PHYSICAL CONCEPTS IN THE DEVELOPMENT OF CONSTITUTIVE EQUATIONS

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The currently proposed viscoplastic material models include in their formulation observed material response but do not generally incorporate principles from thermodynamics, statistical mechanics, and quantum mechanics. In the existing literature, numerous hypotheses have been made for material response based on first principles. Many of these hypotheses have been tested experimentally. Not only must the currently proposed viscoplastic theories be checked against these hypotheses but the experimental basis of these hypotheses must also be checked. The physics of thermodynamics, statistical mechanics and quantum mechanics, including the effects of defects, will be reviewed for their application to the development of constitutive laws.

INTRODUCTION

The currently proposed viscoplastic material models include in their formulation observed material response but do not generally incorporate principles from thermodynamics, statistical mechanics, and quantum mechanics. In the existing literature, numerous hypotheses have been made for material response based on first principles. Many of these hypotheses have been tested experimentally. Not only must the currently proposed viscoplastic theories be checked against these hypotheses but the experimental basis of these hypotheses must also be checked.

As an example of hypotheses commonly accepted but not usually tested, consider the assumption that inelastic deformations in isotropic materials are volume preserving. This is primarily based on the intuitive belief that under large strains the volume must be preserved and on experiments that show the hydrostatic yield stress is much larger than the shear yield stress. Even though many tensile tests on round specimens are performed little attempt is made to check for a change in volume.

The response of engineering materials is generally described in terms of the macroscopic behavior of large numbers of atoms. Such descriptions are semi-empirical in nature and usually neglect the information available from more fundamental theories, such as thermodynamics, statistical mechanics and quantum mechanics. Actually the macroscopic response of materials depends intimately on the quantum mechanical interaction of electrons in neighboring atoms. To illustrate this dependence, the distribution of the outer (valence) electrons of an atom determines the binding energy of the atoms in a solid.

The distribution and motion of these electrons can be calculated using quantum mechanics principles. The response of atoms bound by their outer electrons can be "averaged" using statistical mechanics principles including the effects of defects. The statistical mechanics analysis will result in the thermodynamic mechanical response of the material.

Thermodynamic principles can be examined to determine constraints on the mechanical response of materials. Allen in Ref. 1 presents a clear and concise thermodynamic formulation. From thermodynamics, constraints on the isothermal and adiabatic elastic moduli variation with temperature and strain can be determined based solely on the definitions of the moduli. The second law of thermodynamics has been used to determine the constraints that should exist between state variables. Statistical mechanics can be applied to the determination of material response. This theory has not been extensively applied to solid materials but has been used to determine some relationships.

Quantum mechanics principles also have not generally been applied to the determination of material properties because of the difficulty in analyzing the interaction between electrons in many electron atoms. Recently a new quantum mechanics analysis method, the pseudopotential method, has been developed which examines only the outer valence electrons. The pseudopotential method has been applied not only to electronic proprties but also to mechanical and thermal properties.

The effects of defects on the response of materials can be described using topological and statistical concepts. For example, atomic vibration models near defects dictate that at moderate-to-high strain rates the yield stress should vary linearly with the logarithm of the strain rate. The yield stresses and slip directions in a crystal lattice can be estimated based on atomic configurations, forces, and the effects of defects. Defects themselves can be characterized based on topological considerations of atomic configurations. The topological specifications of many defects and defect types can be described statistically and the macroscopic response of the materials specified.

In the discussion that follows, the thermodynamics of materials will be discussed first including illustrations on the constraints it places on material behavior. The derivation of thermodynamic principles from statistical mechanics is then reviewed. The statistical mechanics results, though, are dependent on the energy levels derived from quantum mechanics principles. The analysis of the response of solid materials directly from quantum mechanics principles is illustrated in the next section. The following section discusses the effects of imperfections and the last section summarizes the conclusions.

THERMODYNAMIC CONSIDERATIONS

Reversible Process Large Strains

Thermodynamic restrictions for systems undergoing reversible processes (e.g., an elastic response) can be quite severe and the restrictions are not readily apparent. For a system of volume, V, the first law of thermodynamics requires the increase in internal energy, $\dot{U}$, to be equal to the heat added, $\dot{Q}$, plus the work done on the system, $\dot{W}$

$$\dot{U} = \dot{Q}+\dot{W} \tag{1}$$

The work done on the system is

$$\dot{W} = \int_V \sigma_{ij} v_{ij} dV \tag{2}$$

where $v_{ij} = 1/2(\dot{U}_{i,j}+\dot{U}_{j,i})$ is the symmetric part of the velocity gradient, and σ_{ij} is the Cauchy or current stress. For a reversible process, the rate of change of entropy is

$$\dot{S} = \frac{\dot{Q}}{T} \tag{3}$$

where T is the temperature.

Consider a uniform closed system; a system with a small volume would be nearly uniform. Refer all quantities to the original configuration. Then

$$\dot{W} = \sigma_{ij} v_{ij} V = \frac{\rho}{\rho_o} S_{ij} V \dot{E}_{ij} \tag{4}$$

where S_{ij} is the Kirchoff stress,

$\dot{E}_{ij}$ is the Lagrangian strain rate,

ρ is the current density, and

ρ_o is the initial density.

Consider the internal energy, u, and entropy, s, per unit mass of the system where

$$M = \rho V \tag{5}$$

is the total mass, then Eqs. (1) and (3) become

$$\dot{u} = T\dot{s} + \frac{1}{\rho_o} S_{ij}\dot{E}_{ij} \tag{6}$$

for a reversible process u and s are functions of the end points of the system and not dependent on the path taken. Using the temperature, and the strain as the state variables

$$u = u(T,\underset{\sim}{E}),\ s=s(T,\underset{\sim}{E}) \tag{7}$$

or

$$\dot{u} = \frac{\partial u}{\partial T}\dot{T} + \frac{\partial u}{\partial E_{ij}}\dot{E}_{ij} = T\dot{s} + \frac{1}{\rho_o} S_{ij}\dot{E}_{ij} \tag{8}$$

$$\dot{s} = \frac{\partial s}{\partial T}\dot{T} + \frac{\partial s}{\partial E_{ij}}\dot{E}_{ij} \tag{9}$$

From Eq. (8)

$$\left.\frac{\partial u}{\partial E_{ij}}\right|_{s=\text{const}} = \frac{1}{\rho_o} S_{ij} \tag{10}$$

This is not convenient if temperature is used as a state variable since entropy will be a function of temperature and strain. Instead defining the Hemholtz free energy as

$$a = u - Ts = a(T,\underset{\sim}{E}) \tag{11}$$

then

$$\dot{a} = -s\dot{T} + \frac{1}{\rho_o} S_{ij}\dot{E}_{ij} = \frac{\partial a}{\partial T}\dot{T} + \frac{\partial a}{\partial E_{ij}}\dot{E}_{ij} \tag{12}$$

or

$$\frac{\partial a}{\partial T} = -s, \quad \frac{\partial a}{\partial E_{ij}} = \frac{1}{\rho_o} S_{ij} \tag{13}$$

From the mixed partials of Eq. (13)

$$\frac{1}{\rho_o} \frac{\partial S_{ij}}{\partial T} + \frac{\partial s}{\partial E_{ij}} = 0 \tag{14}$$

and

$$\frac{\partial S_{ij}}{\partial E_{kl}} = \frac{\partial S_{kl}}{\partial E_{ij}} \tag{15}$$

Consider a linear elastic material

$$S_{ij} = D_{ijkl}[E_{kl} - \alpha_{kl}(T-T_o)] \tag{16}$$

where D_{ijkl}, α_{kl} and T_o are constants. Then from Eq. (15)

$$D_{ijkl} = D_{klij} \tag{17}$$

The symmetry of the stress (if there are no body moments) and strain tensors yields

$$D_{ijkl} = D_{jikl} \tag{18}$$

and

$$D_{ijkl} = D_{ijlk} \tag{19}$$

These results imply that there can be at most 21 elastic constants for a generally anisotropic material. In addition, if the material is assumed to have a specific heat at constant volume (strain), C_v, that is not a function of strain or temperature, then

$$C_v = \frac{1}{M} \frac{\dot{Q}}{\dot{T}} = T \frac{\partial s}{\partial T} = \text{const} \tag{20}$$

All of the thermodynamic functions can now be found for a linear elastic material

$$s = \frac{1}{\rho_o} D_{ijkl} E_{ijkl} \alpha_{kl} + C_v \ln\left(\frac{T}{T_R}\right) \tag{21}$$

$$u = u_o + C_v T + \frac{1}{2\rho_o} D_{ijkl} E_{ij} E_{kl} + \frac{T_o}{\rho_o} D_{ijkl} E_{ij} \alpha_{kl} \tag{22}$$

$$a = u_o + C_v\left[1 - \ln\left(\frac{T}{T_R}\right)\right] + \frac{1}{2\rho_o} D_{ijkl} E_{ij} E_{kl} - \frac{1}{\rho_o} D_{ijkl} E_{ij} \alpha_{kl} (T - T_o) \tag{23}$$

where u_o and T_R are arbitrary constants.

The thermodynamics of reversible processes places restrictions on the manner in which the elastic constants can be defined for nonisothermal loadings. Researchers have sometimes introduced the elastic constants as instantaneous constants, see Ref. 2, where

$$\dot{S}_{ij} = D_{ijkl}\left[\dot{E}_{kl} - \alpha_{kl} \dot{T}\right] \tag{24}$$

From Eq. (13)

$$S_{ij} = \rho_o \frac{\partial a}{\partial E_{ij}} = \rho_o \, a,_{E_{ij}} \tag{25}$$

and

$$\dot{S}_{ij} = \rho_o \left\{\frac{\partial a,_{E_{ij}}}{\partial T} \dot{T} + \frac{\partial a,_{E_{ij}}}{\partial E_{kl}} \dot{E}_{kl}\right\} \tag{26}$$

Comparing Eqs. (26) and (24)

$$\frac{\partial a,_{E_{ij}}}{\partial T} = -\frac{1}{\rho_o} D_{ijkl} \alpha_{kl}, \quad \frac{\partial a,_{E_{ij}}}{\partial E_{kl}} = \frac{D_{ijkl}}{\rho_o} \tag{27}$$

But the mixed partials are equal, therefore

$$\frac{\partial^2 a, E_{ij}}{\partial T \, \partial E_{kl}} = -\frac{1}{\rho_o} \frac{\partial (D_{ijmn}\alpha_{mn})}{\partial E_{kl}} = \frac{1}{\rho_o} \frac{\partial D_{ijkl}}{\partial T}$$

or

$$\frac{\partial D_{ijkl}}{\partial T} + \frac{\partial (D_{ijmn}\alpha_{mn})}{\partial E_{kl}} = 0 \tag{28}$$

Equation (28) implies variations in the elastic moduli with temperature as defined in Eq. (24), will produce variations with strain of the sum $D_{ijmn}\alpha_{mn}$. For an isotropic material

$$D_{ijkl} = 2\mu\delta_{ik}\delta_{jl} + \lambda\delta_{ij}\delta_{kl} \tag{29}$$

and Eq. (28) becomes

$$2\frac{\partial \mu}{\partial T}\delta_{ik}\delta_{jl} + \frac{\partial \lambda}{\partial T}\delta_{ij}\delta_{kl} \frac{\partial [\alpha(2\mu+3\lambda)]}{\partial E_{kl}}\delta_{ij} = 0 \tag{30}$$

If $i \neq j$ in Eq. (30)

$$\frac{\partial \mu}{\partial T} = 0 \tag{31}$$

Hence, the shear modulus cannot vary with temperature! Contracting on i,j in Eq. (30)

$$2\frac{\partial \mu}{\partial T}\delta_{kl} + 2\frac{\partial \lambda}{\partial T}\delta_{kl} + 3\frac{\partial [\alpha(2\mu+3\lambda)]}{\partial E_{kl}} = 0 \tag{32}$$

If $k \neq 1$

$$\frac{\partial[\alpha(2\mu+3\lambda)]}{\partial E_{kl}} = 0 \tag{33}$$

the product $\alpha(2\mu+3\lambda)$ is not a function of shear strain. Contracting Eq. (32) again

$$3\frac{\partial K}{\partial T} + \frac{\partial(\alpha K)}{\partial E_{kk}} = 0 \tag{34}$$

where $K = 1/3\ (2\mu+3\lambda)$ is the bulk modulus.

The restrictions in Eqs. (31), (33) and (34) are mathematically quite severe for elastic (or reversible) processes. Equations equivalent to Eq. (28) are cited in Ref. 3 but the conditions of Eq. (24), are not stated leaving the result confused. If instead of Eq. (24) the stress is given by

$$S_{ij} = D_{ijkl}(T,\underset{\sim}{E})\left[E_{kl} - \alpha_{kl}(T,\underset{\sim}{E})(T-T_o)\right] + S^o_{ij} \tag{35}$$

Then $S_{ij} = S_{ij}(T,\underset{\sim}{E})$ and Eq. (27) are automatically satisfied.

Irreversible Process Small Strains

For irreversible processes thermodynamics is not as clearly defined. Two additional assumptions are made (Ref. 4): (1) the entropy is a function of state, this will hold for sufficiently slow processes, and (2) the second law is extended to the local level. Then for some volume V

$$\frac{D}{Dt}\int_v \rho s dV = -\int_A \phi_i n_i dA + \frac{D}{Dt}\int \rho \mathcal{S} dV \tag{36}$$

where ϕ_i = entropy flow vector,

$\mathcal{S}$ = internal entropy source, and

n_i = is the normal to the surface element dA.

Transforming the surface integral to a volume integral and using the conservation of mass

$$\rho \frac{DS}{Dt} = -\phi_{i,i} + \rho \frac{D\mathcal{S}}{Dt} \tag{37}$$

where the second law now requires

$$\frac{D\mathcal{S}}{Dt} \geq 0 \tag{38}$$

The heat being added to the volume V is

$$\frac{DQ}{Dt} = \int_v [-h_{i,i} + \sigma_{ij} v^D_{ij}] dV = \int \rho \frac{Dq}{Dt} dV \tag{39}$$

where q is the heat added per unit mass in the volume dV

v^D_{ij} is the symmetric part of the velocity gradient which is converted to heat (the dissipative part). The total velocity gradient is

$$v_{ij} = v^c_{ij} + v^D_{ij} \tag{40}$$

and v^c_{ij} represents the part of the velocity gradient that is converted to recoverable internal energy, the conservative part. The internal energy is then governed by

$$\frac{Du}{Dt} = \frac{Dq}{Dt} + \frac{1}{2} \sigma_{ij} v^c_{ij} \tag{41}$$

The change in entropy can be found by proceeding along a reversible path, or

$$\frac{Ds}{Dt} = \frac{1}{T} \frac{Dq}{Dt} = - \frac{h_{i,i}}{\rho T} + \frac{\sigma_{ij} v^D_{ij}}{\rho T} \tag{42}$$

Equivalently

$$\rho \frac{Ds}{Dt} = -\left(\frac{h_i}{T}\right)_{,ii} - \frac{h_i T_{,i}}{T^2} + \frac{\sigma_{ij} v^D_{ij}}{T} \tag{43}$$

Comparing this with Eq. (37)

$$\phi_i = \frac{h_i}{T} \tag{44}$$

and

$$\rho \frac{D\mathcal{S}}{Dt} = -\frac{h_i T_{,i}}{T^2} + \frac{\sigma_{ij} v^D_{ij}}{T} \geq 0 \tag{45}$$

For <u>small</u> strains take

$$v^D_{ij} = \dot{c}_{ij} \qquad v_{ij} = \dot{\varepsilon}_{ij} \tag{46}$$

where $\dot{c}_{ij}$ is the inelastic strain, and

$\dot{\varepsilon}_{ij}$ is the total strain.

For uniform temperature distributions and small strains, Eq. (45) becomes

$$\sigma_{ij} \dot{c}_{ij} \geq 0 \tag{47}$$

Equation (47) is related to Drucker's postulate but in Ref. 5 there is no mention to isothermal conditions. Equation (47) can be extended to states with an initial stress and infinitesimal stress changes, Ref. 3. Note that the condition in Eq. (47) holds only for systems with uniform temperature distributions. Other assumptions in addition to the second law of thermodynamics must be made for Eq. (47) to apply more generally. For example, if linear phenomenological laws are assumed and Gibb's condition for a reversible process is applied, then the internal entropy production must be a positive definite function of the state variables. Consider the functional theory, described in Ref. 6, where

$$\dot{c}_{ij} = \dot{\lambda} \left(\frac{3}{2} S_{ij} - \Omega_{ij}\right) \tag{48}$$

where $S_{ij} = \sigma_{ij} - 1/3\ \sigma_{kk}\delta_{ij}$ on the deviatoric stress, and Ω_{ij} is the equilibrium stress.

Equation (46) requires

$$\frac{3}{2} S_{ij}S_{ij} = 3J_2 \geq S_{ij}\Omega_{ij} \tag{49}$$

For uniaxial loading, Eq. (49) becomes

$$\sigma^2 \geq \sigma\Omega \tag{50}$$

which means if the equilibrium stress and the stress have the same sign then the stress must be larger in absolute value than the equilibrium stress. Experimental evidence shows that Eq. (49) is violated. The reason for the disagreement arises from the fact that all of the inelastic strain is not dissipated initially, which is assumed in Eq. (39). Initially some of the inelastic strain can raise the recoverable internal energy of the material. This rise in recoverable internal energy can be pictured as an atomic arrangement that is at a higher state, as shown in Fig. 1. This higher energy state can be relatively stable, represented by the higher of the two relative minimums. Thermal diffusion of the atoms to a lower state will gradually dissipate some or all of the inelastic strain energy as heat. The quantity, Ω, can now be viewed as representing structural changes in the atomic arrangement of a material.

If Eq. (39) is replaced by

$$\frac{DQ}{Dt} = \int_v \left[-h_{i,i} + \left(\sigma_{ij} - \frac{2}{3}\Omega_{ij}\right)v^D_{ij}\right]dV \tag{39'}$$

Then Eq. (49) will be converted to

$$\frac{2}{3}\dot{\lambda}\left(\frac{3}{2} S_{ij} - \Omega_{ij}\right)\left(\frac{3}{2} S_{ij} - \Omega_{ij}\right) \geq 0 \tag{49'}$$

This is always satisfied since $\dot{\lambda}$ is positive.

STATISTICAL MECHANICS CONSIDERATIONS

From statistical mechanics, which characterize the overall response of large numbers of atoms, many of the postulates and results of thermodynamics can be found. For example, the Onsager reciprocal relation, Ref. 7, for materials with linear phenomenological laws, can be derived from statistical mechanics considerations. Statistical mechanics is based on the assumption that "all microstates of a system that have the same energy are assumed to be equally likely" Ref. 8. By considering two large systems of atoms, A and B, in equilibrium, the probability that the total system, A and B, is at energy E_A+E_B is

$$P_{A+B}(E_A+E_B) = P_A(E_A)P_B(E_B) \tag{51}$$

This follows from the fact that the energy of atoms in system A (or B) where system A and B are each in contact with a thermal reservoir will be independent of the energy of the atoms in system B (or A). From Eq. (51) it can be shown that the probability that a system is at energy, E_K is given by

$$P(E_k) = \frac{1}{Z} e^{-\beta E_k} \tag{52}$$

where $Z = \sum_k e^{-\beta E_k}$ is the partition function, and (53)

β is a parameter to be determined.

To determine this parameter, consider the internal energy which is now defined as the average energy of the system, then

$$U = \bar{E} = \sum_k E_k P(E_k) = \frac{1}{Z} \sum_k E_k e^{-\beta E_k} \tag{54}$$

From Eq. (53)

$$U = -\frac{\partial(\ln Z)}{\partial \beta} \tag{55}$$

For a perfect monitonic gas, Ref. 8, the partition function is

$$Z = V^N \left(\frac{2\pi}{\beta m}\right)^{3N/2} \tag{56}$$

where N is the number of atoms of mass, m, in volume V. From Eq. (55)

$$U = \frac{3N}{2\beta} \tag{57}$$

but the internal energy is also

$$U = \frac{3}{2} NkT \tag{58}$$

where k is Boltzmann's constant. Therefore comparing Eqs. (57) and (58)

$$\beta = \frac{1}{kT} \tag{59}$$

The result in Eq. (59) is general and applies to all systems.

One thermodynamic function, the internal energy, is now determined from the statistical response of the individual atoms. A second function needs to be determined to specify the system. To accomplish this, consider

$$d(\ln Z) = \frac{\partial \ln Z}{\partial \beta} d\beta + \frac{\partial \ln Z}{\partial \varepsilon_{ij}} d\varepsilon_{ij} \tag{60}$$

Substituting for the first partial derivative using Eq. (55) and using

$$U d\beta = d(\beta U) - \beta dU \tag{61}$$

$$d(\ln Z + \beta U) = \beta dU + \frac{\partial \ln Z}{\partial \varepsilon_{ij}} d\varepsilon_{ij} \tag{62}$$

From the first law of thermodynamics (i.e., the conservation of energy) for reversible reactions,

$$dU = TdS + \sigma_{ij}Vd\varepsilon_{ij} \tag{63}$$

Substituting Eq. (62) with (63)

$$d(\ln Z + \beta U) = \frac{1}{k}\, dS + \left[\beta V\sigma_{ij} + \frac{\partial \ln Z}{\partial \varepsilon_{ij}}\right]d\varepsilon_{ij} \tag{64}$$

Equation (64) must hold for arbitrary changes in strain and entropy therefore

$$dS = kd(\ln Z + \beta U) \tag{65}$$

and

$$\sigma_{ij} = -\frac{1}{\beta V}\frac{\partial \ln Z}{\partial \varepsilon_{ij}} = -\frac{kT}{V}\frac{\partial \ln Z}{\partial \varepsilon_{ij}} \tag{66}$$

Statistical mechanics has been applied to the response of solids, (e.g., Refs. 9 and 10). For example, consider a solid to be a collection of N atoms each of which can vibrate in three orthogonal directions. Then if the atoms are assumed to be linear harmonic oscillations, quantum mechanics can be used to determine the possible energy levels in Eqs. (52) and (53). These energy levels are from Ref. 10 or the Appendix.

$$E_i = \left(n_i + \frac{1}{2}\right)h\nu_i \qquad \begin{matrix} n_i = 0,1,2,\ldots,\infty \\ i = 1,2,3,\ldots,3N \end{matrix} \tag{67}$$

where $\nu_i = \frac{1}{2\pi}\sqrt{\frac{k_i}{m_i}}$ is the natural frequency of atom i. The total energy for a state is

$$E = \sum_{i=1}^{3N} E_i$$

and the partition function is

$$Z = \sum_{\text{states}} e^{-\beta E} = \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \cdots \sum_{n_{3N}=0}^{\infty} e^{-\beta(E_1+E_2+\ldots+E_{3N})} \tag{68}$$

Substituting Eq. (67) into Eq. (68) and summing over each N_i

$$Z = \sum_{i=1}^{3N} \frac{e^{-\beta h\nu_i/2}}{1-e^{-\beta h\nu_i}} \tag{69}$$

or

$$\ln Z = \sum_{i=1}^{3N} \left\{ -\frac{\beta h\nu_i}{2} - \ln\left(1-e^{-\beta h\nu_i}\right) \right\} \tag{70}$$

From Eq. (55)

$$U = \sum_{i=1}^{3N} \left(\frac{h\nu_i}{2} + \frac{1}{\beta} \left[\frac{\beta h\nu_i e^{-\beta h\nu_i}}{1-e^{-\beta h\nu_i}} \right] \right) \tag{71}$$

and, at high temperatures β approaches zero ($\beta = 1/kT$)

$$U = \sum_{i=1}^{3N} \left(\frac{h\nu_i}{2} + \frac{1}{\beta} \right) = 3NkT + \sum_{i=1}^{3N} \frac{h\nu_i}{2} \tag{72}$$

the specific heat at constant volume is then

$$C_v = \frac{\partial V}{\partial T} = 3Nk \tag{73}$$

which is the classical thermodynamic result and from experimental data is accurate at high temperatures. For a complete discussion of this result, see Refs. 9 or 10.

The above result does not include the stress strain response. To accomplish this, consider the atoms to be stretched to a new position a distance x_o from their relative equilibrium positions by an external applied force. The energy levels will now increase approximately by

$$\frac{1}{2} k_i x_o^2$$

or

$$E_i = \frac{1}{2} h\nu_i + \frac{1}{2} k_i x_o^2 + n_i h\nu_i \tag{74}$$

is the approximate energy of atom i.

Using $k_i = 4\pi^2 m_i \nu_i^2$ and $x_o = 2a\varepsilon$ where 2a is the distance between atomic centers and ε is the strain. Equation (68) can now be rewritten as

$$E_i = \frac{1}{2} h\nu_i + 8\pi^2 a^2 m_i \nu_i^2 \varepsilon^2 + n_i h\nu_i \tag{75}$$

Assuming the frequencies of each atom in each direction are the same, the Einstein approximation, the partition function becomes

$$\ln Z = 3N \left[-\frac{\beta}{2} h\nu - 8\pi^2 a^2 m \beta \nu^2 \varepsilon^2 - \ln\left(1 - e^{-\beta h\nu}\right) \right] \tag{76}$$

and the stress is from Eq. (66)

$$\sigma = \frac{48N\pi^2 a^2 m\nu^2 \varepsilon}{V} = 48\pi^2 \rho a^2 \nu^2 \varepsilon \tag{77}$$

where $\rho = nm/V$ is the density, then the elastic modulus

$$E = 48\pi^2 \rho a^2 \nu^2 \tag{78}$$

It should be possible to test Eq. (78) against available data.

QUANTUM MECHANICAL APPLICATIONS TO THE RESPONSE OF MATERIALS

In considering the statistical mechanics aspects of material response, quantum mechanics provided the means for determining the energy states of a system. Only the potential energy between neighboring atoms was considered, but actually this potential energy is determined by the chemical bonding between adjacent atoms, which in turn is determined by the outer electrons. Summarizing the mechanical properties of a solid are ultimately tied to the binding energy present in the outer electrons. In the analyses discussed in the section on statistical mechanics, the contribution to the energy of the system from the electrons was neglected; an assumption that generally produces accurate results, as quantum mechanics principles are considerably more important for low mass particles such as electrons than for higher mass particles like atomic nuclei.

Nevertheless the pseudopotential method for describing these outer electrons is being developed,Refs. (12, 13),and shows promise for describing elementary mechanical properties. The pseudopotential method is based on assuming a potential which is approximately correct in the regions where the outer electrons are likely to be. For example, in Ref. (13), the potential energy, V, is assumed to be

$$V(r) = \begin{cases} 0 & r \leq R_e \\ -\frac{e^2}{r} & r > R_e \end{cases} \tag{79}$$

where

r is the distance from an atomic nucleus
e is the charge on an electron, and
R_e is a semi-empirical constant.

The approximation in Eq. (79) is referred to as the empty core model, and is relatively accurate compared with numerical solutions. The approximation is based on the assumption that when a valence electron enters the region of an atom's core electrons that it moves as if there is little change in potential energy.

In Ref. (14), several somewhat more complex approximations to the potential are compared for their accuracy in predicting the bulk moduli of solids and liquids at temperatures from absolute zero to over 1000 deg F. For

example, one theory predicts a bulk modulus for aluminum at room temperature that is within twenty percent of the experimental value and these results are predicted using initially rough analytical calculations. Certainly the pseudopotential method deserves careful examination.

Quantum mechanics has, since the early stages of its development, been applied to the prediction of the interatomic potentials for diatomic hydrogen. Using these results, it has been possible to determine higher order terms in the energy eigenvalues, Ref. (15), as

$$E_n = \left(n + \frac{1}{2}\right) \hbar\nu - \left(\frac{\hbar^2\nu^2}{4D}\right)\left(n + \frac{1}{2}\right)^2 \tag{80}$$

The first term is the same as Eq. (67) used in the discussion on statistical mechanics, the second term is a correction. The constant D is the dissociation energy for the molecule, and the maximum energy level cannot exceed the dissociation energy, or

$$E_{n_{max}} \leq D < E_{n_{max}+1} \tag{81}$$

The second term in Eq. (80) is quite small and has only a small effect on the partition function, Eq. (68). A correction for the angular momentum can also be included in Eq. (80) but again the effect on the partition function is small. Better approximations to the energy levels lead to extremely accurate results for the thermodynamic properties, for example, see Ref. 10.

EFFECTS OF IMPERFECTIONS

In principle it is possible to derive the properties of solids by considering the energy levels of the atoms (and electrons). The discussion on statistical mechanics has been applied to essentially perfect crystals. Imperfections, or defects, have a profound effect on the response of solid materials. These imperfections will generally lower the oscillation frequencies of the atoms to such an extent that they will control the inelastic deformation of the material.

For example, in Ref. (3), it is shown from a consideration of activation energies and dislocation geometry that

$$\sigma(\varepsilon) = f\left[T\left(1-\alpha \ln \frac{\dot{\varepsilon}}{\dot{\varepsilon}_o}\right)\right] \tag{82}$$

where

$\dot{\varepsilon}_o$ and α are constants determined by the dislocation geometries
T is the absolute temperature
$\dot{\varepsilon}$ is the strain rate
σ is the stress, and
f is an arbitrary function

The quantity

$$T_m = T\left(1-\alpha \ln \frac{\dot{\varepsilon}}{\dot{\varepsilon}_o}\right) \tag{83}$$

is referred to as the velocity modified temperature, and has been shown to have some experimental validity.

An important concept employed in the derivation of Eq. (82) is Burgers vector. The Burgers vector is found by comparing a path about a line imperfection (e.g., a screw dislocation) and a closed path in a perfect crystal. The path about the imperfection follows the same atomic path as the path in the perfect crystal. The path about the imperfection then will not close. The vector required to close this path is the Burgers vector.

In a similar manner, it should be possible to represent plane and point imperfections in addition to line imperfections by similar integrations. For example, the line imperfection is described by performing a one dimensional integration. A point imperfection can be described by performing an integration on a surface that surrounds the point and a surface imperfection can be described by taking a difference between two points on each side of the surface. In other words: (1) a zero dimensional (point) imperfection is described by performing a two dimensional (surface) integration, (2) a one dimensional (line) imperfection is described by performing one dimensional integration and (3) a two dimensional imperfection is described by a zero dimensional integration. The sum of the dimension of the imperfection and the dimension of integration required to describe it is always the same number, or

$$n + m = 2 \tag{84}$$

where

n is the dimension of the imperfection
m is the dimension of the integration

Topological descriptions like those resulting in Eq. (84) have been applied to material description (e.g. see Refs. 16-17).

Defects can be classified quantatively by performing the proper integration. Not all defects will be identical and there will be some probabilistic distribution in the quantities used to classify the distributions. These probability distributions will ultimately determine the inelastic response of the material.

CONCLUSIONS

The effects of a defect on the stress-strain law can, in principle, be found by using quantum mechanics to determine the energies from the potential energy of the neighboring atoms. The energies in turn, determine the results from a statistical mechanics analysis. Furthermore, the results of the statistical mechanics analysis determine the thermodynamic response of the material.

Although such a procedure is possible in principle, it is not practical because the results would be overly complex for engineering applications. However, such an approach should produce important results which place constraints on the form of any newly proposed constitutive relations.

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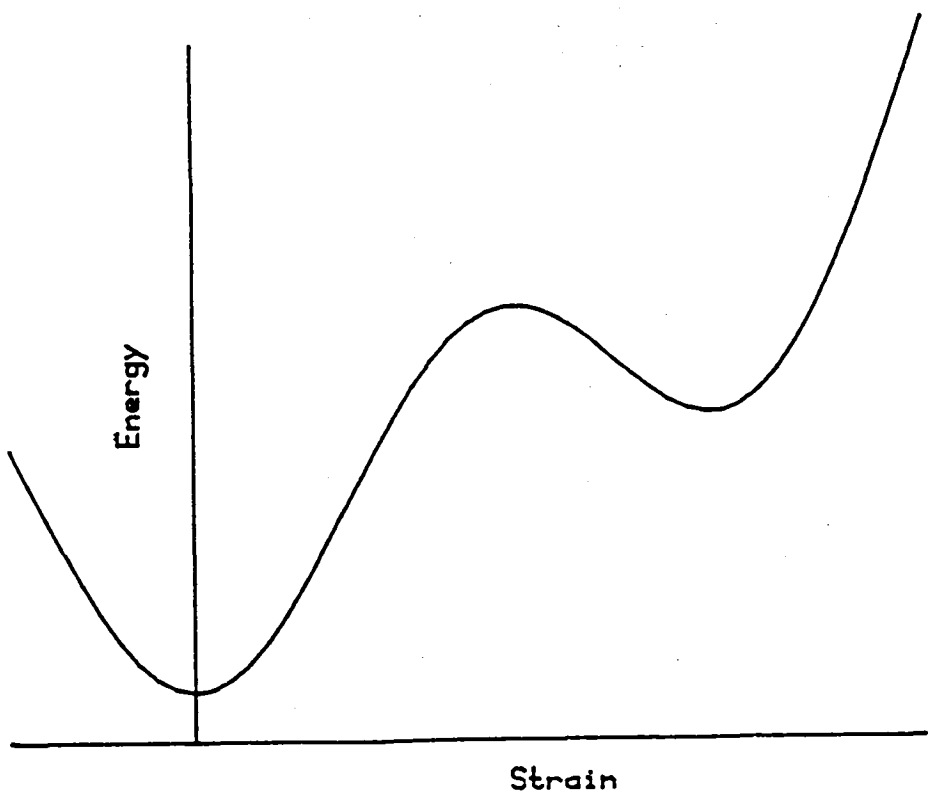

Fig. 1 Hypothetical Internal Energy Variation