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1983 J. Phys. A: Math. Gen. 16 3401

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On the physics of state transition

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Received 4 May 1982, in final form 20 December 1982

Abstract. In the melting of a solid crystalline medium, the shear modulus changes abruptly to zero. This behaviour can be explained firstly by representing the stress tensor in terms of the correlation function and the potential of interaction of the system and secondly by using an extension of Ruelle's criterion for thermodynamic stability.

1. Introduction

It has sometimes been conjectured that the phenomenon of state transition from solid to liquid is simply the spontaneous production of dislocation which becomes thermodynamically feasible at a specific temperature and during a dilating mode (see, e.g., Kosterlitz and Thouless 1973, Nelson and Halperin 1979, Young 1979). The stated conjecture encompasses essentially both the discrete (atomic) aspect of dislocation and the continuum (phenomenological) aspect of temperature and dilatation. Initial thoughts on the melting phenomenon within the scope of this modern and well accepted view may be traced back to Born (1939) who suggested that the fluidity of a melt occurs when one of the elastic moduli vanishes. Observations have also shown that, at the melting point, the shear modulus of perfect crystals jumps discontinuously to zero in the fluid (figure 1). Since dilatation is an integrated consequence of discrete deformation of lattice structure, the proliferation of microscopic grain boundaries in a crystal has a direct influence on the behaviour of the macroscopic scale of displacement. Therefore, the attempt to use defects to explain phase transitions in three dimensions is not completely unrelated to the abrupt change in the shear modulus. In other words, if the discrete formalism reflected through the study of correlation functions can be used to cast a theory of melting, such a theory would not exclude the defect-mediated phase transition hypothesis as another supporting point of view put forth by Mott and Gurney (1939). More generally, the incorporation of microscopic geometry changes to the macroscopic phase behaviour of crystals opens a novel research area which has great accessibility to recent development in the mathematics of singularities. Along the same line of thought, the idea of superfluid transition by proliferation of vortex lines was also advanced by Feynman (1955). For comprehensive literature on the subject one may refer to the recent reviews by Cotterill (1980) and Halperin (1981).

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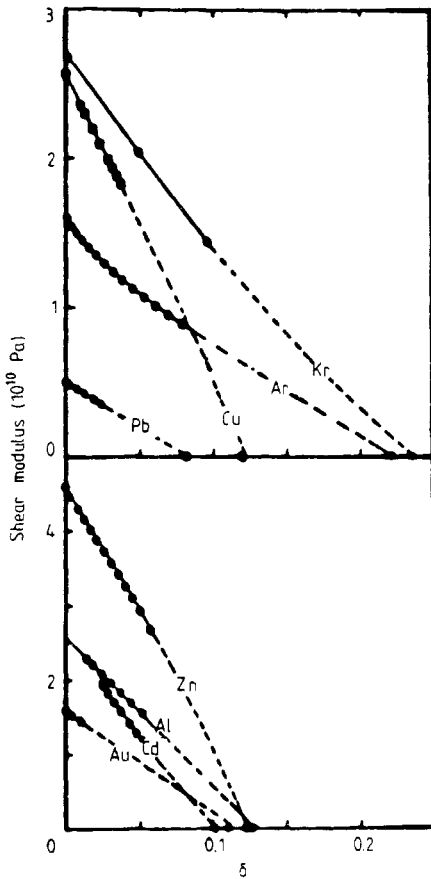


Figure 1. Shear modulus plotted against dilatation δ , both as a function of temperature (adapted from Tallon 1979).

From a different perspective, the study of phase transition in crystals can be regarded as an approximate theory for the melting of a general class of solids (Ruelle 1977b). This conceptual approximation relies largely on the combination of distinct crystalline structures to reconstruct the thermomechanical behaviour of the solid material under consideration. If the idealised reconstruction using surrogate lattice media can reproduce the true medium in a quantitative sense and under strictly defined mathematical conditions, the theoretical implications derived from the study of these structurally simpler models will provide a more precise means to estimate the complex phenomenon of melting, especially at critical limits of material behaviour.

In this technical communication, we restrict our attention to the problem of the melting of monoatomic solid crystals. The phase transition in such media is of first order, and the Helmholtz free energy is discontinuous at the critical threshold of motion. It is relevant to point out that from a continuum mechanics perspective, a conventional stability analysis of the stated problem is not applicable (Ericksen 1980). Herein we will propose the use of correlation functions to explain the abrupt behaviour of the shear moduli. Our arguments will be based on the choice of a measure of the spread of fluctuations, on the relationship between the elastic moduli and the correlation and potential functions of the system, and on the continuum extension of Ruelle's stability criterion. These arguments are feasible because of recent work by the authors on the structural implications of the stress representation (Abi-Ghanem and Nguyen 1982, 1983).

2. Measure of disorder

In statistical mechanics, a correlation function of the system may be viewed as a macroscopic indicator of microscopic irregularities. Experimentally, such a function may be determined by x-ray diffraction. At the phase transition point, the correlation function behaves discontinuously and possesses new qualitative properties. As an indicator of disorder (Tabor 1981), it will signify the domain of validity of a continuous description for a deforming medium.

3. Relationship between the elastic moduli and the correlation function

In the following, we will review briefly the method that leads to the establishment of a relationship between the linear elastic moduli, the correlation functions and the interatomic pair potential. For more details, see Abi-Ghanem and Nguyen (1982).

In linear elasticity, the stress tensor T_{kl} is expressed in terms of the strain tensor ϵ_{ij} as

$$T_{kl} = \kappa_{kl}(T^* - T) + c_{ijkl}\epsilon_{ij}, \quad i, j, k, l = 1, 2, 3 \tag{1}$$

where $\epsilon_{ij} = \frac{1}{2}(u_{i,j} + u_{j,i})$, (u_i) and $(u_{i,j})$ are the displacement field and its gradient, respectively; $(T^* - T)$ is the infinitesimal temperature change, c_{ijkl} and κ_{kl} are the elastic and stress-temperature moduli, respectively. Repeating indices denote the summation notation.

Let V be a closed portion of a material body. The statistical mechanics stress tensor is given by

$$\pi_{kl} = -k \frac{T}{v} f_l(q_k; T) \delta_{kl} + \frac{1}{2v^2} \int_V \frac{1}{r} \phi'(r) g_2(x_m, q_m; T) x_{kx_l} dx_1 dx_2 dx_3, \tag{2}$$

$k, l, m = 1, 2, 3$, where δ_{kl} is the Kronecker symbol, $r = |(x_1, x_2, x_3)|$, (x_k) is the local vectorial distance with origin (q_k) , $g_2(x_k, q_k; T) \equiv F_2((q_k) - \frac{1}{2}(x_k), (q_k) + \frac{1}{2}(x_k); T)$ and $f_1(q_k; T)$ are the two-particle and one-particle distribution functions, respectively (parametrised by the thermodynamic variables and necessarily form invariant under the symmetries of the crystalline structure), v is the specific volume, T is the absolute temperature, k is the Boltzmann constant, and $\phi(r)$ is the interaction potential of the particles; the prime denotes the derivative d/dr .

The stress tensor expression given in (1) will result from the relation

$$T_{kl} = \pi_{kl}^* - \pi_{kl} \tag{3}$$

where the asterisk denotes the post-deformation quantity of π_{kl} with respect to additional change in external factors.

On the other hand the constitutive theory in the gradient approximation of the displacement field leads to the following representation of the distribution functions:

$$f_1^*(q_m^*; T^*) = F(\mathcal{F}(V); q_m, T) \tag{4a}$$

$$g_2^*(x_m^*, q_m^*; T^*) = G(\mathcal{F}(V); x_m, q_m, T) \tag{5a}$$

where the notation

$$\mathcal{F}(V') \triangleq \{[u_{i,j}(q'_m), (T^* - T)(q'_m)]: (q'_m) \in V' \subseteq V\}$$

designates a field of displacement and temperature gradients over the space V' , F and G are functionals satisfying

$$F(\{(0, 0)\}; q_m, T) \equiv f_1(q_m; T)$$

$$G(\{(0, 0)\}; x_m, q_m, T) \equiv g_2(x_m, q_m; T).$$

For the local approximation $\mathcal{T}(\{q_m\})$ of $\mathcal{T}(V)$, (4a) and (5a) become

$$f_1^*(q_m^*; T^*) \approx F + (\partial F / \partial u_{i,j})_T u_{i,j} + (\partial F / \partial T)(q_m)(T^* - T) \tag{4b}$$

$$g_2^*(x_m^*, q_m^*; T^*) \approx G + (\partial G / \partial u_{i,j})_T u_{i,j} + (\partial G / \partial T)(q_m)(T^* - T); \tag{5b}$$

the terms on the right-hand side of (4b) and (5b) are evaluated at the values of the argument equal to $((0, 0); q_m, T)$ and $((0, 0); x_m, q_m, T)$, respectively. Subsequently this short-hand notation will be used.

From (1) and (3) we obtain the elastic modulus formula

$$c_{ijkl} = \frac{1}{4}(\Gamma_{ijkl} + \Gamma_{jikl} + \Gamma_{ijlk} + \Gamma_{klij}) \tag{6}$$

where

$$\begin{aligned} \Gamma_{ijkl} = & k \frac{T}{v} \left[F \delta_{ij} - \left(\frac{\partial F}{\partial u_{i,j}} \right)_T \right] \delta_{kl} - \frac{1}{2v^2} \delta_{ij} \int_V \frac{1}{r} \phi'(r) G x_k x_l \, dx_1 \, dx_2 \, dx_3 \\ & + \frac{1}{v^2} \delta_{ij} \int_V \frac{1}{r} \phi'(r) G x_k x_i \, dx_1 \, dx_2 \, dx_3 \\ & + \frac{1}{2v^2} \left[\int_V \frac{1}{r} \phi'(r) \left(\frac{\partial G}{\partial u_{i,j}} \right)_T x_k x_l \, dx_1 \, dx_2 \, dx_3 \right. \\ & \left. + \int_V \frac{1}{r} \left(\frac{1}{r} \phi'(r) \right)' G x_i x_j x_k x_l \, dx_1 \, dx_2 \, dx_3 \right]. \end{aligned} \tag{7}$$

Hence the Helmholtz free energy ψ becomes

$$\begin{aligned} \rho_0 \psi = & \left\{ -\frac{k}{2v} \left[F + T \left(\frac{\partial F}{\partial T} \right)_{(q_m)} \right] u_{k,k} + \frac{1}{4v^2} u_{k,l} \int_V \frac{1}{r} \phi'(r) \left(\frac{\partial G}{\partial T} \right)_{(q_m)} x_k x_l \, dx_1 \, dx_2 \, dx_3 \right\} \\ & \times \left(\frac{\partial T}{\partial u_{i,j}} \right)_S u_{i,j} + \frac{kT}{2v} \left[F u_{i,i} - \left(\frac{\partial F}{\partial u_{i,j}} \right)_T u_{i,j} \right] u_{k,k} \\ & - \frac{1}{4v^2} u_{i,i} u_{k,l} \int_V \frac{1}{r} \phi'(r) G x_k x_l \, dx_1 \, dx_2 \, dx_3 \\ & + \frac{1}{2v^2} u_{i,i} u_{k,l} \int_V \frac{1}{r} \phi'(r) G x_k x_i \, dx_1 \, dx_2 \, dx_3 \\ & + \frac{1}{4v^2} u_{i,j} u_{k,l} \left[\int_V \frac{1}{r} \phi'(r) \left(\frac{\partial G}{\partial u_{i,j}} \right)_T x_k x_l \, dx_1 \, dx_2 \, dx_3 \right. \\ & \left. + \int_V \frac{1}{r} \left(\frac{1}{r} \phi'(r) \right)' G x_i x_j x_k x_l \, dx_1 \, dx_2 \, dx_3 \right] \end{aligned}$$

with the assumption that the initial density has the form

$$\rho_0 \approx (m/v)F$$

where m is the mass of one particle.

4. Extended Ruelle's stability criterion for a continuum

From a discrete system point of view, Ruelle (1977a) gave a definition of the stability of an interaction and an equivalent statement concerning the convergence of the grand partition. Physically, his condition aims at preventing the collapse of infinitely many particles into a bounded region by choice of an appropriate type of interaction. More rigorously, the residual energy resulting from the repulsive and attractive forces between the particles of the system must possess a lower bound to ensure thermodynamic stability. We will present his criterion in an integral form using the two-particle distribution as a weighting function. Our intention is to account for the manner in which the energy is shared by different parts of the medium. Immediate structural implications will follow.

Definition. Let ϕ be a real symmetric upper semi-continuous function $V_0 \subseteq \mathbb{R}^3$. We say that the interaction ϕ is stable if

$$\text{vol}(V) \int_V \phi(r) G \, dx_1 \, dx_2 \, dx_3 > 0 \tag{8}$$

holds for every $V \subseteq V_0$ with a bounded measure $\text{vol}(V)$.

Strictly speaking, the interaction stability implies that the right-hand side of (8) should denote the minimum internal energy stored in the system. This is a non-positive quantity which may be regarded as constant under the thermomechanical setting of our analysis. The constant value arises from the fact that, as the system approaches instability, the internal energy approaches a negative limit from above. In this sense, such a constant represents the self-energy of the crystalline system locally. Consequently we may adopt the above form of inequality without loss of clarity. Furthermore, we notice that when G is a sum of the Dirac distribution function supported by the set of equilibrium positions, (8) indicates that the potentials are positive definite and this fact is well recognised in lattice dynamics.

We now establish the restrictions on G . We start by expressing (8) in the coordinates of the deformed configuration, denoted by the asterisk of the solid body and then use the estimates

$$\text{vol}(V^*) \approx \text{vol}(V)(1 + u_{i,i}) \tag{9}$$

$$\phi(r^*) = \phi(r) + r^{-1} x_i x_j u_{i,j} \phi'(r) + \frac{1}{2} r^{-2} x_i x_j x_m x_n u_{i,j} u_{m,n} \phi''(r) \tag{10}$$

where the double prime denotes d^2/dr^2 . Thus, we obtain

$$\begin{aligned} (1 + 2u_{k,k}) \int_V \left(\phi(r) + \frac{1}{r} \phi'(r) x_i x_j u_{i,j} + \frac{1}{2r^2} x_i x_j x_m x_n u_{i,j} u_{m,n} \phi''(r) \right) \\ \times \left[G + \left(\frac{\partial G}{\partial u_{m,n}} \right)_T u_{m,n} + \left(\frac{\partial G}{\partial T} \right) (q_m)(T^* - T) \right] dx_1 \, dx_2 \, dx_3 > 0 \end{aligned}$$

or

$$\begin{aligned} \int_V \phi(r) G \, dx_1 \, dx_2 \, dx_3 + (T^* - T) \int_V \phi(r) \left(\frac{\partial G}{\partial T} \right)_{(q_m)} dx_1 \, dx_2 \, dx_3 \\ + u_{i,j} \left[\int_V \phi(r) \left(\frac{\partial G}{\partial u_{i,j}} \right)_T dx_1 \, dx_2 \, dx_3 + 2\delta_{im} \delta_{jm} \int_V \phi(r) G \, dx_1 \, dx_2 \, dx_3 \right] \end{aligned}$$

$$\begin{aligned}
 & + \int_V \frac{1}{r} \phi'(r) G_{x_i x_j} dx_1 dx_2 dx_3 \Big] \\
 & + u_{i,j} u_{m,n} \left[\int_V \frac{1}{r} \phi'(r) \left(\frac{\partial G}{\partial u_{m,n}} \right)_T dx_1 dx_2 dx_3 \right. \\
 & + 2\delta_{mk} \delta_{nk} \int_V \phi(r) \left(\frac{\partial G}{\partial u_{i,j}} \right)_T dx_1 dx_2 dx_3 \\
 & + 2\delta_{mk} \delta_{nk} \int_V \frac{1}{r} \phi'(r) x_i x_j G dx_1 dx_2 dx_3 \\
 & \left. + \int_V \frac{1}{2r^2} \phi''(r) x_i x_j x_m x_n G dx_1 dx_2 dx_3 \right] \\
 & + u_{i,j} (T^* - T) \left[\int_V \frac{1}{r} \phi'(r) x_i x_j \left(\frac{\partial G}{\partial T} \right)_{(q_m)} dx_1 dx_2 dx_3 \right. \\
 & \left. + 2\delta_{ik} \delta_{jk} \int_V \phi(r) \left(\frac{\partial G}{\partial T} \right)_{(q_m)} dx_1 dx_2 dx_3 \right] > 0 \tag{11}
 \end{aligned}$$

where, at most, quadratic terms of the displacement and temperature gradients variables are retained.

The latter inequality is valid for arbitrary small values of $(T^* - T)$, $u_{i,j}$ and, in view of the internal energy approaching the self-energy near the thermodynamical instability as mentioned earlier, for all $V \subseteq V_0$, it leads to

$$\int_V \phi(r) G dx_1 dx_2 dx_3 > 0 \tag{12a}$$

$$\int_V \phi(r) \left(\frac{\partial G}{\partial T} \right)_{(q_m)} dx_1 dx_2 dx_3 > 0 \tag{12b}$$

$$\begin{aligned}
 & \int_V \phi(r) \left(\frac{\partial G}{\partial u_{i,j}} \right)_T dx_1 dx_2 dx_3 + 2\delta_{ij} \int_V \phi(r) G dx_1 dx_2 dx_3 \\
 & + \int_V \frac{1}{r} \phi'(r) x_i x_j G dx_1 dx_2 dx_3 = 0 \tag{12c}
 \end{aligned}$$

$$\int_V \frac{1}{r} \phi'(r) x_i x_j \left(\frac{\partial G}{\partial T} \right)_{(q_m)} dx_1 dx_2 dx_3 = 0 \tag{12d}$$

$$\int_V \frac{1}{2r^2} \phi''(r) G_{x_i x_j x_m x_n} dx_1 dx_2 dx_3 + \int_V \frac{1}{r} \phi'(r) \left(\frac{\partial G}{\partial u_{m,n}} \right)_T x_i x_j dx_1 dx_2 dx_3 > 0 \tag{12e}$$

for all $i, j, m, n = 1, 2, 3$.

From the above independent relations, some properties of the two-particle distribution function may be observed. Firstly, the correlation function is *a priori* susceptible to the nature of the local law of interaction; while it provides a structural description of the lattice, it will also try to adapt itself to any qualitative change in the potential function and will recast the system into a new and stable geometry. Secondly, the aforementioned restrictions are of a global type and a new mode of interaction would necessarily invalidate them. Finally, at a critical point the mode of behaviour of G

can be classified with respect to the external parameters. Both the potential and correlation functions may be approximated by stable unfoldings, possibly of different topological structures. An abrupt change of the energy level causes the discontinuity of the correlation function. Whilst the reverse is not true, and such a case occurs if the solid material undergoes a plastic deformation instead of melting, it can still be concluded that a singular mode of response of G is a necessary and sufficient condition for a global or local disorder. From this discussion and Thom's (1982) hypothesis of local state, we conjecture the following: the degree of determinism of a process is linked to the coupling nature of the local potential and the geometry of the correlation function. This geometry and the global energy of the system may be regarded as coexisting entities which complement one another and together give a unique signature to the medium.

5. Melting of a crystalline solid

To obtain a quantitative evaluation of the moduli at the onset of melting, we use the fact that a simple fluid is a material whose isotropy group is the full unimodular group (Truesdell 1966). Thus, we conclude the disappearance of (12). An illustration is now given for an isotropic elastic medium.

In the spherical coordinates, (12) takes the following form

$$\int_0^R r^2 \phi(r)g(r; T, v) dr > 0 \quad \int_0^R r^2 \phi(r) \left(\frac{\partial G}{\partial T} \right)_{(q_m)} dr > 0 \tag{13a, b}$$

$$\int_0^R r^2 \phi(r)g(r; T, v) dr > 0 \tag{13a}$$

$$\int_0^R r^2 \phi(r) \left(\frac{\partial G}{\partial T} \right)_{(q_m)} dr > 0 \tag{13b}$$

$$3 \int_0^R r^2 \phi(r) \left(\frac{\partial G}{\partial u_{i,i}} \right)_T dr + 6 \int_0^R r^2 \phi(r)g(r; T, v) dr + \int_0^R r^3 \phi'(r)g(r; T, v) dr = 0 \tag{13c}$$

$$\int_0^R r^3 \phi'(r) \left(\frac{\partial G}{\partial \mathbf{F}} \right)_{(q_m)} dr = 0 \tag{13d}$$

$$\int_0^R r^4 \phi''(r)g(r; T, v) dr + 6 \int_0^R r^3 \phi'(r) \left(\frac{\partial G}{\partial u_{i,i}} \right)_T dr > 0 \tag{13e}$$

where R is the radius of the sphere V ; G and its derivatives are evaluated at $[(0, 0); r, T, v]$, and $G[(0, 0); r, T, v] \equiv g(r; T, v)$.

The Lamé constants are expressed by

$$\lambda = k \frac{T}{v} \left[F - v \left(\frac{\partial F}{\partial v} \right)_T \right] - \frac{4\pi}{5v^2} \int_0^\infty r^3 \phi'(r)g(r; T, v) dr + \frac{2\pi}{15v^2} \int_0^\infty r^4 \phi''(r)g(r; T, v) dr \tag{14a}$$

$$\mu = \frac{8\pi}{15v^2} \int_0^\infty r^3 \phi'(r)g(r; T, v) dr + \frac{2\pi}{15v^2} \int_0^\infty r^4 \phi''(r)g(r; T, v) dr \tag{14b}$$

and the bulk modulus becomes

$$K = \lambda + \frac{2}{3}\mu$$

$$= k \frac{T}{v} \left[F - v \left(\frac{\partial F}{\partial v} \right)_T \right] - \frac{4\pi}{9v^2} \int_0^\infty r^3 \phi'(r) g(r; T, v) dr + \frac{2\pi}{9v^2} \int_0^\infty r^4 \phi''(r) g(r; T, v) dr. \quad (15)$$

At the melting temperature, equations (13) are reduced to equalities. In free thermal expansion of the body $u_{i,j}$ is a linear function of $(T^* - T)$ and consequently the shear modulus μ vanishes. Physically the body does not sustain any shear, and this new state of the medium is, in fact, a characteristic of simple liquids.

6. Conclusion

The geometry of the correlation function determines the type of singular response of a medium. At the critical threshold of motion, it is possible to characterise the direction of the evolution of the system to a new state and, by using the extended stability criterion, to evaluate the elastic moduli.

In a forthcoming paper we will apply the concept presented to investigate the onset of irregular behaviour in solids.

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