DOI: 10.1478/AAPP.981A4

AAPP | Atti della Accademia Peloritana dei Pericolanti
Classe di Scienze Fisiche, Matematiche e Naturali
ISSN 1825-1242

Vol. 98, No. 1, A4 (2020)

ON THE FRAGILITY OF COMPLEX MATERIAL SYSTEMS

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Abstract. In this work we investigate, from both a macroscopic and a microscopic point of view, the fragility degree of complex material systems. In particular, we integrate a microscopic and a macroscopic approach. The former is formulated in the framework of non-equilibrium thermodynamics in order to obtain the phenomenological equations for the heat flux and viscous pressure tensor, as functions of the absolute temperature T and of the small strain tensor, in the isotropic case, where the shear viscosity is supposed to depend on T_g/T. The latter is connected with a macroscopic definition of fragility, operatively introduced by Angell for glass-forming systems, and with the definition of thermal restraint, based on elastic incoherent neutron scattering data. On that score literature data of viscosity, as a function of concentration and temperature, and literature data of elastic intensity data are correlated with the system fragility and with the system thermal restraint. The obtained results are of interest for a wide range of innovative materials, such as, for example, carbon nanotubes and bioprotectant systems.

1. Introduction

Materials science is nowadays a fascinating area of research that is often at the cutting edge of science and engineering. This discipline requires both developing new materials and improving on existing ones, and has important applications also for advancing other fields of research. An example is furnished by carbon nanotubes, which are one of the most promising materials today for energy storage, electronics, medicine, engineering. Carbon nanotubes, besides having excellent electrical conductivity, can withstand high working temperatures, and offer a high strength-to-weight ratio. From the structural point of view, carbon nanotubes are constituted by graphene sheets, consisting of single carbon atomic layers, within a honeycomb framework, that can be rolled to form a tube with a nanometer diameter (Ebbesen *et al.* 1996; Yu *et al.* 2010; Liu *et al.* 2013; Venkataraman *et al.* 2019). A second relevant example is furnished by bioprotectant molecules. In nature, particular complex biological systems present a suspended life, passing into a vitreous state of suspended animation under stress conditions (drying and freezing) depending on the temperature and pressure of the environment where these cellular systems live. Cryptobiosis, from Greek kriptos, which means both "hidden" and "coated", refers to a particular state of organisms, during which hidden levels of metabolic functions are maintained form ending prohibitive surrounding conditions. In fact, these complex systems can survive for long periods and after rehydration recover full viability. Given the wide variety and the increasing number of innovative material systems, in many applicative fields, it is of paramount importance to characterize both the system structural sensitivity and the rigidity degree for temperature changes (Magazù *et al.* 1989; Jannelli *et al.* 1996; Faraone *et al.* 1999; Branca *et al.* 2005; Minutoli *et al.* 2007; Cannuli *et al.* 2018).

In this paper a macroscopic model, based on the classical irreversible thermodynamics, is developed to obtain the phenomenological equations for the heat flux q_α and the viscous pressure tensor $P^{(vi)}_{\alpha\beta}$ and to indagate, at macroscopic level, on the fragility degree in glass forming hydrogen bonded systems. In particular, in Section 2, choosing as independent variables the temperature T and the small strain tensor $\varepsilon_{\alpha\beta}$, the expressions for q_α and $P^{(vi)}_{\alpha\beta}$ are derived as functions of these variables. The anisotropic case and also the isotropic case (where the material systems under considerations have thermal and mechanical properties invariant respect to all rotations and inversions of the axes frame) are studied. The results obtained in this thermodynamic scenario are connected to a quantitative approach to define the fragility, operatively, from a macroscopic point of view and the Arrhenius law, for the viscosity η versus T_g/T, where T is the absolute temperature and T_g the glass transition temperature, is discussed. Angell's classification of glass-forming systems is revisited. In Section 3 literature viscosity measurements performed by a set of viscometers as a function of concentration and temperatureand elastic neutron scattering measurements are discussed. It is found that the fragility degree is inversely proportional to the system thermal restraint.

2. Macroscopic point of view to describe fragility

In this Section to introduce the concept of fragility in a macroscopic context, we assume that the glass forming hydrogen bonded system under consideration is a *thermo-viscous isotropic* system, whose thermal and mechanical behaviour can be studied using the procedures of non-equilibrium thermodynamics (see de Groot and Mazur 1962; Kluitenberg 1984; Ciancio 2009; Jou and Lebon 2010; and Restuccia and Kluitenberg 1987, 1988, in which media with more variables are treated). In particular, we suppose that the physical properties of these material systems we are deal with can be illustrated deriving the phenomenological equations for the heat flux q_α and the viscous pressure tensor $P^{(vi)}_{\alpha\beta}$, assumed dependent functions on two suitable independent variables, chosen in such a way to characterize the physical behaviour of these systems, and constituting the thermodynamic state vector, *i.e.*, the internal energy density e, linked to the absolute temperature T by a caloric equation, and the small strain tensor $\varepsilon_{\alpha\beta}$, defined by

$$\varepsilon_{\alpha\beta} = \frac{1}{2}\left(\frac{\partial u_\alpha}{\partial x^\beta} + \frac{\partial u_\beta}{\partial x^\alpha}\right) \quad (\alpha,\beta = 1,2,3), \tag{1}$$

with u_α the displacement field. Introducing the deviator tensor $\tilde{\varepsilon}_{\alpha\beta}$ and the scalar (or spherical) part ε of $\varepsilon_{\alpha\beta}$ in the following way

$$\tilde{\varepsilon}_{\alpha\beta} = \varepsilon_{\alpha\beta} - \frac{1}{3}\varepsilon\delta_{\alpha\beta} \quad \varepsilon = \frac{1}{3}\varepsilon_{\gamma\gamma}, \quad (\alpha,\beta,\gamma = 1,2,3), \tag{2}$$

where Einstein convention for the dummy indices is used, $\varepsilon_{\alpha\beta}$ can be written in the form

$$\varepsilon_{\alpha\beta} = \tilde{\varepsilon}_{\alpha\beta} + \varepsilon\delta_{\alpha\beta}, \text{ with } \tilde{\varepsilon}_{\gamma\gamma} = 0. \tag{3}$$

The following expressions are also true

$$\varepsilon = \frac{1}{3}\operatorname{div}\boldsymbol{u} \quad \tilde{\varepsilon}_{\alpha\beta} = \frac{1}{2}\left(\frac{\partial u_\alpha}{\partial x^\beta} + \frac{\partial u_\beta}{\partial x^\alpha} - \frac{2}{3}\delta_{\alpha\beta}\operatorname{div}\boldsymbol{u}\right), \tag{4}$$

and because $\varepsilon_{\alpha\beta}$ is symmetric also $\tilde{\varepsilon}_{\alpha\beta}$ is symmetric.

Thus, let us introduce the first law of thermodynamics for the considered media in the following form

$$\frac{de}{dt} = -\operatorname{div}\boldsymbol{q} + P_{\alpha\beta}\frac{d\varepsilon_{\alpha\beta}}{dt}, \tag{5}$$

where we have disregarded the energy source, the mechanical pressure tensor is symmetric and the operator $\frac{d}{dt}$ indicates the material derivative with respect to time, defined by

$$\frac{d}{dt} = \frac{\partial}{\partial t} + v_\gamma \frac{\partial}{\partial x^\gamma}, \tag{6}$$

with $\frac{\partial}{\partial t}$ the local derivative with respect to time and x_i $(i = 1,2,3)$ Cartesian coordinates. In the following the standard Cartesian tensor notation in a rectangular coordinate system, in a current configuration $\mathscr{K}_t$, will be used.

Let us assume that the specific entropy s (*i.e.*, the entropy per unit of mass) is a function of the internal energy and the small strain tensor

$$s = s(e, \varepsilon_{\alpha\beta}). \tag{7}$$

We shall define the absolute temperature T and the equilibrium pressure tensor $P^{(eq)}_{\alpha\beta}$ in terms of the partial derivatives of s respect to the corresponding conjugate variables in the form

$$T^{-1} = \frac{\partial s}{\partial e}\left(e, \varepsilon_{\alpha\beta}\right), \tag{8}$$

$$P^{(eq)}_{\alpha\beta} = -\rho T \frac{\partial s}{\partial \varepsilon_{\alpha\beta}}\left(e, \varepsilon_{\alpha\beta}\right). \tag{9}$$

From Eqs. 7- 9 we obtain for the differential of s, multiplied by T, the following expression, called Gibbs relation,

$$T ds = de - vP^{(eq)}_{\alpha\beta} d\varepsilon_{\alpha\beta}, \tag{10}$$

where the definition of specific volume v, given by $\rho = 1/v$, is used.

From Eq. 10 it follows that

$$T\frac{ds}{dt} = \frac{de}{dt} - vP^{(eq)}_{\alpha\beta}\frac{d\varepsilon_{\alpha\beta}}{dt}. \tag{11}$$

Inserting Eq. 5 into Eq. 11 we have

$$\rho\frac{ds}{dt} = T^{-1}\left(-\operatorname{div}\boldsymbol{q} + P^{(vi)}_{\alpha\beta}\frac{d\varepsilon_{\alpha\beta}}{dt}\right), \tag{12}$$

where $P^{(vi)}_{\alpha\beta}$ is the viscous (irreversible) pressure tensor defined by

$$P^{(vi)}_{\alpha\beta} = P_{\alpha\beta} - P^{(eq)}_{\alpha\beta}. \tag{13}$$

From Eq. 12 we derive the balance equation for the entropy

$$\rho \frac{ds}{dt} = -\operatorname{div}\boldsymbol{J}^{(s)} + \sigma^{(s)}, \tag{14}$$

where $\boldsymbol{J}^{(s)} = T^{-1}\boldsymbol{q}$ is the entropy flux and $\sigma^{(s)}$ is the internal entropy production per unit volume and per unit time, given by

$$\sigma^{(s)} = T^{-1}\left(\boldsymbol{q}\cdot\boldsymbol{X}^{(q)} + P^{(vi)}_{\alpha\beta}\frac{d\varepsilon_{\alpha\beta}}{dt}\right). \tag{15}$$

In Eq. 15 the field $\boldsymbol{X}^{(q)}$ is defined by

$$\boldsymbol{X}^{(q)} = -T^{-1}\operatorname{grad} T. \tag{16}$$

In Eq. 15 the internal entropy source $\sigma^{(s)}$ (a non-negative quantity) is zero if the system under consideration is in thermodynamic equilibrium, where $\operatorname{grad} T$ and $\frac{d\varepsilon_{\alpha\beta}}{dt}$ are null. From Eq. 15 it is seen that the entropy production is given by two contributions: the first term arises from the heat conduction, the second is connected with the gradient of velocity field ($\frac{d\varepsilon_{\alpha\beta}}{dt}$ is the symmetric part of the velocity gradient), giving rise to viscous effects. Also from Eq. 15 it is seen that the expression of $\sigma^{(s)}$ is a bilinear form composed of sum of terms, where each term is the inner product of two factors of which one is the *flux* and the other is the *thermodynamic force*, or the *affinity*, conjugate to the flux.

Following a standard method of non-equilibrium thermodynamics we derive for the considered medium, supposed anisotropic in a first step of the thermodynamic procedure, the following phenomenological equations

$$q_\alpha = L^{(q,q)}_{\alpha\beta}X^{(q)}_\beta + L^{(q,vi)}_{\alpha\beta\gamma}\frac{d\varepsilon_{\beta\gamma}}{dt}, \tag{17}$$

$$P^{(vi)}_{\alpha\beta} = L^{((vi),q)}_{\alpha\beta\gamma}X^{(q)}_\gamma + L^{(vi,vi)}_{\alpha\beta\gamma\zeta}\frac{d\varepsilon_{\gamma\zeta}}{dt}. \tag{18}$$

Equations 17 and 18 describe irreversible processes inside the medium and represent the generalizations of Fourier's law and Newton's law, respectively. Furthermore, in their right-hand sides the second term in Eq. 17 and the first term in Eq. 18 describe cross effects between heat conduction and mechanical viscosity. The quantities $\boldsymbol{L}$ are phenomenological tensors. In particular, $L^{(q,q)}_{\alpha\beta}$ is the second order tensor of the heat conductivity, $L^{(vi,vi)}_{\alpha\beta\gamma\zeta}$ is the tensor of order four of the viscosity, $L^{(q,vi)}_{\alpha\beta}$ and $L^{(vi,q)}_{\alpha\beta}$ are second order tensors connected with the interaction between thermal and viscous phenomena. From experiments it is possible to know the values of these phenomenological coefficients. By virtue of the symmetry of $\varepsilon_{\alpha\beta}$, from Eq. 9 it follows that also $P^{(eq)}_{\alpha\beta}$ is a symmetric tensor and then from Eq. 13 the viscous stress tensor $P^{(vi)}_{\alpha\beta}$ is also a symmetric tensor. Thus, we obtain the following symmetry relations for the phenomenological tensors

$$L^{(q,vi)}_{\alpha\beta\gamma} = L^{(q,vi)}_{\alpha\gamma\beta}, \quad L^{(vi,q)}_{\alpha\beta\gamma} = L^{(vi,q)}_{\beta\alpha\gamma}, \tag{19}$$

$$L^{(vi,vi)}_{\alpha\beta\gamma\zeta} = L^{(vi,vi)}_{\beta\alpha\gamma\zeta} = L^{(vi,vi)}_{\alpha\beta\zeta\gamma} = L^{(vi,vi)}_{\beta\alpha\zeta\gamma}. \tag{20}$$

Since $\boldsymbol{q}$ and $\frac{d\varepsilon_{\alpha\beta}}{dt}$ are odd functions under time reversal and $\boldsymbol{X}^{(q)}$ and $\tau^{(vi)}_{\alpha\beta}$ are even functions under time reversal, the Onsager-Casimir reciprocity relations read

$$L^{(q,q)}_{\alpha\beta} = L^{(q,q)}_{\beta\alpha}, \quad L^{(vi,vi)}_{\alpha\beta\gamma\zeta} = L^{(vi,vi)}_{\gamma\zeta\alpha\beta}, \quad L^{(q,vi)}_{\alpha\beta\gamma} = -L^{(vi,q)}_{\beta\gamma\alpha}. \tag{21}$$

The relations 19-21 reduce the number of independent components of the phenomenological tensors.

Inserting expressions 17 and 18 for $\boldsymbol{q}$ and $\tau^{(vi)}_{\alpha\beta}$ in Eq. 15, by virtue of symmetry and Onsager-Casimir reciprocity relations, we obtain for the entropy production the following form

$$\sigma^{(s)} = T^{-1}\left\{L^{(q,q)}_{\alpha\beta} X^{(q)}_{\alpha} X^{(q)}_{\beta} + L^{(vi,vi)}_{\alpha\beta\gamma\zeta} \frac{d\varepsilon_{\alpha\beta}}{dt}\frac{d\varepsilon_{\gamma\zeta}}{dt}\right\}. \tag{22}$$

Equation 22 shows that the entropy production is a quadratic form in the components of the time derivatives of the gradient of the temperature and in the components of the time derivative of the strain tensor. Furthermore, the second law of thermodynamics establishes that the entropy production is a positive definite quadratic form, *i.e.*,

$$\sigma^{(s)} \geq 0. \tag{23}$$

From its positive definite character (see Famà *et al.* 2019, for detailed dicussions and calculations regarding this character) some inequalities may be derived for the components of the phenomenological coefficients. For instance, we have

$$L^{(q,q)}_{\alpha\alpha} \geq 0, \quad L^{(vi,vi)}_{\alpha\beta\alpha\beta} \geq 0 \tag{24}$$

and by virtue of symmetry and Onsager-Casimir relations also we obtain

$$L^{(vi,vi)}_{\alpha\beta\beta\alpha} \geq 0, \quad L^{(vi,vi)}_{\beta\alpha\alpha\beta} \geq 0, \quad L^{(vi,vi)}_{\beta\alpha\beta\alpha} \geq 0. \tag{25}$$

The existence of spatial symmetry properties in the considered material systems may simplify the form of the phenomenological equations 17 and 18 in such a way that the Cartesian components of the fluxes do not depend on all the Cartesian components of the thermodynamic forces (a statement called Curie symmetry principle, see de Groot and Mazur 1962). Thus, we shall assume that the media taken into account have symmetry properties such that they are isotropic with respect to all rotations and inversions of the frame of axes. In this case for the second order tensor $L^{(q,q)}_{\alpha\beta\gamma}$, the three order tensors $L^{(q,vi)}_{\alpha\beta\gamma}$ and $L^{(q,vi)}_{\alpha\beta}$ and the fourth order tensor $L^{(vi,vi)}_{\alpha\beta\gamma\zeta}$ we have (Jeffreys 1931; de Groot and Mazur 1962):

$$L^{(q,q)}_{\alpha\beta} = L^{(q,q)}\delta_{\alpha\beta}, \quad L^{(q,vi)}_{\alpha\beta\gamma} = 0, \quad L^{(q,vi)}_{\alpha\beta\gamma} = 0,$$

$$L^{(vi,vi)}_{\alpha\beta\gamma\zeta} = \frac{1}{2}\eta_s\left(\delta_{\alpha\gamma}\delta_{\beta\zeta} + \delta_{\beta\gamma}\delta_{\alpha\zeta}\right) + \frac{1}{3}\left(\eta_v - \eta_s\right)\delta_{\alpha\beta}\delta_{\gamma\zeta}, \tag{26}$$

where η_v is the volume viscosity and η_s is the shear viscosity. Using the isotropy relations in Eq. 26, the phenomenological equations 17 and 18 take the form

$$q_\alpha = -\lambda\,\mathrm{grad}\,T, \tag{27}$$

$$P^{(vi)}_{\alpha\beta} = \eta_s \frac{d\tilde{\varepsilon}_{\alpha\beta}}{dt} + \eta_v \frac{d\tilde{\varepsilon}}{dt}\delta_{\alpha\beta}, \tag{28}$$

where we have introduced the thermal conductivity $\lambda = T^{-1}L^{(q,q)}$ and we have used the definitions in Eqs. 2, 3 and 16. Equations (27) and (28) represent, respectively, Fourier heat equation and Navier-Stokes equation for isotropic thermoviscous media. In this paper we have supposed that the Fourier heat equation describes the thermal disturbances, having infinite velocity and diffusive character. Other thermodynamic theories and studies regard descriptions of propagation of thermal signals having finite velocity, where, for example, the relaxation time of the heat flux towards its thermodynamic equilibrium value is taken into consideration and the thermal disturbances are fast (see, for instance, Muschik and Restuccia 2006; Jou and Lebon 2010; and also Ciancio and Restuccia 2019, where the classical irreversible thermodynamics (CIT) with internal variables was applied). In our case we have used the CIT theory without internal variables (de Groot and Mazur 1962), because we have focused our attention only on the viscous phenomena.

Substituting the phenomenological laws 27 and 28 in the expression 15 for the entropy production we have

$$\sigma^{(s)} = T^{-1}\left\{T^{-2}L^{(q,q)}(\operatorname{grad} T)^2 + \eta_s\left(\frac{d\tilde{\varepsilon}_{\alpha\beta}}{dt}\right)^2 + 3\eta_v\left(\frac{d\tilde{\varepsilon}}{dt}\right)^2\right\}. \tag{29}$$

From Eq. 29 it is seen that the entropy production is a non-negative bilinear form in the components of the gradient of temperature, the components of of the time derivative of the deviator of the strain tensor and the time deriative of the scalar part of this tensor. In the case of considered media we suppose $\eta_s(T_g/T)$ depending on T_g/T, *i.e.*, $\eta_s(T_g/T)$, and neglecting the contribution $\eta_v \frac{d\tilde{\varepsilon}}{dt}\delta_{\alpha\beta}$, given by the spherical part of $\frac{d\tilde{\varepsilon}}{dt}$, calling by η the shear viscosity η_s and by $P^{(vi)}_{\eta\alpha\beta}$ the shear viscous contribution of $P^{(vi)}_{\alpha\beta}$, we have

$$P^{(vi)}_{\eta\alpha\beta} = \eta(T_g/T)\frac{d\tilde{\varepsilon}_{\alpha\beta}}{dt}. \tag{30}$$

The dependence of the phenomenological coefficient η on (T/T_g) is new in the literature and starting from the phenomenological equation 30 for the viscous pressure tensor $P^{(vi)}_{\eta\alpha\beta}$, it is possible to connect this thermodynamic scenario to a quantitative approach to define the fragility m, operatively defined as

$$m = \left.\frac{d\log\eta}{d(T_g/T)}\right|_{T=T_g}, \tag{31}$$

where T is the absolute temperature, η is the shear viscosity.

Taking into account the definition 31, there exists an Angell's classification of glass-forming systems "strong" and "fragile" of particular relevance (Angell *et al.* 1994; Angell 1995) that is based on the choice of an invariant of the shear viscosity that at $T = T_g$ has the value $\eta\left(\frac{T_g}{T}\right)\Big|_{T=T_g} = \eta(1) = 10^{13} poise$ (being T_g a scaling temperature) (Angell 1997). Furthermore, the deviation from the celebrated Arrhenius law is connected with the degree of the the fragility of the system, defined as structural sensitivity to temperature changes in approaching T_g.

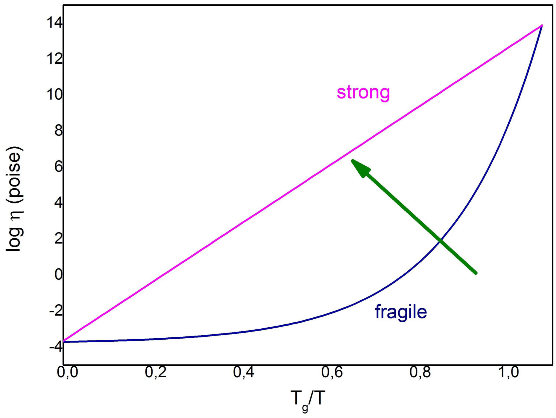

FIGURE 1. Angell's plot which reports the two limit cases: strong and fragile behaviors.

In this paper, in a macroscopic frame we illustrate this fragility property assuming that the physical law describing η versus T_g/T, *i.e.*, $\eta = \eta(T_g/T)$ has the following form:

$$\frac{d\eta}{d(T_g/T)} = m\eta \tag{32}$$

where the positive fragility m is an "increasing coefficient of η" and $\frac{d\eta}{d(T_g/T)}$ represents the rate of η with the respect to T/T_g. From (32), by separation of variables, we have:

$$\frac{d\eta}{\eta} = md\left(\frac{T_g}{T}\right). \tag{33}$$

In the hypothesis in which m is a constant, we obtain Arrhenius law. In fact, by an integration we have

$$\int_{\eta_0}^{\eta} d\log\eta = m\int_{T_g/T_0}^{T_g/T} d\left(\frac{T_g}{T}\right), \tag{34}$$

where we have indicated by η_0 and T_0 the values of η and T at a reference state, that is also an equilibrium thermodynamic state. From (38) after integration, we obtain:

$$\log\eta = \log\eta_0 + m(T_g/T), \tag{35}$$

where we have continued to call by T_g/T the difference $T_g/T - T_g/T_0$. Equation (35) represents a straight line in the plan $(\log\eta, T_g/T)$ (see Fig. 1). The slope (trigonometric tangent) of this straight line is a constant m. From (35) we obtain

$$\log\frac{\eta}{\eta_0} = m(T_g/T), \tag{36}$$

from which we derive the celebrated law of Arrhenius type, with m constant

$$\eta = \eta_0 e^{m(T_g/T)}. \tag{37}$$

2.1. Experimental data and discussion. In the following we discuss the trehalose-water system, which has a huge number of application in the biophysics field due to its bioprotectant effectiveness (Branca *et al.* 1999, 2001, 2002; Magazù *et al.* 2012). Viscosity measurements were performed by a set of viscometers as a function of volume fraction and temperature. Figure 2 shows the viscosity behaviour as a function of volume fraction at four different temperature values, *i.e.*, T=25°C, 45°C, 65°C and 85°C.

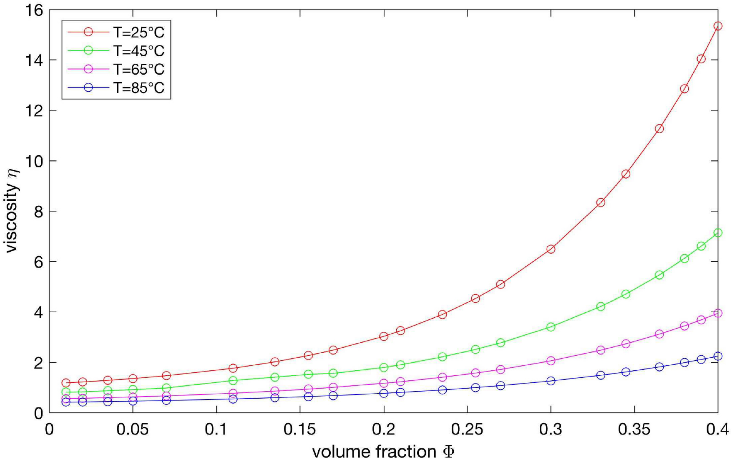

FIGURE 2. Viscosity data versus volume fraction for four different temperatures. As it can be seen, in the high diluited regime, by increasing the volume fraction the viscosity temperature dependence increases.

The difficulties encountered in measuring fragility increase by approach the glass transition temperature and can be overcome by Elastic Incoherent Neutron Scattering (EINS) (Minutoli *et al.* 2008; Magazù *et al.* 2013a; Migliardo *et al.* 2013). In order to extract quantitative information from the $I_{EINS}(T)$, behaviors it is possible to use the following expression:

$$I_{\mathrm{EINS}}(T) = \frac{Ae^{-B(T-T_0)}}{1+e^{-B(T-T_0)}} + C - DT, \tag{38}$$

where A denotes the amplitude factor connected with the global thermal intensity behavior, *i.e.*, with the system thermal restraint or resilience. It should be noticed that this quantity is not connected with a local behavior but represents a global property of the system. B is associated with the transition steepness, passing from smaller to higher values when the transition becomes more and more abrupt. As it can be inferred by the following RENS (Resolution Elastic Neutron Scattering) approach, T_0 represents the inflection temperature, corresponding to the temperature value for which the system relaxation time equals the instrumental resolution time (Caccamo *et al.* 2018a,b; Magazù *et al.* 2018). On this concern such a temperature value should occur at different values for the different systems. As a final point, $C - DT$ characterizes the low temperature vibrational contribution (Magazù *et al.* 2011; Magazù *et al.* 2013b). The analysis of the thermal restraint as a function of

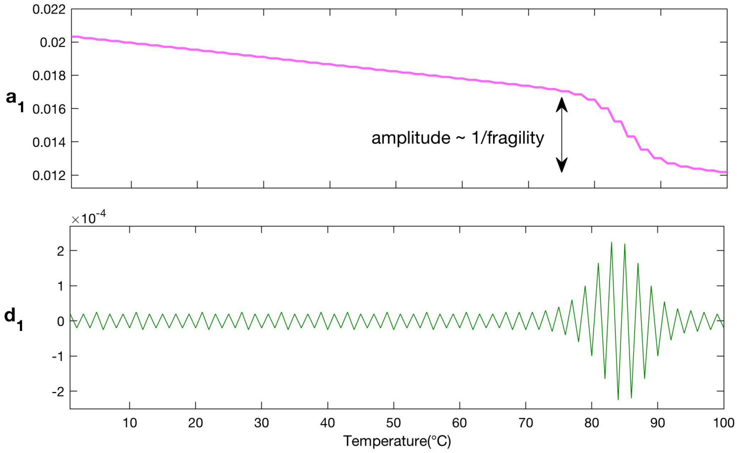

FIGURE 3. Elastically scattered intensity of trehalose as a function of temperature after the decompostion by wavelet analysis.

temperature performed on different glass-forming systems showed that a lower fragility, namely by a higher structural resistance to temperature changes, is connected with a higher value of the force field constant and with a lower amplitude A, *i.e.*, with a higher system thermal restraint. In order to better analyse the signal a Discrete Wavelet Transform has been employed. Such a method allows to decompose the signal into approximation coefficients (a_c) and detail coefficients (d_c). In particular, Fig. 3 shows the approximation coefficient (a_1) and the detail coefficient (d_1) resulting from the Daubechies wavelet analysis (Caccamo and Magazù 2018; Mezei *et al.* 2019; Caccamo *et al.* 2020).

3. Microscopic description of fragility

We observe that in a microscopic frame the fragility is given by the thermodynamic and kinematic operative definition

$$m = \frac{\Delta C_p(T_g)}{\Delta \mu} \tag{39}$$

where $\Delta C_p(T_g)$ is the heat capacity at glass transition temperature T_g, $\Delta\mu$ is the potential energy barrier height (see Eq. 31). The complexity of the energy landscape variation with temperature can be correlated with the number of minima of the potential energy hypersurface, *i.e.*, its degeneracy degree and with the average energy height barriers. These topological features determine the structural sensitivity to temperature changes, *i.e.*, the "fragility".

A small heat capacity variation $\Delta C_p(T_g)$ characterizes the strongest systems, whereas a large deviation from Arrhenius law and a large heat capacity variation $\Delta C_p(T_g)$ characterize the most fragile ones (Zellner 1979; Gosálvez *et al.* 2005). In the all embracing Angell's portrayal plot, between the two limit cases, strong and fragile, intermediate behaviours can be interpreted in terms of different kinematic and thermodynamic contributions, $\Delta C_p(T_g)$.

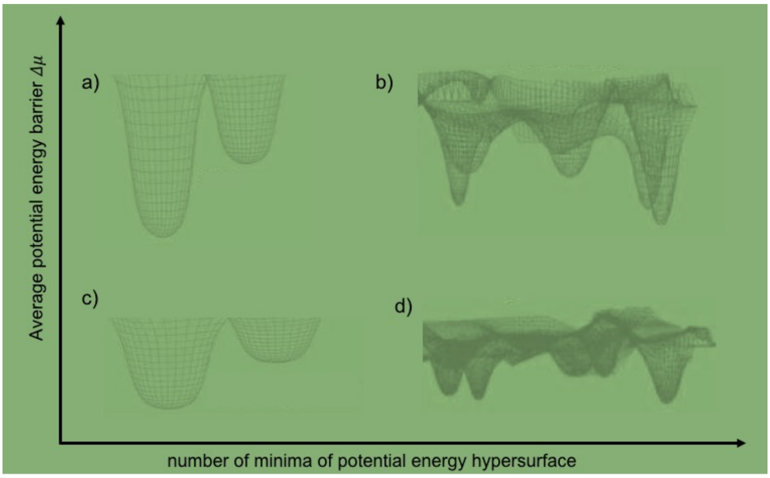

FIGURE 4. Qualitative sketch of potential energy hypersurface behavior in glass forming system. The abscissa reports the number of minima of potential energy hypersurface while the ordinate reports the potential energy hypersurface height.

More specifically, in Fig. 4 a qualitative sketch is shown:

- thermodynamically strong - $\Delta C_p(T_g)$ - and kinetically fragile systems (non-Arrhenius behaviour) are characterized by a low minima density and low energy barriers;
- vice-versa thermodynamically fragile - large $\Delta C_p(T_g)$ - and kinetically strong systems (Arrhenius behaviour) show a high hyper-surface configurational degeneracy and high barrier heights.

Conclusions

In this work a quantitative mathematical approach to investigate the fragility degree in complex material systems has been developed. On this purpose, using the procedures of the classical irreversible thermodynamics explicit expressions for the phenomenological equations for the heat flux and the viscous pressure tensor were derived, describing the thermal and mechanical properties of the media under consideration, and in the isotropic case the shear viscosity was supposed dependent on (T_g/T). This thermodynamic panorama was linked to the operative macroscopic definition of the fragility and Arrhenius law, connected with the fragility of the material systems under consideration, was discussed. The approaches clearly show that the system fragility degree is inversely proportional to the system thermal restraint.

Acknowledgements

The authors acknowledge the “National Group of Mathematical Physics” (GNFM-INdAM); M.T.C. acknowledges the AIM Project.

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Communicated 23 June 2016; manuscript received 31 May 2017; published online 18 May 2020