A MECHANICAL AND THERMODYNAMICAL THEORY OF NON-LINEAR RELAXATION BEHAVIOUR OF SOLIDS

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A theory is worked out describing relaxation as a diffusion process of molecular groups over potential barriers. Mechanical and thermodynamical properties resulting from this model are calculated. On the basis of this theory deviations from linearity (i.e. proportionality between stress and strain) may be related to properties of the potential holes and barriers in which the diffusion process takes place.

The reaction of a viscoelastic system on external forces shows retardation. It has often been suggested that such a behaviour may be interpreted on a molecular scale by the migration of molecular groups from one equilibrium position to another.[1]

Such a picture is essentially a one-particle model analogous to the models introduced in the theory of liquids. The movement of certain kinds of molecular groups is considered. Their migration is assumed to be responsible for the mechanism of retarded deformation. The molecules surrounding these groups are not included explicitly in the calculation. Their influence is described by a potential field $V(q)$ in which the movement of the groups takes place. The rate of migration of the molecular groups between two potential holes, separated by a barrier, is calculated. Up to now this has always been done by the theory of reaction rates under the very questionable assumption of thermal equilibrium between the particle density in the holes and on the barrier. In our theory the rate of migration is calculated on the basis of a diffusion theory.

The consequences of this picture are discussed in detail. Even while starting from a very general model quite definite conclusions are reached due to the restrictions imposed by thermodynamics. The model leads to a single retardation time for the resulting creep deformation; at larger stresses it shows non-linear viscoelastic behaviour, viz., a stress dependence of the retardation time and of the ultimate compliance.

On the other hand, one must expect that our one particle model will describe the most simple retardation phenomena only. For the description of more complicated processes a distribution of retardation times is necessary. For linear behaviour, this is obtained by means of a distribution function of the parameters of the model. However, the combination of different retardation processes presents a difficult problem outside the region of linear behaviour which is as yet unsolved.

On the other hand even our simple molecular picture shows traits also occurring in experiment, e.g. a decrease of the retardation time with increasing external force. We are confident therefore that the mechanical and thermodynamical properties resulting from our one particle model give some indication of the behaviour, even of complicated systems.

THERMODYNAMICAL DISCUSSION OF THE RELAXATION PROCESS

A viscoelastic bar under the action of a constant longitudinal force shows retarded deformation to a new equilibrium position. This creep may be interpreted on a molecular scale as the migration of certain molecular groups to new

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equilibrium positions. Before an external force is applied, the molecular groups are distributed according to a Boltzmann distribution in the potential field V originating from the surrounding molecules. $V(q)$ is a function of the position vector q. This potential field may show holes, separated by barriers. It is the migration of the molecular groups over these barriers which causes the phenomenon of retarded deformation.

The external force tends to establish a new equilibrium distribution of the molecular groups, which are responsible for the creep of the material. These new equilibrium positions may be described as a new Boltzmann distribution of the molecular groups in a potential field $V(q) - v(\sigma, q)$. For a one-dimensional model v would be equal to σq; in our case v is an as yet unknown function of the external force σ and the position vector q. Some information on v may be obtained on the basis of statistical thermodynamics. Let the spatial distribution of the molecular groups considered be given by the density $\rho(q, \sigma, T, t)$. For the new equilibrium distribution ρ is given by

$$\rho = C(\sigma, T) \exp\left\{ - \frac{V(q) - v(\sigma, q)}{kT} \right\}, \tag{1}$$

where C is determined from the normalization condition

$$\int_{-\infty}^{+\infty} \rho \, dq = 1. \tag{2}$$

The length of the bar l is related in some way to the distribution function ρ. It may be defined quite generally

$$l = \int_{-\infty}^{+\infty} g(\sigma, q) \rho \, dq, \tag{3}$$

where g is an unknown function of σ and q.

It should be noted that V, v and g are assumed to be independent of T. This means that all temperature influences apart from those acting via the Boltzmann factor in (1) have been neglected.

For an experiment under a constant external force σ the obvious thermodynamic functions to be defined are the entropy S and the enthalpy H:

$$S = -k \int_{-\infty}^{+\infty} \rho \log \rho \, dq,$$

$$H = \int_{-\infty}^{+\infty} (V - v) \rho \, dq. \tag{4}$$

When comparing two states of equilibrium for different σ (and T) the basic thermodynamic relation

$$TdS = dH + l d\sigma \tag{5}$$

should be obeyed.

By substitution of (1) in the definitions (3), (4) and (5) the following relation between v and g is obtained

$$g = \partial v / \partial \sigma. \tag{6}$$

The internal energy U is

$$U = H + \sigma l = \int_{-\infty}^{+\infty} \left(V - v + \sigma \frac{\partial v}{\partial \sigma} \right) \rho \, dq. \tag{7}$$

We are interested in materials for which the instantaneous deformation due to the process considered is small as compared with the retarded deformation, i.e. a change of l is mainly due to a change of ρ.

If we restrict ourselves to this case g in (3) is a function of q only and the following expressions are obtained for g, v and U

$$ g = f(q); \quad v = \sigma f(q); \quad U = \int_{-\infty}^{+\infty} V\rho \, dq. \tag{8} $$

THE DIFFUSION THEORY

The migration of molecular groups in the field $V - v$ is described as a diffusion process, governed by the Smoluchowski diffusion equation.[2] In order to simplify the resulting formulae the calculations will be restricted to a one-dimensional model (co-ordinate q). No essential features are lost by this restriction. The Smoluchowski equation reads

$$ -\frac{\partial \rho}{\partial t} = \frac{1}{f} \frac{\partial}{\partial q} \left\{ F\rho - kT \frac{\partial \rho}{\partial q} \right\}. \tag{9} $$

In our special case the force F is defined by

$$ -F = \frac{dV}{dq} - \frac{\partial v}{\partial q}, \tag{10} $$

while f is a friction factor, defined as the ratio between F and the systematic velocity of the molecular groups. This friction factor ensures the thermal coupling between the molecular groups considered and the rest of the system which does not appear explicitly in the calculations. If f is large enough, temperature equilibrium (i.e. a Boltzmann distribution of the momenta of the molecular groups) remains established in a first approximation, even while the diffusion process is set in motion.[2] The diffusion process for our special model was treated by one of us [3] with the following results.

Two states, 1 and 2, are defined, corresponding to two potential holes 1 and 2. The numbers of particles in these states are

$$ n_1 = \int_{-\infty}^{q_t} \rho \, dq \quad \text{and} \quad n_2 = \int_{q_t}^{+\infty} \rho \, dq, \tag{11} $$

where q_t indicates the value of q at the top of the potential barrier, separating the two holes. This definition of two separate states has a physical meaning only, if the height of the barrier is large compared with kT. The following equations for n_1 and n_2 may be derived from (9) [3]

$$ -\dot{n}_1 = \dot{n}_2 = K_1 n_1 - K_2 n_2, \tag{12} $$

where the reaction rates K_i $(i = 1, 2)$ are found as [3]

$$ K_i = kT \left/ \left\{ f \int_{\text{barrier}} \exp\left(\frac{V-v}{kT}\right) dq \int_{\text{hole } i} \exp\left(-\frac{V-v}{kT}\right) dq \right\}. \right. \tag{13} $$

By means of (12) and (13) the change of n_1 and n_2 may be calculated if V and v are known. The derivation of (13) is based on the assumption that the height H of the barrier is so large as compared with kT that the particles in each hole are approximately distributed according to Boltzmann's formula, while the density ρ on the barrier is so low that it may be neglected.

These assumptions amount to

$$ = \rho \quad \begin{cases} \dfrac{n_1(t)}{I_1} \exp\left(-\dfrac{V-v}{kT}\right) & \text{in hole 1,} \\[2ex] 0 & \text{on the barrier,} \\[2ex] \dfrac{n_2(t)}{I_2} \exp\left(-\dfrac{V-v}{kT}\right) & \text{in hole 2,} \end{cases} \tag{14} $$

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where n_1 and n_2 are solutions of (12) normalized by the relation $n_1 + n_2 = 1$, while I_1 and I_2 are defined as

$$I_i = \int_{\text{hole } i} \exp\left(-\frac{V-v}{Tk}\right) dq \quad (i = 1, 2). \tag{15}$$

Substitution of (14) in (3)-(5) yields the length and the thermodynamic properties of the bar as functions of time.

EXPLICIT CALCULATION OF THE DEFORMATION AND THE THERMODYNAMIC FUNCTIONS FOR A SPECIAL MODEL

The general formulae of the previous sections are now applied to a simple, rectangular model consisting of two holes and a barrier (cf. fig. 1). For the deformation v of this field the following assumption is made

$$v = \begin{array}{l} \nearrow C_1\sigma \quad \text{in hole 1,} \\ \rightarrow C_t\sigma \quad \text{on the barrier,} \\ \searrow C_2\sigma \quad \text{in hole 2,} \end{array} \tag{16}$$

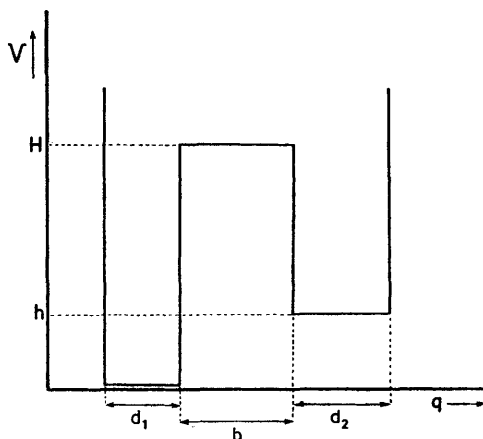where C_1, C_2 and C_t may be functions of q, but not of σ (cf. (8)).

FIG. 1.—Potential energies of holes and barrier.

The introduction of functions of q would be physically justified only for a model in which the detailed structure of the holes as a function of q is considered. Therefore the C are treated as constants in our rectangular model. The mechanical and thermodynamical functions may now be expressed in the constants of the model (cf. fig. 1) and n_1 and n_2. In the results the following abbreviations, related to the molecular entropies and free energies in the states 1, 2 and t, are used :

$$
\begin{array}{lll}
S_1 = k \log d_1, & F_1 = -TS_1, & \phi = (F_2 - F_1)/2, \\
S_2 = k \log d_2, & F_2 = -TS_2 + h, & \psi = F_t - (F_1 + F_2)/2. \\
S_t = k \log b, & F_t = -TS_t + H, &
\end{array} \tag{17}
$$

For the sake of clearness the free enthalpy, $F_i - C_i\sigma$, is given in fig. 2 as a function of the co-ordinate q in the deformed state. For the undeformed state an analogous figure is obtained by putting $\sigma = 0$. It should be observed that the molecular free energies and enthalpies, introduced above, do not include the terms related to the particle density n_1 or n_2.

The following expressions are obtained for the total internal energy and the total entropy

$$U = n_2 h,$$

$$S = - k(n_1 \log n_1 + n_2 \log n_2) + n_1 S_1 + n_2 S_2. \tag{18}$$

The differential eqn. (12) yields an expression for n_1,

$$n_1 = n_1{}^0 + (n_1^\infty - n_1{}^0)\{1 - \exp(- t/\tau\}, \tag{19}$$

where $n_1{}^0$, n_1^∞ are the values of n_1 in the undeformed, deformed state of equilibrium.
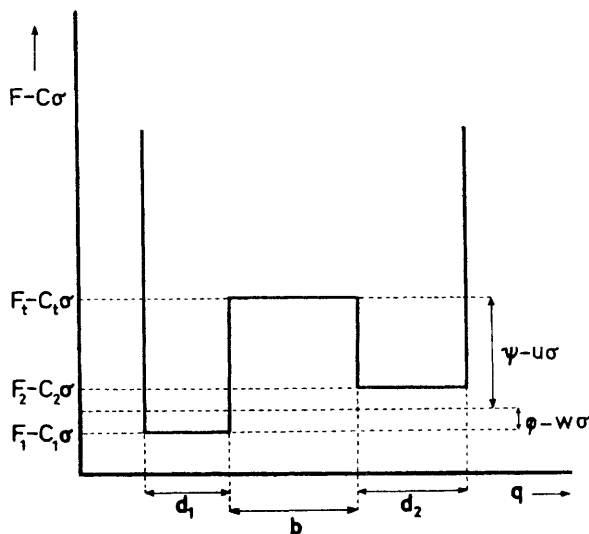

FIG. 2.—Free enthalpies of holes and barrier in the deformed state (undeformed state for $\sigma = 0$).

The retardation time $\tau (\tau^{-1} = K_1 + K_2)$ and the final elongation Δl of the bar are found as

$$\tau = \frac{f b^2 \exp(\psi - u\sigma/kT)}{2\,kT \cosh(\phi - w\sigma/kT)}, \tag{20}$$

$$\Delta l = l^\infty - l^0 = \frac{w \sinh(w\sigma/kT)}{\cosh(\phi/kT) \cosh(\phi - w\sigma/kT)}, \tag{21}$$

where $\qquad u = C_t - (C_1 + C_2)/2, \quad w = (C_2 - C_1)/2. \tag{22}$

Using (22), the following expressions for $n_1{}^0$ and n_1^∞ are found:

$$n_1{}^0 = \frac{\exp(\phi/kT)}{2 \cosh(\phi/kT)}; \quad n_1^\infty = \frac{\exp[(\phi - w\sigma)/kT]}{2 \cosh[(\phi - w\sigma)/kT]}. \tag{23}$$

The retardation time τ contains the friction factor f, originating from the diffusion theory. The expression $\psi - u\sigma$ in the exponent gives the difference between the free enthalpy of the transition state t and the mean free enthalpy of states 1 and 2. The expression $\phi - w\sigma$ in the denominator gives the difference between the free enthalpies of states 1 and 2.

It is interesting to compare (20) with the expression for the reaction rate resulting from the so-called transition state method [4]

$$K = 1/\tau = (kT/h) \exp(- \Delta F/kT), \tag{24}$$

where $\qquad \Delta F = F_t - F_1.$

Eqn. (24) is derived by assuming thermodynamic equilibrium between the top of the barrier and a single hole.

On the contrary, our equation is derived from a discussion of a diffusion process, while the questionable assumption of equilibrium between hole and barrier is avoided. Moreover, our treatment includes the forward as well as the backward diffusion process.

DISCUSSION OF THE RETARDATION TIME AND OF THE FINAL ELONGATION

A viscoelastic material shows linear behaviour if the retardation time τ is independent of σ, and the elongation Δl is proportional to σ.

A development of expressions (20) and (21) for τ and Δl with respect to σ gives

$$\tau = \tau_0 \left[1 + \frac{\sigma w}{kT} \left\{ \tanh \frac{\phi}{kT} - \frac{u}{w} \right\} \right.$$
$$\left. + \left(\frac{\sigma w}{kT} \right)^2 \left\{ \frac{u^2}{2w^2} - \frac{1}{2} + \left(\tanh \frac{\phi}{kT} \right)^2 - \frac{u}{w} \tanh \frac{\phi}{kT} \right\} + \ldots \right]. \quad (25)$$

$$\Delta l = \frac{w}{(\cosh \phi/kT)^2} \left[\frac{\sigma w}{kT} + \left(\frac{\sigma w}{kT} \right)^2 \tanh \frac{\phi}{kT} + \ldots \right], \quad (26)$$

where
$$\tau_0 = \frac{fb^2 \exp(\psi/kT)}{2kT \cosh(\phi/kT)} \quad (27)$$

is the retardation time for $\sigma = 0$.*

Now a material for which the retardation time has a term linear in σ (cf. (25)) does not even show linear behaviour for small values of σ. Moreover, it behaves differently for extension and for compression. A linear region may be defined if the factors $\sigma w/kT$ in (25) and $(\sigma w/kT)^2$ in (26) vanish, i.e., if

$$\phi = 0 \quad \text{and} \quad u = 0. \quad (28)$$

As may be seen from fig. 2, the condition $\phi = 0$ means that the free enthalpies of the two holes in the undeformed state ($\sigma = 0$) are equal. This may be realized by various combinations of length and breadth of the potential holes of fig. 1. The introduction of the free enthalpies in fig. 2 greatly simplifies the discussion as it combines depth and breadth of the holes in a single variable. The condition $u = 0$ means that the free enthalpy change caused by the deformation has the same absolute value but the opposite sign for holes 1 and 2.

A model obeying conditions (28) will be called a symmetrical model. The development of τ and Δl is much simplified for such a model

$$\tau = \tau_{00} \left[1 + \left(\frac{\sigma w}{kT} \right)^2 \left(-\frac{1}{2} \right) + \ldots \right], \quad (29)$$

$$\Delta l = w \left(\sigma w/kT + \ldots \right), \quad (30)$$

where
$$\tau_{00} = \frac{fb^2}{2kT} \exp \left(\frac{\psi}{kT} \right), \quad (31)$$

is the retardation time under zero stress for a symmetrical model.*

The value of σ for which

$$\sigma w/kT = 1 \quad (32)$$

may now be called the limit of linearity. Indeed for this order of magnitude of σ the material shows non-linear behaviour.

* This retardation time may be determined by means of recovery measurements after arbitrary stress histories.

In fig. 3 and 4 the retardation time τ and the final deformation Δl are given as functions of σ for $u = 0$ (antisymmetrical free enthalpy change, cf. fig. 2) and for various values of ϕ (different values of initial enthalpy difference of the holes,
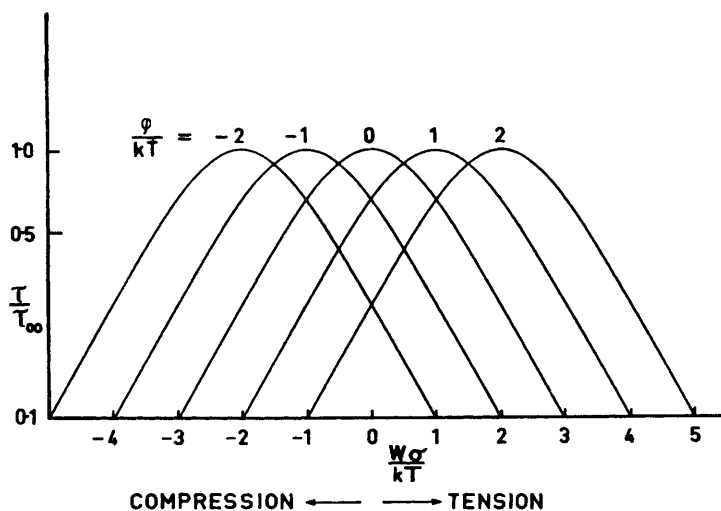

FIG. 3.—Retardation time as a function of external force for various free energy differences of the holes.
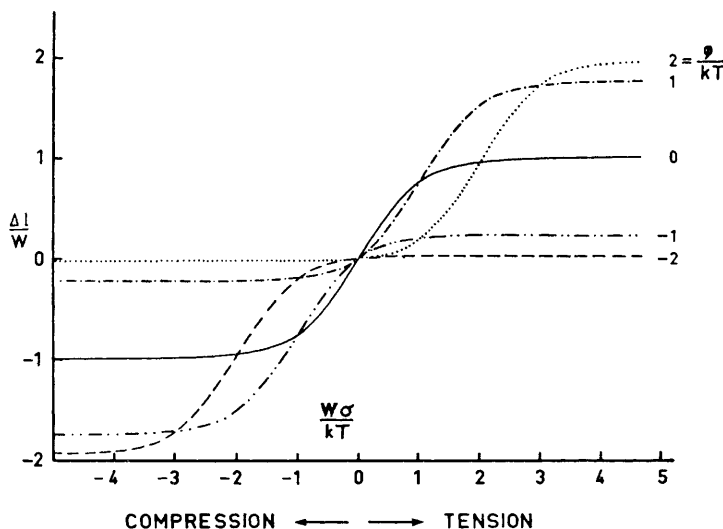

FIG. 4.—Final elongation as a function of external force for the cases of fig. 3.

cf. fig. 2). From fig. 3 it may be observed that for positive ϕ the value of τ increases with increasing σ. This behaviour may be understood by observing that for positive ϕ the retardation is mainly determined by the larger migration rate K_2. This rate decreases with increasing σ and the retardation time increases. For negative ϕ the argument applies to K_1 and the retardation time decreases.

  The final deformation (fig. 4) shows a curious dissymmetry. The reason is that for positive ϕ the particles are mainly in hole 1, even for the undeformed state. Compression does not change much in this situation. For negative ϕ the particles are mainly in hole 2 and they remain so at extension. Obviously phenomena related to the asymmetry of the holes are observable for anisotropic materials (e.g. fibres) only.

[1] cf. Burte and Halsey, *Textile Res. J.*, 1947, **17,** 465. This paper contains a model similar to ours. However, the diffusion theory is not used for the calculation of the migration rates, while no thermodynamical discussion of the model is given.
[2] Kramers, *Physica*, 1940, **7,** 284.
[3] Brinkman, *Physica*, 1956, **22,** 29, 149.
[4] Pelzer and Wigner, *Z. physik. Chem.*, *B*, 1932, **15,** 445. Eyring, *J. Chem. Physics*, 1935, **3,** 107. Evans and Polanyi, *Trans. Faraday Soc.*, 1935, **31,** 875.