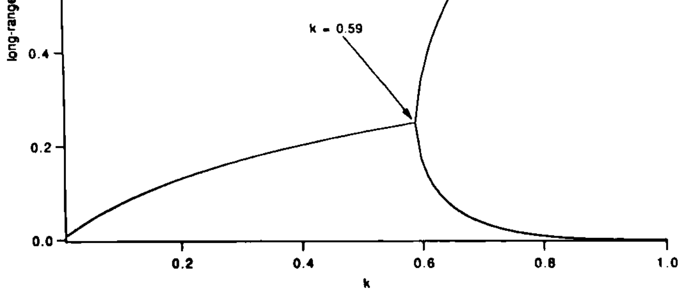


FIGURE 13 Bifurcation diagram for polyimide adhesive showing point of instability.

display both temporal and spatial instability. However, it is important to recognize that while the presence of an instability is a necessary condition for this type of interphase formation it is not sufficient. It is clear from an inspection of Equation (12) that the spatial symmetry of the concentration is not broken and that while the magnitude of change of concentration in a given volume element will be affected by the source term, the gradient in concentration will not be affected. In order to exhibit a propagating instability the symmetry of Equation (12) must be broken by a statistical fluctuation term. In the most general case the magnitude and symmetry of these fluctuations will have an important bearing on the range and structure of the interphase and in this sense it is the nature of these very small-scale fluctuations which should be the object of our primary interest. For present purposes it is merely necessary to recognize that such a term will be responsible for the final overall pattern. Accordingly, we may write

$$\frac{d\alpha}{dt} = \nabla D \nabla \alpha + \frac{d\alpha'}{dt} + \frac{d\alpha''}{dt} \tag{13}$$

where $d\alpha''$ is the very small fluctuation in concentraion due to atomic level fluctuations in the local concentration. Notice also that, in order to be strictly correct, we should replace the $\nabla\alpha$ term with the gradient in the chemical potential. This will take account of specific chemcial interactions but this aspect will not be pursued here.

Also, the gradient will be different in the direction normal to the surface. Local variations in surface chemical structure and morphology will thus be reflected in short-distance effects in this term. The important point for our purpose is the recognition that it is the potential instability associated with the second term on the right-hand side of Equation (13) which provides a driving force for interphase formation. While this term gives rise to the bifurcation, it is the third term, the small fluctuation term, which governs the spatial variation in concentration. In order to illustrate these effects we have solved Equation (13) using kinetic data approximating the polyimide PMR-15. Two sets of boundary conditions were used, namely the ring and the hard wall. The former corresponds to a one-dimensional representation of an infinite, i.e., bulk system, while the latter corresponds to conditions more representative of a bondline.

In each case, 100 volume elements were considered corresponding to a system length of 100 microns. The diffusion coefficient was fixed at the value 0.001 and the time step for the calculation was 6 sec. The numerical scheme for the solution of Equation (13) is outlined in the Appendix.

In our solution of Equation (13), the resin was heated to close to the point of instability, starting from a completely uncured state. A small fluctuation was then applied. It is this small fluctuation which couples to the nonlinear source term and gives rise to the microscopic gradients which result eventually in a long-range variation in the density. This is shown in Figure 14 for both the ring and wall system, where it is seen that, under suitable conditions, concentration or density variations may extend for many microns. The observation of such a pattern is usually termed morphology so that the model embodied in Equation (13) apparently captures the essential physics of how morphology, i.e., spatial inhomogeneity, develops from initially homogeneous adhesive systems. Notice that the morphology close to the wall is different from that in the

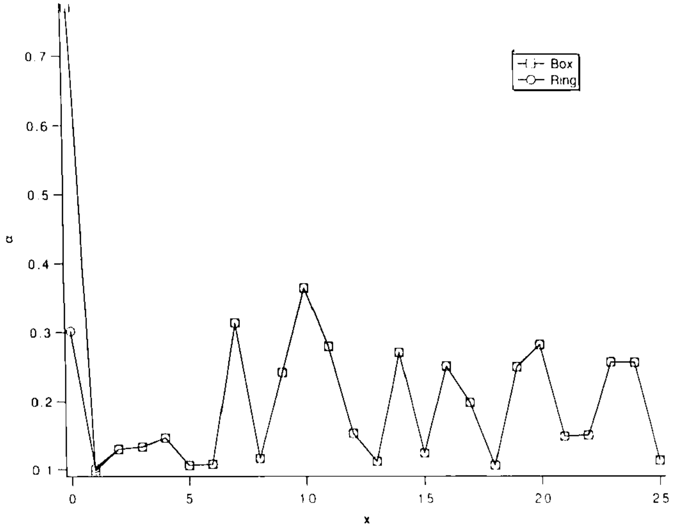


FIGURE 14 Model calculation of the generalized density profile for a system in a ring —O— (i.e., with no boundary effects) and in a box —☐—.

bulk. The essential point is that it is very small perturbations associated with fluctuations on an atomistic scale, i.e., the dα''/dt term, which couple to the nonlinear term and are thereby amplified in both magnitude and range.

We have concentrated here on the effects of reactivity for, after all, real adhesives do undergo cure reactions. It is, however, worth pointing out that nonlinearity may also arise by virtue of the gradient in the chemical potential term and this will always be present in the interphase. Also, the instability has the effect of amplifying the very small fluctuations due to atomic motions and in this respect the bulk large-scale morphology is a reflection of the tiny atomistic fluctuations. As discussed earlier, these can be calculated using quantum mechanical and molecular dynamics methods so that we have, in fact, the essential theoretical apparatus required to bridge the gap in the distance scales.

Acknowledgement

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Note Added in Proof

In recent experimental studies Strålin and Hjertberg, (*J. Adhes. Sci. Technol.* **6**, 1233 1992; *J. Adhes.* **41**, 51, 1993) have found that a well bonded oxy-hydroxide (psuedoboehmite) interface promotes strong bonds. This is full agreement with our model calculations (Figure 8). The authors would like to thank Dr. Geoffrey Dearnaley RFS for bringing these references to our attention.

NOTATION USED

W_A	Work of adhesion
W^{LW}	Lifshitz-van der Waals contribution to the work of adhesion
W^{AB}	Lewis acid-base contribution to the work of adhesion
f	Enthalpy to free energy conversion factor
N	Number of moles
ΔH	Molar enthalpy change
σ_s^{LW}	Lifshitz-van der Waals contribution to the surface free energy of the solid
σ_a^{LW}	Lifshitz-van der Waals contribution to the surface free energy of the adhesive
ΔS	Entropy change
i	The square root of -1
$\lvert\Psi\rangle$	Quantum-mechanical wave function
H	Hamiltonian operator
$v(r)$	Potential energy of the system
∇^2	Del squared operator-the gradiant operator dotted with itself
M	Mass of the system
$u(r)$	Potential energy of the system as a function of position
ε	Depth of the minimum in the potential energy well
σ	Collision diameter of the atomic pair in the Lennard-Jones potential
$\bar{F}_i$	Force on the ith atom
$\sum_j$	Summation over j
∇	The gradient operator
α	Degree of cure
k	Rate constant
m, n	Constants
t	Time
$\Delta\varepsilon$	Activation energy
β	Boltzmann's constant
T	Absolute temperature
$f^n(\alpha)$	The n^{th} iterate of a function of α, $f(\alpha)$
D	Diffusion constant

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APPENDIX

The solution of Equation (15) is, in principle, straightforward. Expanding α in terms of the spatial coordinate

$$\alpha(x+\Delta x)=\alpha(x)+\frac{\mathrm{d}\alpha}{\mathrm{d}x}\Delta x+\frac{1}{2}\frac{\mathrm{d}^2\alpha}{\mathrm{d}x^2}(\Delta x)^2+\cdots \tag{A1}$$

and

$$\alpha(x-\Delta x)=\alpha(x)-\frac{\mathrm{d}\alpha}{\mathrm{d}x}\Delta x+\frac{1}{2}\frac{\mathrm{d}^2\alpha}{\mathrm{d}x^2}(\Delta x)^2-\cdots \tag{A2}$$

Adding Equations (A1) and (A2) and rearranging terms gives the second difference equation

$$\frac{\mathrm{d}^2\alpha}{\mathrm{d}x^2}=\frac{1}{(\Delta x)^2}\{\alpha(x+\Delta x)-2\alpha(x)+\alpha(x-\Delta x)\}. \tag{A3}$$

Notice that the cubic term vanishes and Equation (A3) is accurate to order $\sim(\Delta x)^4$. Similarly,

$$\alpha(t+\Delta t)=\alpha(t)+\frac{\mathrm{d}\alpha}{\mathrm{d}t}\Delta t+\frac{1}{2}\frac{\mathrm{d}^2\alpha}{\mathrm{d}t^2}(\Delta t)^2+\cdots \tag{A4}$$

Using Equations (A3) and (A4) one may write the Fickian term

$$\alpha(x,t+\Delta t)=\alpha(x,t)+\frac{D\Delta t}{(\Delta x)^2}\{\alpha(x+\Delta x,t)-2\alpha(x,t)+\alpha(x-\Delta x,t)\}. \tag{A5}$$

For a given time step, Δt, and mesh size, Δx, Equation (A5) provides a convenient solution when initial conditions are given. The reactive term in Equation (13) is given by Equation (8) with $m=0$ and $n=3$, which may be written

$$\alpha'(x,t+\Delta t)=\alpha'(x,t)=k[1-\alpha'(x,t)]^3\Delta t. \tag{A6}$$

In a given volume element at time t the total $\alpha_{\mathrm{T}}(\mathrm{x},\mathrm{t})$ is the sum of the diffusive, reactive and fluctuation terms

$$\alpha_T(x,t)=\alpha(x,t)+\alpha'(x,t)+\alpha''(x,t). \tag{A7}$$

For simplicity we have set $\alpha''(x,t)$ at the small value $\pm 10^{-4}$ and applied this perturbation to each volume element in the bulk system. Near the surface the fluctuations was $\pm 10^{-3}$. Notice that far from the bifurcation point this term rapidly decays and the system reacts essentially uniformly. Close to the point of bifurcation the normally small fluctuation may be sufficient to bring the system into the unstable regime and these small fluctuations may grow. Also, it is plausible to assume that fluctuations near a surface will be different from that in the bulk so that such tiny effects may have macroscopic consequences. Clearly, a lot of work needs to be done in relation to quantifying the precise magnitude and symmetry of such fluctuations. For present purposes it is sufficient to note that it is the size of the fluctuation relative to the distance from the point of bifurcation which is of central import- ance, for as one approaches the "critical" point even an infinitesimal fluctuation can grow.

Finally, it is important that D, Δt and Δx be chosen such that the solution to Equation (A7) is numerically stable.[31] In the present case we have chosen these values to be qualitatively illustrative and numerically stable without attempting to model a particular material.