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LATTICE DEFECTS AS LOTKA-VOLTERRA SOCIETIES

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Abstract

Since the early part of this century the Lotka-Volterra or predator-prey equations have been known to simulate the stability, instability, and persistent oscillations observed in many biological and ecological societies. These equations have been modified in many ways and have been used to model phenomena as varied as childhood epidemics, enzyme reactions, and conventional warfare. In the work to be described, similarities are drawn between various lattice defects and Lotka-Volterra (LV) societies. Indeed, grain boundaries are known to "consume" dislocations, inclusions "infect" grain boundaries, and dislocations "annihilate" dislocations. Several specific cases of lattice defect interaction kinetics models are drawn from the materials science literature to make these comparisons. Each model will be interpreted as if it were a description of a biological system. Various approaches to the modification of this class of interaction kinetics will be presented and discussed. The earliest example is the Damask-Dienes treatment of vacancy-divacancy annealing kinetics. This historical model will be modified to include the effects of an intermediate species and the results will be compared with the original model. The second example to be examined is the Clark-Alden model for deformation-enhanced grain growth. Dislocation kinetics will be added to this model and results will be discussed considering the original model. The third example to be presented is the Ananthakrishna-Sahoo model of the Portevin-Le Chatelier effect that was offered in 1985 as an extension of the classical Cottrell atmosphere explanation. Their treatment will be modified by inclusion of random interference from a pesky but peripheral species and by allowing a rate constant to be a function of time.

Introduction

The early works of Malthus [1,2] and Verhulst [3,4] were concerned that a population can evolve in number faster than crops can be grown and reaped to feed the individuals comprising the population. As direct consequences of their works come the terms "Malthusian" (exponential) and "logistic" (saturable) growth. These matters prompted considerable effort [5] in modeling the evolution of species populations that was crowned by a small report by Lotka that went largely unnoticed and unappreciated [6]. Lotka, who was trained as a chemist, used the law of mass action to suggest that autocatalytic chemical reactions could sustain damped oscillation. Later Lotka [7] demonstrated that his system of kinetic equations exhibited sustained oscillation and simulated a type of biological coupling that is now referred to as the predator-prey model. Independently, and with probabilistic reasoning, the famous Italian mathematician, Volterra [8] arrived at similar equations for the description of biological interactions. The Lotka-Volterra (LV) equations are a coupled set of nonlinear ordinary differential equations for the rate of evolution of two interdependent populations. They are usually written as

$$\frac{dx}{dt} = k_1 x - k_2 xy$$

$$\frac{dy}{dt} = -k_3 y + k_4 xy$$

where x is the relative density (concentration) of species 1, y is the concentration of species 2, t is time, and the k_i are rate constants. Lotka demonstrated that these equations can exhibit sustained oscillations but conjectured that the conditions necessary would only occur rarely in real situations. Indeed, evidence for sustained oscillation did not appear in the chemical literature until decades later [9] because chemists believed (wrongly) that such oscillations were a violation of the second law of thermodynamics. The LV set, and modifications thereof, did receive the attention of mathematicians who appreciated that the RHS possesses terms that capture life's aspects including birth, competitive interaction, disease, and death. These aspects and algebraic terms can be found in many of the models used in materials science to describe the evolution of lattice defect populations. For example, the Gilman-Li equation [10,11] for dynamic recovery of dislocation density has the precise form as the Verhulst description of logistic population growth. Consequently, the purpose of this work is to explore the similarities among three lattice defect models, taken from the materials science literature, and LV type equations. The three models will also be modified by employing the same criticisms and techniques used by mathematicians, biologists, etc. to examine what new behavior might be exhibited.

The earliest example of an evolutionary lattice defect model the author could find in the literature is the Dienes-Damask treatment [12,13] of vacancy annealing kinetics. This historical model will be modified to include the effects of an intermediate species and the results will be compared with the original model. The second example to be examined is the Clark-Alden model [14] for deformation-enhanced grain growth. Vacancy-dislocation interaction kinetics will be added to this model and results will be discussed considering the original model. The third example to be presented is the Ananthakrishna-Sahoo model [15] of the Portevin-Le Chatelier effect that was offered as a kinetic description of the classical Cottrell atmosphere explanation. Their treatment will be modified by inclusion of a random interference from a pesky but peripheral species known to most experimenters.

Biological Interpretation Of Lattice Defect Interactions

The designation "genus" is used in biology to describe a group or class of species with common characteristics. In materials science we are accustomed to 4 genus categories of lattice defects; point, line, surface, and volume. The term "phylum" is used in biology to describe descendants or related members of a given genus. In materials science we have vacancies, interstitial impurities, and substitutional atoms belonging to the "point" genus, edge, screw, partial dislocations, and disclinations in the "line" genus, stacking faults, grain and twin boundaries in the "surface"

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genus, and voids, precipitates, and inclusions in the "volume genus." The kinetics of interaction between these various lattice defects also shares certain similarities with biological interactions. As mentioned above, the Verhulst equation was one of the first to describe the evolution of populations. This equation takes the form

$$\frac{dx}{dt} = ax(1 - \frac{x}{x_s})$$

where a is a rate constant and x_s is the maximum number of individuals supportable by the population. The interpretation of this simple expression is typically that individuals are "born" at a rate proportional to its current size and are "crowded out" at a rate proportional to $-x^2$. The population of the United States, shown in Fig. 1, is shown fitted with the logistic model so it can be stated, with some degree of accuracy, that the Gilman-Li equation can be used to predict the future population trends of our country! With use of an "eyeball" fit of the data the Gilman-Li equation predicts that the U.S. will saturate at 335 million citizens and will reach 98% of that limit by the year 2085.

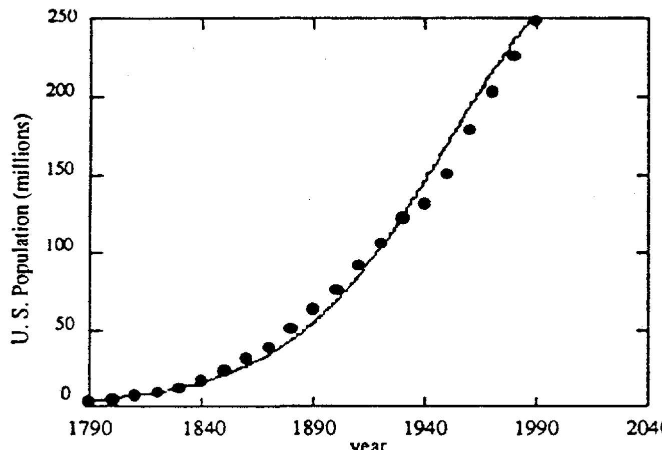

Fig. 1- Data from the U. S. Census Bureau on the population of the United States beginning in the year 1790 fitted with the Gilman-Li equation. The saturation population of the U.S. is predicted to be 335 million.

Depending on the application, alternate terminology for the algebraic terms in rate equations can be found, for example, the "kill" rate in cannibalistic society would be proportional to $-x^2$, while in the Gilman-Li model the term "immobilization" is appropriate. In a population of two species a term like $-xy$ is usually used to simulate the "consumption" rate of one species by another and with a positive sign the term indicates that one of the species "thrives" upon the other. These interpretations are those used in the LV predator-prey model. Alternate algebraic forms for the same terminology can be found. For example, it is easy to see that terms like x^2 or xy can also represent birth rate. Immigration and emigration into societies are often represented by constants, death by natural causes by $-x$, and the rate of infection of a healthy population by a diseased species is often described by xy. Regardless of the application, these models usually find swift and appropriate criticism even when the models appear successful in simulating experimental data. Of course this is to be desired because improvements to the models generally follow. Criticism of the LV equations has included the lack of population size dependence (logistic behavior), individual uniformity (no age, sex or virility), and no heredity or delay effects. Modifications to the LV equations (and other similar models) have included higher dimensionality (more than 2 species), inclusion of higher order terms (e.g. x^2y), and additional effects such as diffusion, convection, and fluctuation. In the following, three models for the kinetic evolution of lattice defects will be examined and modified with the intention of continuing the analogy with LV-like equations.

The Dienes-Damask Model

In their 1961 paper Dienes and Damask (DD) modeled the annealing kinetics of excess monovacancies and divacancies in a pure lattice [13]. The excess concentrations were assumed to have been created by quenching from an elevated temperature. Written as a chemical reaction their model reads

$$V + V \overset{k_1}{\underset{k_2}{\Leftrightarrow}} D$$

$$V \xrightarrow{k_3} sinks$$

$$D \xrightarrow{k_4} sinks$$

and from the law of mass action the associated kinetics are

$$\frac{dV}{dt} = k_2 D - k_1 V^2 - k_3 V \quad (1a)$$

$$\frac{dD}{dt} = \frac{1}{2} k_1 V^2 - (\frac{1}{2} k_2 + k_4) D \quad (1b)$$

where V and D are the excess atomic fractions of monovacancies and divacancies, respectively. With use of the rate constants and initial conditions provided by DD the rate equations were numerically integrated and are shown in Fig. 2.

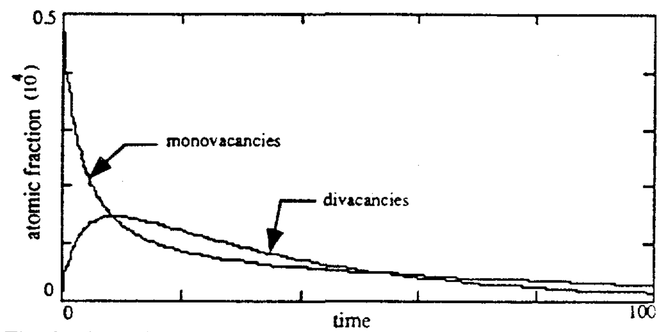

Fig. 2- Numerical solutions to the Dienes and Damask model for annealing of excess mono and divacancy populations.

This set of reactions, especially the two leading terms in eqs. (1), need a biological interpretation and this will be provided after discussing a modified Dienes-Damask model.

A Modified Dienes-Damask Model

To create a simple modification of the DD model an "immigration" term could be added to eq. (1a). In reality this term might be the result of radiation exposure that creates monovacancies at a constant rate such that steady state concentrations of both defects would be observed after a sufficiently long anneal. These steady state values have been calculated and are shown plotted versus the immigration term in Fig. 3. Note that depending on the size of this term the relative ratio of the steady state concentrations changes significantly which suggests that the properties (e.g., resistivity)

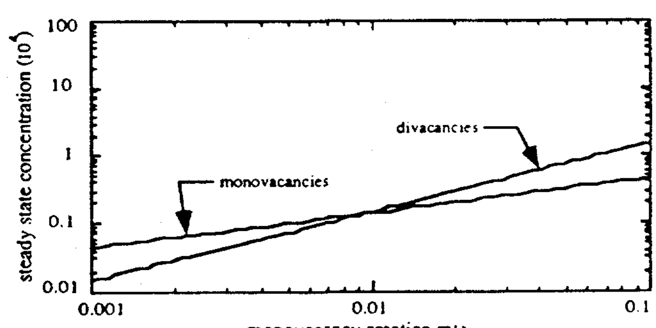

Fig. 3- The steady state values of the mono and divacancy is a function of the "immigration" rate of monovacancies.

of each defect type could be studied by proportionation. This model can be modified further by assuming that the monovacancies initially form an intermediate species that is locally stable relative to the monovacancies but unstable relative to the divacancy. These defects could form if only partial, but metastable, lattice relaxation occurred along a particular lattice direction. The probability of their formation would be sensibly equal to that of the divacancy and their expected life would depend on the rate constants. Viewed as a chemical reaction the model would be

$$V + V \underset{k_2}{\overset{k_1}{\Leftrightarrow}} E$$

$$E \underset{\gamma}{\overset{\beta}{\Leftrightarrow}} D$$

$$V \overset{k_3}{\rightarrow} sinks$$

$$E \overset{k_4}{\rightarrow} sinks$$

$$D \overset{k_4}{\rightarrow} sinks$$

and the rate equations would be

$$\frac{dV}{dt} = \alpha + k_2 E - k_1 V^2 - k_3 V \qquad (2a)$$

$$\frac{dE}{dt} = \frac{1}{2}k_1 V^2 - (\frac{1}{2}k_2 + k_4 + \beta)E + \gamma D \qquad (2b)$$

$$\frac{dD}{dt} = -(k_4 + \gamma)D + \beta E \qquad (2c)$$

where α is the immigration term discussed above. The initial conditions for V and D were taken from DD as were the rate constants k_i. These data were supplemented by arbitrary values for α, β, and γ, and an initial condition for the intermediate species that equaled that for the divacancy. The numerical solutions are shown in Fig. 4. As expected, the defects seek steady states that reflect the magnitude of the immigration term and the rate constants. If performed, the experiment could be used to provide evidence for the existence of an intermediate species. A possible

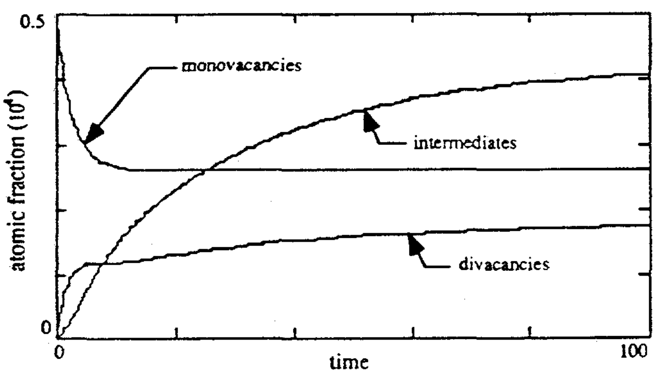

Fig. 4- The Dienes-Damask model with constant immigration and an intermediate species, E. The rate constants, k_i, are those used in Fig. 2 above while $\alpha = 0.04$, $\beta = 0.2$, and $\gamma = 0.05$.

biological interpretation of the modified DD equations are offered by a model for the process of marriage. People (V) meet, fall in love, and become engaged ($V + V \rightarrow E$). After a period of time they either decide to get married ($E \rightarrow D$) or agree to separate ($E \rightarrow V + V$). Unfortunately, some marriages also end in separation (γ) or divorce (k_4).

The Clark-Alden Model

Microstructural evolution and strain localization during mechanical testing at elevated temperatures occur in a wide variety of metal alloys. Dynamic recrystallization is a vivid example of the coupling of microstructure and deformation that can, under certain conditions of temperature and strain rate, yield oscillatory behavior[16,17]. Another well-known example of this coupling is strain-enhanced grain growth during superplastic deformation[18-22]. Modeling of this process has been based on the grain growth analysis of Clark and Alden (CA)[14] which, in turn, received guidance from the early work of Girafalco and Grimes[23]. The fundamental idea is that grain boundary mobility is directly proportional to the excess vacancy concentration that is augmented by continuous deformation. The alloy of interest to CA was Sn-1% Bi that was known to be superplastic and which exhibited normal grain growth. They considered a small, polycrystalline volume of this material that is subject to a shear strain rate, $\dot{\varepsilon}$, and as a result has an excess atom fraction of vacancies, n_v. CA argued that the rate of change of the vacancy population can be described by

$$\frac{dn_v}{dt} = k_1\dot{\varepsilon} - k_2 n_v \qquad (3a)$$

where k_1 and k_2 are rate constants and the first term on the RHS describes vacancy production by the deformation process and the second term describes vacancy annihilation at sinks. Grain growth was described by

$$\frac{dL}{dt} = \frac{k_3(n_v + n_o)}{L} \qquad (3b)$$

where L is grain size, n_o is the equilibrium atom fraction of vacancies, and k_3 is a rate constant. These equations demand that if deformation should stop, the excess vacancy population will decay to zero and the rate of grain growth will revert to its normal form. After making the following substitutions

$x = \frac{n_v}{n_o}$, $y = \frac{L}{L_o}$, $\tau = 10^3 t$, $\alpha = \frac{10^{-3}}{n_v}k_1$, $\beta = 10^{-3}k_2$, and $\gamma = 10^{-3}\frac{n_v}{L_o^2}k_3$ the CA equations become

$$\frac{dx}{d\tau} = \alpha\dot{\varepsilon} - \beta x \qquad (4a)$$

$$\frac{dy}{d\tau} = \gamma\frac{1 + x}{y}. \qquad (4b)$$

where L_o is the initial grain size. Numerical solutions to eqs. (4a) and (4b) are shown in Fig. 5, are similar to those determined analytically by CA, and clearly indicate that deformation assists grain growth according to their model. The initial conditions were $x = 0$ and $y = 1$.

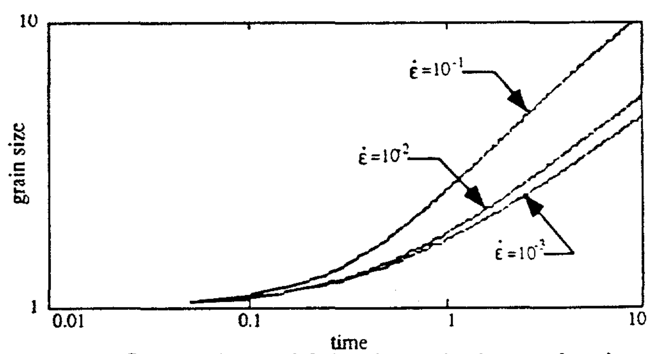

Fig. 5- The Clark-Alden model showing grain size as a function of time for various applied strain rates.

A Modified Clark-Alden Model

The results of many grain growth experiments suggested to Burke[24] and later Grey and Higgins[25] that growth is limited by impurities and other effects to a grain size, D_e. So, in modifying the CA model the process of grain growth will first be made logistic. A third species, glissile dislocations, will also be added since constant strain rate testing generates these as well and it has been suggested that dislocations support grain growth through pipe diffusion[26, 27]. To describe the evolution of the dislocation population during constant strain rate testing (utilized by CA) the model of Peczak and Lutton will be used[28]. This model has the form

$$\frac{d\rho}{dt} = \dot{\varepsilon}(k_a\rho^{1/2} - k_b\rho)$$

where ρ is the mobile dislocation density. If the steady state dislocation density, $\rho_o = (\frac{k_a}{k_b})^2$, is used to define a dimensionless dislocation density, the modified CA model becomes

$$\frac{dx}{d\tau} = \alpha\dot{\varepsilon} - \beta x \quad (5a)$$

$$\frac{dy}{d\tau} = \gamma(1+x)(1+\delta z)(\frac{1}{y} - \frac{1}{y_\infty}) \quad (5b)$$

$$\frac{dz}{d\tau} = \phi\dot{\varepsilon}(z^{1/2} - z). \quad (5c)$$

where y_∞ is the dimensionless grain size limit and the Greek letters are rate constants. The numerical solutions were obtained with initial conditions given by $(10^{-3}, 1, 10^{-3})$ and are shown in Fig. 6. At a strain rate of $\dot{\varepsilon} = 10^{-2}$, dislocations contribute to grain growth as expected from the model. There was considerable controversy[26,27] over whether dislocations do

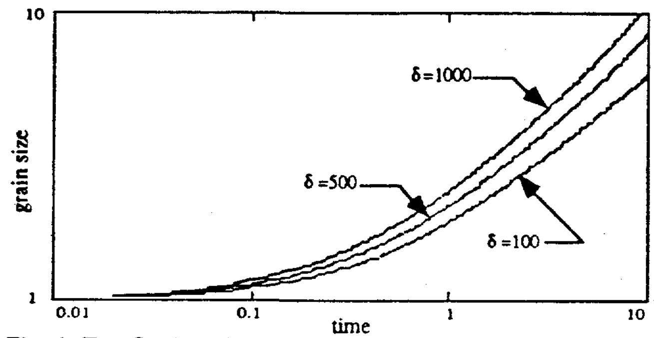

Fig. 6- The Clark-Alden model modified as suggested by Brown [26,27] showing additional grain size enhancement due to the dislocations created by strain and pipe diffusion of vacancies.

contribute in this fashion, but it is not the purpose of this report to resolve this issue but only to continue the analog described earlier. The biological interpretation of eq.(5a) is one involving immigration and natural death. By transforming variables according to $y = n^{-1}$ and $z = v^2$ it can be shown that eq. (5b) becomes the logistic equation with a quadratic birth term and eq. (5c) becomes describable as immigration and natural death.

The Ananthakrishna-Sahoo Model

Step-like serrations observed on stress-strain curves are commonly referred to as the Portevin-Le Chatelier effect. The classical mechanism used to explain this phenomenon is due to Cottrell[29] and involves the thermodynamic attraction of impurities or alloy components to dislocation cores. This segregation stabilizes the dislocations and the Cottrell atmosphere of secondary atoms such that if a critical stress is applied the dislocations break away from the atmosphere and provide a local burst of plastic strain. Biologists would describe this as a dislocation species gradually being polluted in a manner that affects their normal behavior. Ananthakrishna and Sahoo (AS) developed a method to describe the formation of this atmosphere, with use of Volterra's ideas on heredity, and applied it to the phenomenon of stair-case creep which is another manifestation of the Portevin-Le Chatelier effect [15, 30]. In dimensionless form their equations read

$$\frac{dx}{dt} = (1-a)x + y - xy - bx^2 \quad (6a)$$

$$\frac{dy}{dt} = b(kbx^2 - xy - y + az) \quad (6b)$$

$$\frac{dz}{dt} = c(x - z) \quad (6c)$$

where a, b, c and k are constants while x, is the glissile density, y the sessile density, and z is the density "polluted" by the Cottrell atmosphere. These equations have remarkable properties and, as pointed out by AS, are similar to an oscillator known as the "Oregonator" [31]. AS showed that if the constants take certain limited values a stable limit cycle is obtained, as shown in Fig. 7,

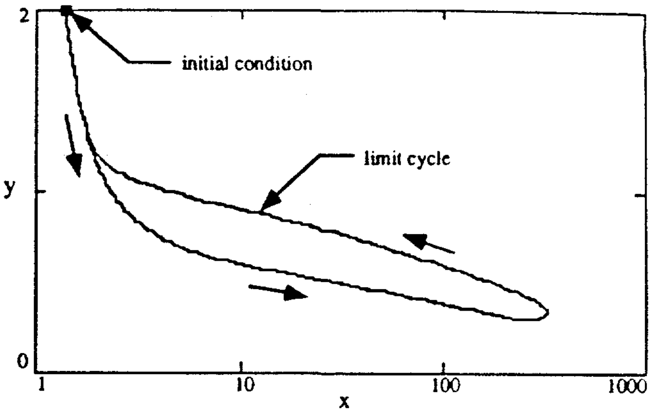

Fig. 7- The limit cycle of the Ananthakrishna-Sahoo model of the Portevin-Le Chatelier effect showing large amplitude oscillation of glissile and small amplitude oscillation of sessile dislocations.

in which the glissile dislocations oscillate in number density with very large amplitude and sessile dislocations oscillate with small amplitude. The density of polluted dislocations also oscillates with time. By integrating the glissile dislocation density over time (to obtain the strain by means of the Orowan equation) AS were able to show that an increasing step-like function is obtained that is reminiscent of stair-case creep. Equations (6) are also capable of exhibiting chaotic behavior.

A Modified Ananthakrishna-Sahoo Model

It can be shown that if the constants in eqs.(6) are modified to any significant degree the limit cycle loses its stability and the dislocations cease oscillating. Within this range of stable limit cycle behavior small fluctuations of the rate constants and, consequently, dislocation densities should be expected in a physical sense. The affect of this intrusion of experimental justice is a more disorderly appearing limit cycle and a noisy dislocation density versus time curve. Ananthakrishna[30] states that the coefficient "a" in eqs. (6) refers to the concentration of solute atoms that participate in the immobilization of glissile dislocations. It stands to reason that these atoms are liberated when "polluted" dislocations break loose and that the concentration of these atoms might oscillate as well. They would also be expected to drift and be adsorbed by other sinks such as grain boundaries, inclusions, vacancies, etc. In this circumstance, the effective concentration of solute atoms would continuously decrease and at some critical value of the coefficient a the limit cycle would become unstable. Figure 8 shows an arbitrary

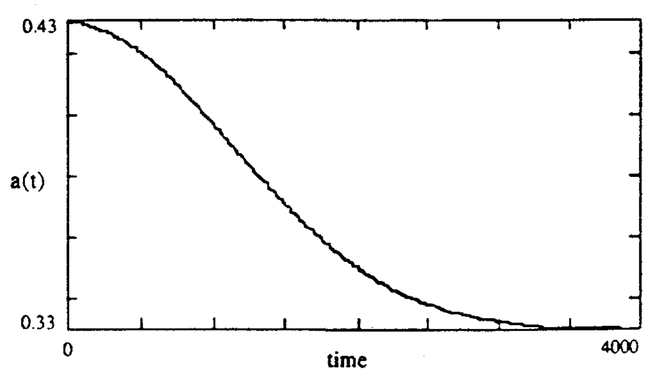

Fig. 8- An arbitrary decrease of the coefficient that is proportional to the solute atom concentration plotted from the value (0.43) used by AS to a value that makes the limit cycle unstable.

decrease of this coefficient, now viewed as a function of time, beginning with the value used by AS and ending at a value that makes the limit cycle unstable. A suitable model would assure that solute atoms are conserved. The solution to eqs. 6 begins as it did in the AS model but after a certain induction period, oscillation of glissile dislocations ceases as shown in Fig. 9. The limit cycle as well begins as before but the oscillations spiral into a "sickly" but persistent steady state as shown in Fig. 10.

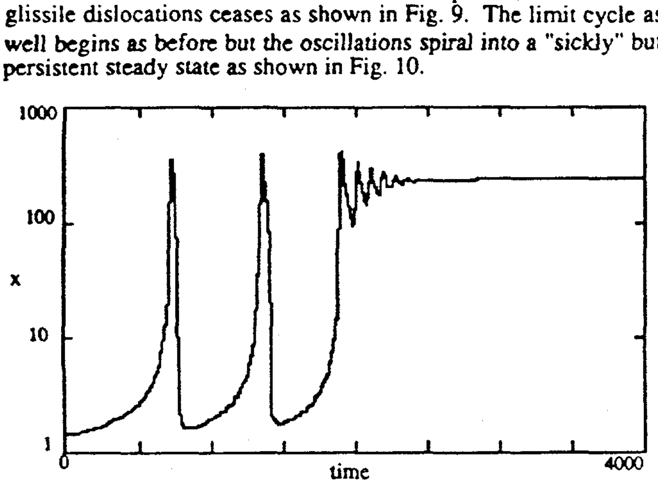

Fig. 9- The glissile dislocation density oscillation as affected by the continuous depletion of solute atoms at other sinks. Similarity to the cessation of a heart beat can be discerned.

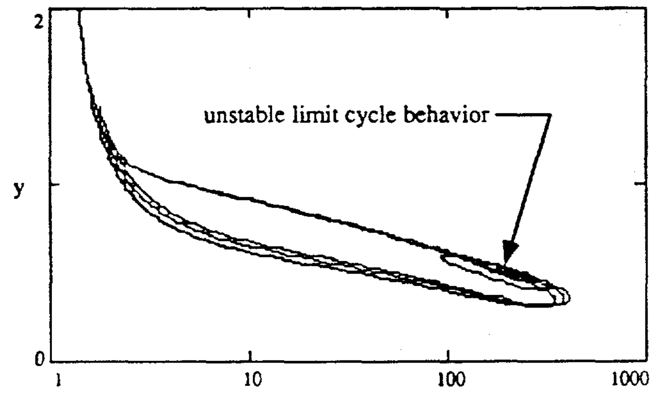

Fig. 10- The Ananthakrishna-Sahoo limit cycle gradually shifts and becomes unstable as the solute concentration dips below a critical value.

Equations (6) are replete with biological interpretation. In eq. (6a) we see the various birth and death terms along with the competitive, feeding, and crowding terms discussed earlier. Taken together the equations exhibit a symbiotic relationship with x thriving on y, y thriving on x and z, and z thriving on x. It is curious that the more mobile species, x, falls prey to the polluted species, z. In the animal kingdom it is usually the slow species that provides sustenance to the predator. Equation (6b) shows that the slow species is a predator as well and survives on the very abundance of the mobile species but not without an occasional loss of its own in the encounter. In the laboratory we would ordinarily interpret the fluctuation term as evidence of Murphy's Gremlin. In the biological world it could be interpreted as spurious influence from other species not incorporated into the model. The continuous depletion of the solute concentration could be interpreted as a deadly virus that consumes a crucial gland until biological rhythms are destroyed and the system wanes to a static and relatively lifeless existence that we call steady state.

Summary and Conclusions

In this report an attempt has been made to interpret and modify existing temporal models for lattice defects in the manner of a biologist or epidemiologist. In the process no attempt has been made to justify the original models or validate the modified models. It was found that the three chosen models could be modified in several ways and that it was tempting to include them all. However, this temptation was resisted and only rather simple modifications were made to each of the three original models. Only modifications that made physical sense were considered. For example, a biologist might be concerned about the age factor in population dynamics but the properties of an "old" and a "young" vacancy or dislocation are probably quite similar so this was not considered.

The Dienes-Damask model could have been modified by including interstitial and substitutional species but this has been done, at least in part [32,33]. The simple addition of an immigration term gave the surprising result that the steady state ratio of vacancies to divacancies can be controlled. One could argue that if radiation or plastic deformation were the physical embodiment of this term more complicated behavior would be expected than is described by the modified Dienes-Damask equations. This kind of critical commentary is analogous to that found in the biological literature and suggests that mechanisms and models can and will always be improved. The addition of an intermediate species was biologically inspired and analogous to adding grasshoppers to the coyote-rabbit Lotka-Volterra society. The expected life of the intermediate species is, of course, unknown but one can certainly imagine an energy diagram having three descending wells in succession and can certainly write down the reactions taking place between species in these wells. The analogy with the institution of marriage was convenient if not useful.

The Clark-Alden model could also have been modified in several ways. The modification chosen came strictly from the materials science literature [24,27,28] and can be nicely transformed into an easily interpretable biological society. It was very tempting to add vacancy-dislocation interaction terms to eqs. (5a) and (5c) to complicate the society. In view of the remarkable effects that ultrasonic energy has on thermokinetic phenomena [34,35] the addition of another dislocation source term, perhaps as an immigration, would be worth investigation. As it stands the modified Clark-Alden model described in eq. (5) does capture grain growth enhancement and might be useful if the 1960's controversy was revisited.

The Ananthakrishna-Sahoo model is one possessing a chemical analogy in the "Oregonator" which is a model of the Belousov-Zhabotinskii [36] oscillating chemical reaction. Its interpretation as a biological system is obvious if it is examined term by term which was done in this report. If examined as a whole it is difficult to imagine a particular biological society that would display the same properties because of the many terms involved. It was, therefore, decided to imagine it as a single living, breathing, pulsating creature that is susceptible to infection by a growing and toxic intruder. Despite the stability (will to live) of its limit cycle the AS system eventually succumbs without the appropriate antibody.

Analogies between e.g., mechanical and electrical systems and the equations used for their description are well known in science and engineering. Models of systems should be and are constantly improved as new information becomes available. Improvements to models also arise from the alternative perspectives that analogies provide. Other models from the materials science literature that seem to lend themselves to this comparison are the terrace-ledge-kink model of a surface, deformation in amorphous materials, and the kinetics of the order-disorder transformation. While it might be presumptuous for a non-biologist to have drawn the above comparisons between lattice defects and biology it has been an enjoyable and informative exercise.

Acknowledgements

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