Materials Science and Engineering A 521–522 (2009) 6–11

Contents lists available at ScienceDirect

Materials Science and Engineering A

journal homepage: www.elsevier.com/locate/msea

# Mechanical properties of simple condensed matter

A.V. Granato *

*University of Illinois at Urbana-Champaign, Department of Physics, 1110 W. Green St., Urbana, IL 61801, USA*

ARTICLE INFO

*Article history:*
Received 7 August 2008
Accepted 17 September 2008

*Keywords:*
Glasses
Liquids
Interstitials

ABSTRACT

Many mechanical properties of glasses and liquids, such as the large shear susceptibility compared to the compressibility, seem strange and unexpected. However, they are basically the same as those found for irradiated crystals at low defect concentrations. This finding is predicted by the Interstitialcy Theory of Condensed Matter (ITCM). According to the ITCM, a liquid is a crystal containing a few percent of interstitialcies (dumbbell configuration), while a glass is a frozen liquid. Recent computer simulations have supported this assertion. Among thermodynamic properties, changes of the shear modulus $G$ and entropy $S$ play a key role in explaining the physics of condensed matter. The sensitivity of measured shear modulus changes is typically about four orders of magnitude greater than that of the entropy. Simple mechanical models can be given for the mechanical properties. The large entropy of melting of the elements provides a proof that the agents of melting are interstitialcies. Shear modulus measurements provide strong evidence for the ITCM.



## 1. Introduction

The shear modulus $G$ (measuring shape change at constant volume) is given as a second derivative of the free energy, as are the bulk modulus $B$ (volume change at constant shape) and the specific heat $C$. Some of the most characteristic features of the changes in properties in and between the solid, liquid and glassy phases of condensed matter are given by $G$ and $C$. We focus here on $G$. The specific heat has been discussed in more detail elsewhere [1]. Changes of the shear modulus can be measured with a precision typically about four orders of magnitude greater than that of the specific heat or entropy. The in-phase response of condensed matter to a periodic external stress gives the elastic constants. The out-of-phase response gives the internal friction; these are related through a Kramers–Kronig relation [2,3].

The earliest theory of matter was given by Aristotle (340–350 BC) [4] as in Fig. 1. His elements of earth, water, air and fire remain more or less in place today, being replaced by the more modern terms of solids, liquids, gases and thermal excitation, respectively. The earth remains the ground state. The theory is simple, explains everything, but predicts nothing. The latter fact excludes it from what is required of a theory today.

The mechanical properties of condensed matter are often described in terms of simple one-dimensional models consisting of springs, dash pots, and mass points, as in Fig. 2. The first such model was given by Hooke [5], in 1678. In three-dimensional matter, the spring constant K represents the shear modulus $G$ or bulk modulus $B$.

In 1867, Maxwell [6] added a dash pot with viscosity $\eta$ to allow for viscous flow to give the equation of motion:

$$\eta\dot{\varepsilon} + G\varepsilon = \sigma \tag{1}$$

where $\sigma$ is the applied stress and $\varepsilon$ is the total strain. This defines a time constant $\tau = \eta/G$ which is still much used today. For a step function stress of duration $T$, or a periodic stress of period $T$, this model provides a unification of solid and liquid-like behavior, with the response solid-like for $T \ll \tau$ and liquid-like for $T \gg \tau$.

In 1907, Einstein [7] used a simple spring and mass point model to provide a unification of mechanical and thermal properties. The frequency $\omega = \sqrt{G/\rho}$ defined an Einstein temperature $\theta$ through the new quantum-mechanical relation $\hbar\omega = k\theta$. He realized that there is no truly static state, even at zero temperature, since there is a zero-point motion. For temperatures, $T < \theta$, for example, room temperature in diamond, the oscillator is not fully excited, and the specific heat is less than the classical Dulong–Petit [8] value of $3R$, where $R$ is the gas constant. This represents a macroscopic observation of the wave nature of matter.

By adding a parallel combination of a dash pot and spring, Snoek, in 1941 [9], was able to describe the behavior of carbon in iron (C/Fe). This is the prototypical example of a dipolar point-defect system. Zener later generalized this effect to other materials, thereby establishing what is now known as the standard anelastic solid [10]. Analogous to dielectric effects, the relationship between the in-phase and out-of-phase response to a periodic stimulus is known as a Debye relaxation.

* Fax: +1 217 244 8544.
*E-mail address:* granato@illinois.edu.

0921-5093/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.msea.2008.09.147

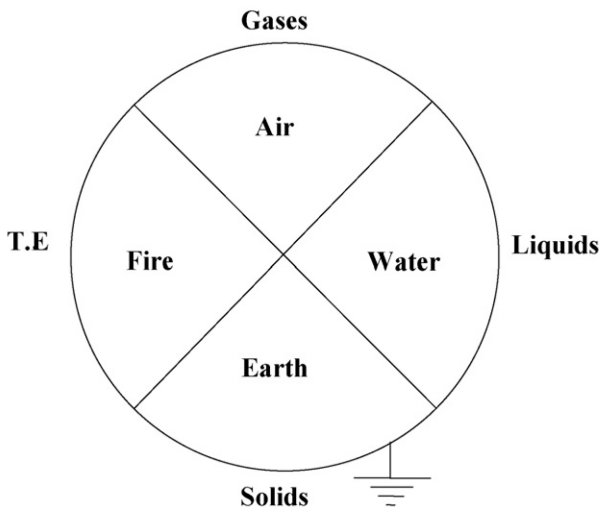


**Fig. 1.** Illustration of Aristotle's theory of matter [4].

In 1946, Frenkel published a book called the "Kinetic Theory of Liquids" [11] that describes some of his research of the previous 20 years. Frenkel's explicit mention of Condensed Matter (see for example the preface) may be the first general use of the term that has come to describe the largest part of research in physics today. Frenkel recognized that liquids near the melting point, and far from the critical point, are more solid-like than gas-like. He realized that a suitable model for condensed matter needed to be a crystal containing intrinsic point defects, either "holes" (vacancies) or "dislocated atoms" (interstitials). At the time, little was known about the properties of these defects and he proceeded supposing they were vacancies. Since that time, it has been found that vacancies cannot account for the entropy of melting; this will be discussed further, subsequently. Then, interstitials are the only possibility.

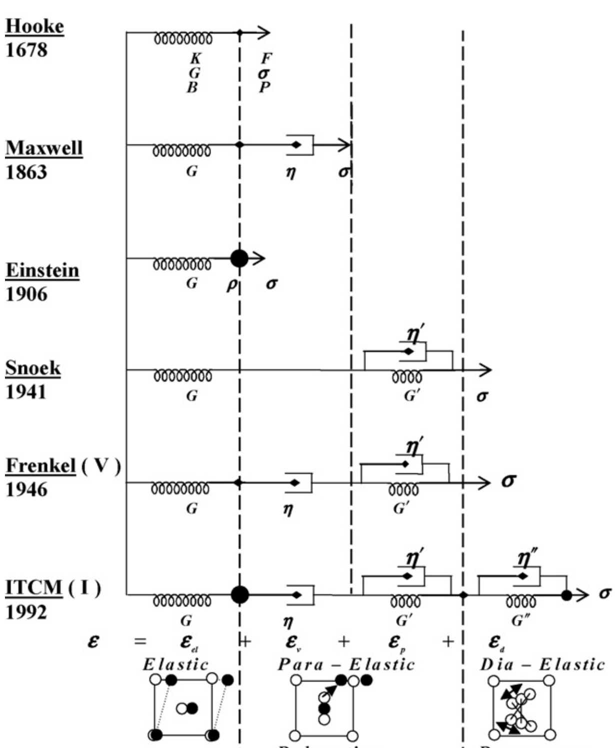


**Fig. 2.** Condensed matter models from Hooke [5] through ITCM (1992).

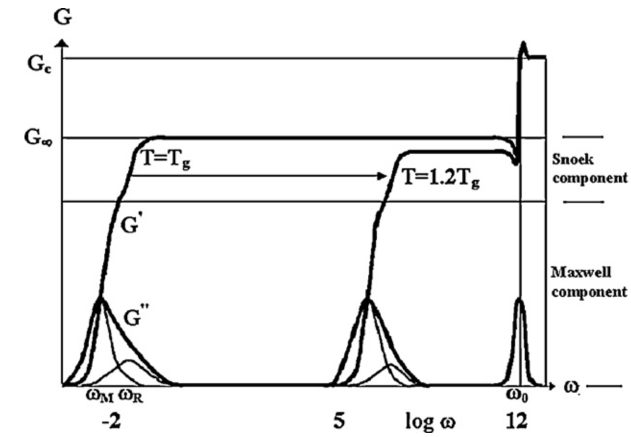


**Fig. 3.** Frequency dependence of shear modulus—In-phase shear modulus ($G'$) and out-of-phase component ($G''$) versus log $\omega$ at $T$ = Tg, and 1.2 Tg. There is a high frequency resonance and low frequency relaxation. The resonance is relatively insensitive while the relaxation is strongly sensitive to temperature [13].

This is the basis of the ITCM [12]. It requires an additional parallel spring—dash pot in the model. This represents a dipole oscillation without diffusion. By analogy with magnetic effects, this is a diaelastic effect in contrast to the para-elastic behavior obtained when the dipole diffuses through the material. It accounts, among other things, for the fact that the so-called "infinite" frequency shear modulus $G_\infty$ for a periodic stress in the Maxwell relation is less (typically by about 30%) than the crystalline value [13] (Fig. 3). The frequency dependence for the in-phase shear modulus $G'$ and the out-of-phase component $G''$for the ITCM model is also shown in the figure. There is a resonance at a frequency $\omega_0 \sim 10^{12}$, with a relaxation at lower frequencies consisting of a superposition of a Snoek-type and Maxwell-type relaxation. The Snoek effect represents an interstitialcy making a single jump and the Maxwell term represents multiple jumps. The resonance is relatively insensitive while the relaxation is strongly sensitive to temperature changes.

## 2. The entropy of melting

The large observed entropy of melting provides a proof that the agents of melting must be interstitials in simple close-packed metals. Melting must require thermally excited intrinsic defects. The only thermally accessible defects are vacancies and interstitials. Dislocations are not equilibrium defects. The entropy of melting is given by $\Delta S_m = L/T_m$, where $L$ is the latent heat and $T_m$ is the melting temperature. For most elements, it has been realized since the nineteenth century to be about 10 J/mole K or about 1.15$R$ (Table 1). This is known as Richards's Rule [14]. The vibrational entropy of vacancies of a few metals became known in the 1960s [15], and its value (~2) is simply too small by an order of magnitude to account for the entropy of melting. This means that interstitials must be the agents of melting.

Table 2 shows typical experimental results for the large vibrational entropy $S_V$ [16,17], and that the shear modulus change should also be anomalously large [18] compared to the volume change. Both these effects are accounted for by the dia-elastic resonance element in the diagram for the ITCM model in Fig. 2.

**Table 1**
Ratio of entropy of melting to volume change $\Delta S_m = L/T_m$ (e.g. Cu).

| | at Tm | Vac |
|---|---|---|
| $\Delta S/R$ | 1.15 | 2 |
| $\Delta V/V$ | 0.45 | 0.8 |
| $\frac{\Delta S/R}{\Delta V/V}$ | 26 | 2.5 |