

# Probing cooperative liquid dynamics with the mean square displacement

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(Received 19 November 2013; revised manuscript received 25 September 2014; published 21 October 2014)

Literature data for picosecond mean square displacements show that the anharmonicity explains only about half of the fragility (with different fractions for different glass formers). The other half must be ascribed to the Adam-Gibbs mechanism of a growing cooperatively rearranging region. One can measure both influences separately by a simultaneous measurement of liquid and crystal in the coexistence region.

DOI: [10.1103/PhysRevE.90.042312](https://doi.org/10.1103/PhysRevE.90.042312)

PACS number(s): 64.70.pm, 63.50.-x

## I. INTRODUCTION

The microscopic reason for the spectacular slowing down of the structural relaxation time scale at the glass transition is a very controversial topic [1–11]. If one models the flow in terms of a thermally activated process, one has to postulate a flow barrier which increases drastically with decreasing temperature.

There are two possible physical mechanisms for such an energy barrier increase. One of them is the Adam-Gibbs mechanism [1] of a growing cooperatively rearranging region. Recent numerical work has corroborated the existence of a growing dynamic length scale [12–14], supporting the Adam-Gibbs explanation. Numerical simulations of model glass formers allow higher-order correlation functions to be calculated. From these (and also in other alternative ways [14]), the length scale of the cooperative dynamics can be extracted [12,13]. This, in turn, has led to the development of new experimental techniques to measure the dynamic length scale in real glass formers [7–9], which are now supposedly even able to test the Adam-Gibbs hypothesis of a flow energy barrier proportional to the number of atoms in the cooperatively rearranging region [10,11].

An alternative explanation in terms of the “elastic model” attributes the strong flow barrier increase on cooling (the fragility) to the anharmonic increase of the short time shear modulus [2–4], reflected in a strong decrease of the mean square displacement on the neutron scattering time scale of picoseconds to nanoseconds [15,16]. At present, both the elastic model [2–4] and the cooperativity model [9–11] claim to be able to explain the full fragility alone.

The present paper intends to reconcile the two conflicting views on the fragility, showing that one has to take both influences into account. It gives a recipe to measure both the temperature dependence of the volume of the cooperatively rearranging region and the anharmonicity from the neutron scattering mean square displacements of liquid and crystal.

After this introduction, Sec. II presents a critical survey of the anharmonicity evidence. It is shown that the picosecond mean square displacements from neutron scattering

measurements in the literature explain only about one-half of the fragility. Section III returns to an old description of the viscosity of selenium [17] in terms of the picosecond mean square displacements of liquid and crystal in their coexistence region, providing it with a physical explanation in terms of the Adam-Gibbs cooperativity. The explanation implies that one can determine the two sources of the fragility separately by such a measurement. The description is applied to two other examples, orthoterphenyl and glycerol. Section IV discusses and concludes the paper.

## II. CRITICAL SURVEY OF THE ANHARMONICITY EVIDENCE

### A. General considerations

Let us first recall the connection between shear modulus and mean square displacement. If one takes the glass former to be a Debye solid and uses the high temperature approximation, the mean square displacement in *one* spatial direction reads

$$\langle u^2 \rangle = \frac{3k_B T}{M\omega_D^2}, \quad (1)$$

where  $M$  is the average atomic mass and  $\omega_D$  is the Debye frequency.

The Debye frequency is given by the longitudinal sound velocity  $v_l$  and the transverse sound velocity  $v_t$ ,

$$\omega_D^3 = \frac{18\pi^2}{v(1/v_l^3 + 2/v_t^3)}, \quad (2)$$

where  $v = a^3$  is the atomic volume. Taking a typical ratio  $v_l/v_t$  of 1.8, one gets the mean square displacement

$$\langle u^2 \rangle = 0.159 \frac{k_B T}{Gv} a^2, \quad (3)$$

where  $G = Mv_t^2/v$  is the shear modulus. Equation (3) shows that within the Debye approximation,  $G$  is indeed an equivalent quantity to  $T/\langle u^2 \rangle$ .

Note that the application of Eq. (3) to the crystal allows an alternative formulation of the Lindemann criterion [18] in terms of the average shear modulus of the crystal. The Lindemann criterion postulates that a crystal melts when the

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mean square displacement amplitude reaches one-tenth of the interatomic distance  $a$ .

Following Olsen and Dyre [3], we define the fragility in terms of the negative logarithmic derivative  $I$  of the flow barrier  $E_b$  with respect to temperature at atmospheric pressure [ $I = (m - 16)/16$  in terms of the usual measure  $m$  of the fragility [19]]. The flow barrier should be proportional both to  $N_{\text{corr}}$ , the number of atoms in a cooperatively rearranging region, and to  $T/\langle u^2 \rangle$ . Therefore,

$$I = -\frac{\partial \ln E_b}{\partial \ln T} = I_{\text{coop}} + I_{\text{anh}}, \quad (4)$$

with the cooperativity coefficient

$$I_{\text{coop}} = -\frac{\partial \ln N_{\text{corr}}}{\partial \ln T} \quad (5)$$

and the anharmonicity coefficient

$$I_{\text{anh}} = \frac{\partial \ln \langle u^2 \rangle}{\partial \ln T} - 1 = -\frac{\partial \ln G}{\partial \ln T}. \quad (6)$$

The equality of the two anharmonicity coefficients  $I_{\text{anh}}$  from the mean square displacement and from the shear modulus is based on the Debye approximation, a purely vibrational argument. Nevertheless, we will see in the comparison to experimental data below that it seems to hold for relaxations as well.

But we will also see that the anharmonicity coefficients depend on the time scale, increasing at longer times by the influence of the relaxations. From a theoretical point of view, one should choose the mean square displacement on the time scale of a picosecond to judge the anharmonicity of the flow barrier. A picosecond is a reasonable estimate for the time it takes to pass the barrier (the waiting time for the necessary local accumulation of thermal energy is obviously much longer). The picosecond mean square displacement includes the effect of vibrations, but excludes the effect of relaxations. If one includes relaxations, one must expect to see a larger anharmonic change than the relevant one on the barrier passage time scale.

## B. Mean square displacements

Figure 1 shows measurements of the mean square displacements in polybutadiene below and above the glass transition temperature. The lower values [20] were measured both for protonated and deuterated samples on the time-of-flight spectrometer IN6 with a resolution width of 0.2 meV, excluding all relaxation with relaxation times longer than a few picoseconds and thus reflecting essentially only the vibrational spectrum. The higher values [21] were obtained on the backscattering spectrometer IN10 with a resolution of 1  $\mu\text{eV}$ , including the fast relaxations with relaxation times up to a nanosecond, which obviously make a very sizable contribution to the mean square displacement at the glass transition.

To determine the anharmonicity from these curves, the values above  $T_g$  are fitted in terms of a parabola. The slope at  $T_g$  determines  $\partial \ln \langle u^2 \rangle / \partial \ln T$ . One gets  $3.6 \pm 0.9$  for the backscattering data and  $2.7 \pm 0.5$  for the time-of-flight data (the larger error bar for the backscattering value comes from the stronger curvature). This indicates a larger anharmonicity

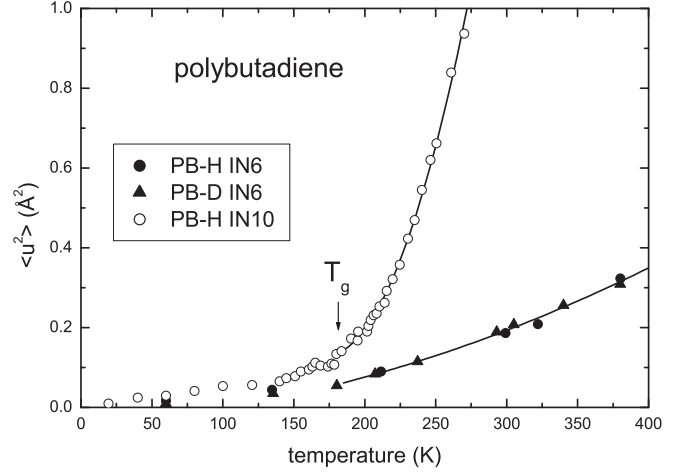


FIG. 1. The temperature dependence of the mean square displacement in glassy and liquid polybutadiene from measurements on the time-of-flight spectrometer IN6 with picosecond resolution [20] and on the backscattering spectrometer IN10 with nanosecond resolution [21]. The lines are parabolic fits of the data above the glass temperature  $T_g$ .

coefficient for the relaxations, a difference which is not quite resolved within experimental error.

But there has been a recent dedicated study able to resolve this difference [16]. It showed a smaller anharmonicity coefficient for the backscattering spectrometer IN13, with a resolution corresponding to 0.4 ns, than for the IN10, with a factor of ten better resolution, a difference clearly out of the error bars for three different glass formers, i.e., glycerol, dibutylphthalate (DBP), and decahydroisoquinoline (DHIQ).

Table I lists the anharmonic coefficient  $I_{\text{anh}}$  determined from neutron measurements in the literature for eight glass formers, taking the lower IN13 values from the work of the Roskilde group [16] in order to keep as close as possible to the

TABLE I. Anharmonic and cooperative fractions of the full fragility  $I = (m - 16)/16 = I_{\text{anh}} + I_{\text{coop}}$  in eight glass formers, determined from the logarithmic derivative of the mean square displacement at the glass temperature  $T_g$ . The values for  $m$  are taken from Refs. [19] and [16].

Substance	$m$	$I$	$\partial \ln \langle u^2 \rangle / \partial \ln T$	$I_{\text{anh}}$	$I_{\text{coop}}$
glycerol	53	2.3	$2.0 \pm 0.1^{\text{a}}$	1.0	$1.2 \pm 0.1$
dibutylphthalate	69	3.3	$2.6 \pm 0.5^{\text{a}}$	1.6	$1.7 \pm 0.5$
DHIQ	160	9.0	$2.2 \pm 0.5^{\text{a}}$	1.2	$7.8 \pm 0.5$
$\text{B}_2\text{O}_3$	32	1.0	$2.2 \pm 0.3^{\text{b}}$	1.2	$-0.2 \pm 0.3$
orthoterphenyl	81	4.1	$3.1 \pm 0.4^{\text{c}}$	2.1	$2.0 \pm 0.4$
1,4-polybutadiene	84	4.3	$2.7 \pm 0.5^{\text{d}}$	1.7	$2.6 \pm 0.5$
selenium	87	4.4	$3.1 \pm 0.2^{\text{e}}$	2.1	$2.3 \pm 0.2$
polystyrene	139	7.7	$2.0 \pm 0.3^{\text{f}}$	1.0	$6.7 \pm 0.3$

<sup>a</sup>Ref. [16].

<sup>b</sup>Ref. [22].

<sup>c</sup>Ref. [23].

<sup>d</sup>Ref. [20].

<sup>e</sup>Ref. [17].

<sup>f</sup>Ref. [24].

relevant picosecond range. The resulting value for  $I_{\text{anh}}$  is never larger than 2.1, showing that one needs a strong cooperativity contribution for very fragile glass formers. Only in  $\text{B}_2\text{O}_3$ , a strong network glass former, is the whole fragility due to the anharmonicity within experimental error. Generally, one has to reckon with a strong cooperativity contribution, in particular for fragile glass formers.

This has also been seen in a recent data collection of mean square displacements [15], which had to postulate a proportionality of the logarithm of the viscosity to  $\alpha + \beta/\langle u^2 \rangle + \gamma/\langle u^2 \rangle^2$ . The term  $\gamma/\langle u^2 \rangle^2$  introduces a similar effect as the temperature dependence of  $N_{\text{corr}}$  and tends to dominate the behavior at  $T_g$ .

In view of the clear result of Table I, the question arises: Why does one often see the full fragility in shear modulus measurements [2–4]? This will be the subject of the next section.

### C. Shear moduli

Measurements of the temperature dependence of the short time shear modulus  $G$  of the undercooled liquid offer an independent way to determine the influence of the anharmonicity on the flow barrier via the logarithmic temperature derivative of the shear modulus [see Eq. (6)].

It has been shown [2–4] that this recipe explains the full fragility  $I$  in many glass formers, contradicting the conclusion of the preceding section. This holds even for one of the glass formers in Table I: selenium. Calculating the shear modulus of selenium from ultrasonic data [25] above the glass temperature of 304 K, one finds  $I_{\text{anh}} = 4.9 \pm 0.5$ , which explains the full fragility within experimental error. Obviously, the shear modulus of liquid selenium is a factor of two to three more anharmonic than the mean square displacement.

In this section, we will argue that the discrepancy is not due to a different anharmonicity coefficient of the shear modulus, but rather due to the different time scale of its determination. The mean square displacement of selenium [17] was measured on the picosecond scale, i.e., the shear modulus [25] in the MHz range, where it is influenced by all relaxations with relaxation times shorter than a microsecond.

In fact, if one takes the GHz shear modulus from Brillouin light scattering data for the transverse sound waves, one reproduces the values of Table I within experimental error: for glycerol [26],  $I_{\text{anh}} = 0.8 \pm 0.2$ , for  $\text{B}_2\text{O}_3$  [27],  $I_{\text{anh}} = 1.5 \pm 0.3$ , and for polybutadiene [28],  $I_{\text{anh}} = 1.7 \pm 0.2$ .

Polybutadiene is an example where one also has mechanical measurements at low frequencies [29]. The real part of the shear modulus around 60 kHz yields again a rather large value for the anharmonicity coefficient,  $I_{\text{anh}} = 6 \pm 1$ .

In this case, the reason is immediately visible in the mechanical data: The measurements show a large secondary relaxation peak which stretches far beyond 60 kHz and which increases its amplitude rapidly with rising temperature. This implies that the real part of the shear modulus at 60 kHz decreases much more rapidly than the Brillouin one because it is not only weakened by the vibrational softening, but also by the increasing secondary relaxation. Consistent with this explanation, the Brillouin shear modulus [30] at the glass transition is 1.7 GPa, decidedly larger than the mechanical

one of 1.1 GPa [29] at 60 kHz. Like the comparison of backscattering spectrometers with different resolution [16], this result shows clearly that the secondary relaxations have a much larger anharmonicity coefficient than the vibrations.

An even larger difference between the  $I_{\text{anh}}$  values from the mean square displacement and from ultrasonic measurements is found in polystyrene. Ultrasonic MHz data [31] show a decrease of the real part of the shear modulus at  $T_g$ , consistent with  $I_{\text{anh}} = 4 \pm 0.2$ , a factor of four larger than the value in Table I.

From these findings, one concludes that the measured anharmonicity coefficient depends on the time scale, in particular in substances with a pronounced secondary relaxation. The time scale argument explains the experimental finding of a proportionality of the flow barrier to the MHz or kHz shear modulus alone in many substances [2–4]. In contrast, the temperature dependence of the light scattering Brillouin shear modulus in the GHz range is too weak to explain the full fragility, which is the same result as the one from the picosecond mean square displacements in Table I.

### III. A SEPARATE MEASUREMENT OF BOTH INFLUENCES

If one admits the presence of both influences on the fragility, cooperativity, and anharmonicity, the question arises how to measure both of them separately. As will be seen, the question is answered by a 20-year-old determination [17] of the mean square displacements in glassy, liquid, and crystalline selenium (Fig. 2). The logarithmic derivative of the liquid  $\langle u^2 \rangle$  at  $T_g = 304$  K is 3.1, explaining 2.1 units of the total fragility  $I = 4.4$  (see Table I). Thus more than half of the fragility remains unexplained and must be attributed to a decrease of  $N_{\text{corr}} \propto 1/T^{2.5}$  (note that this information on the volume of the cooperatively rearranging region comes directly from the pair correlation function; it is not necessary to invoke higher correlations [7–10]).

But there is a second independent way to extract the temperature dependence of the cooperative volume from the data in Fig. 2. The mean square displacement of the

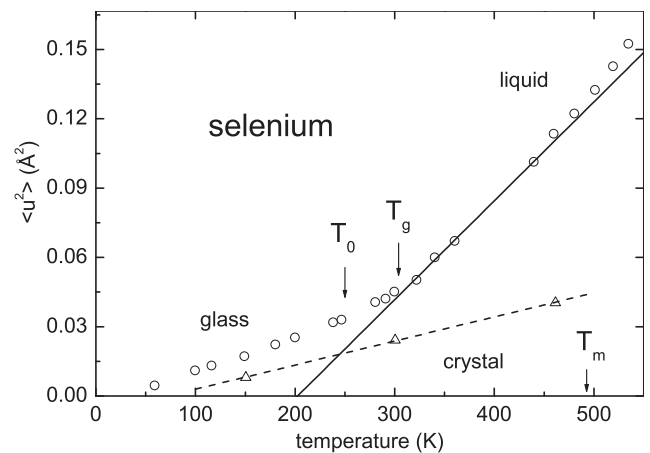


FIG. 2. The mean square displacements in crystalline, glassy, and liquid selenium [17]. Note that the liquid data extrapolate to the crystalline ones at the Vogel-Fulcher temperature  $T_0$ .

undercooled liquid extrapolates to the one of the crystal at 245 K, close to the Kauzmann temperature of 240 K where the excess entropy over the crystal extrapolates to zero and the Vogel-Fulcher temperature of 251 K where the viscosity extrapolates to infinity [32]. In fact, one finds the relation [17]

$$\ln \frac{\eta}{\eta_0} = \frac{u_0^2}{\langle u^2 \rangle - \langle u_c^2 \rangle}, \quad (7)$$

which describes the viscosity  $\eta$  in terms of the two parameters  $u_0 = 1.59 \text{ \AA}$  and  $\eta_0 = 0.31 \text{ mPas}$ . It holds over 18 decades of viscosity variation, from the aging regime below  $T_g$  up to a temperature high above the melting temperature, providing a much better fit of the viscosity than any Vogel-Fulcher law. Note that a linearization of both  $\langle u^2 \rangle$  and  $\langle u_c^2 \rangle$  around  $T_g$  converts this relation into the Vogel-Fulcher law  $\log \eta/\eta_0 \propto 1/(T - T_0)$ , thus identifying the Vogel-Fulcher temperature  $T_0$  with the point where the extrapolated mean square displacement of the liquid reaches the crystalline one. The fit parameter  $\eta_0$  has the value which one expects for a gas of noninteracting selenium atoms at the liquid density. The parameter  $u_0$  measures the thermal vibration amplitude which has to be reached to make the influence of the interatomic potential negligible. This provides the Vogel-Fulcher law with two parameters which have a well-defined physical meaning.

The good agreement suggests that  $1/N_{\text{corr}}$ , which according to Adam and Gibbs [1] is proportional to the structural entropy difference between liquid and crystal, is also proportional to the mean square displacement difference between liquid and crystal. To get the observed proportionality, one has to postulate

$$1/N_{\text{corr}} \propto \frac{\langle u^2 \rangle - \langle u_c^2 \rangle}{\langle u^2 \rangle} \quad (8)$$

to obtain

$$\log \eta/\eta_0 \propto \frac{E_b}{T} \propto \frac{N_{\text{corr}}}{\langle u^2 \rangle} \propto \frac{1}{\langle u^2 \rangle - \langle u_c^2 \rangle}. \quad (9)$$

If Eq. (9) is generally valid, then the measurement of liquid and crystal mean square displacements on the picosecond scale allows one to determine the influences of cooperativity and anharmonicity on the fragility separately.

The scheme works very well for selenium, but one cannot help wondering whether it will also work in other substances. The difficulty is that simultaneous mean square displacement measurements for liquid and crystal of the same substance are rare. The only other example is orthoterphenyl (OTP) [23], but this has been measured on the backscattering instrument IN13 with a high resolution corresponding to a rather long time of about 200 picoseconds. The mean square displacements [23] in Fig. 3(a) show a much stronger curvature at  $T_g$  than those of selenium. Nevertheless, if one fits  $\langle u^2 \rangle$  in terms of a third order function [the continuous line in Fig. 3(a)] and  $\langle u_c^2 \rangle$  in terms of a second order function in temperature [the dashed line in Fig. 3(a)], one finds again the proportionality shown by the continuous line in Fig. 3(b). The fit with  $u_0 = 0.62 \text{ \AA}$  and  $\eta_0 = 0.2 \text{ Pas}$  fails above  $T_m$ , but still covers 12 decades of viscosity variation.

There is no further comparison of crystal and liquid mean square displacements in the literature. What one can do, how-

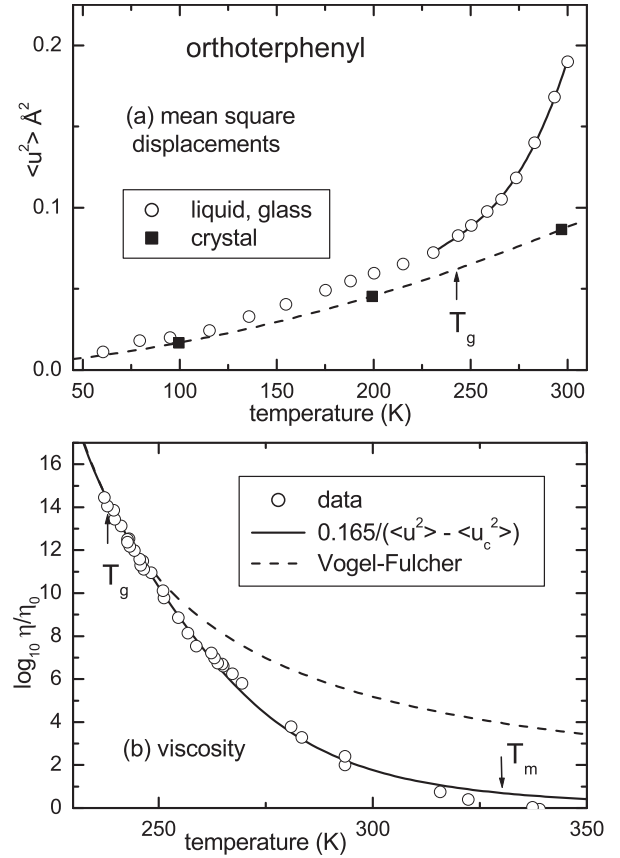


FIG. 3. (a) The mean square displacements in crystalline, glassy, and liquid orthoterphenyl [23]. The lines are the corresponding fits. (b) Proportionality of the logarithm of the viscosity [33]  $\eta/\eta_0$  with  $\eta_0 = 0.2 \text{ Pas}$  to the inverse difference between liquid and crystalline mean square displacements (the continuous line). The dashed line is the Vogel-Fulcher relation.

ever, is to take the crystalline mean square displacement from separate measurements. In glycerol, for example, there is a prediction for the crystalline mean square displacement on the basis of neutron and Raman data [34], which can be combined with the measured liquid mean square displacements [35]. In this substance, one has the advantage that one can compare the  $N_{\text{corr}}$  values from the mean square displacements to those determined from the nonlinear dielectric susceptibility [9,10].

Figure 4(a) shows the mean square displacements of liquid [16,35] and crystalline glycerol [34]; Fig. 4(b) shows the fit with  $u_0 = 1.0 \text{ \AA}$  and  $\eta_0 = 1.6 \text{ mPas}$ . In this case, the fit again works well up to temperatures high above the melting point, probably because the mean square displacements of Wuttke *et al.* [35] are measured in the picosecond range as they should be. Like in selenium and orthoterphenyl, the liquid mean square displacement is more strongly curved than the crystalline one, indicating that neither  $N_{\text{corr}}$  nor the viscosity does really diverge at a nonzero Kauzmann temperature, in agreement with other measurements [37–42].

The results for  $N_{\text{corr}}$  in glycerol are compared in Fig. 5 with those obtained from the nonlinear dielectric measurements [9,10]. The temperature dependence is clearly different (neither technique delivers absolute values, but one can

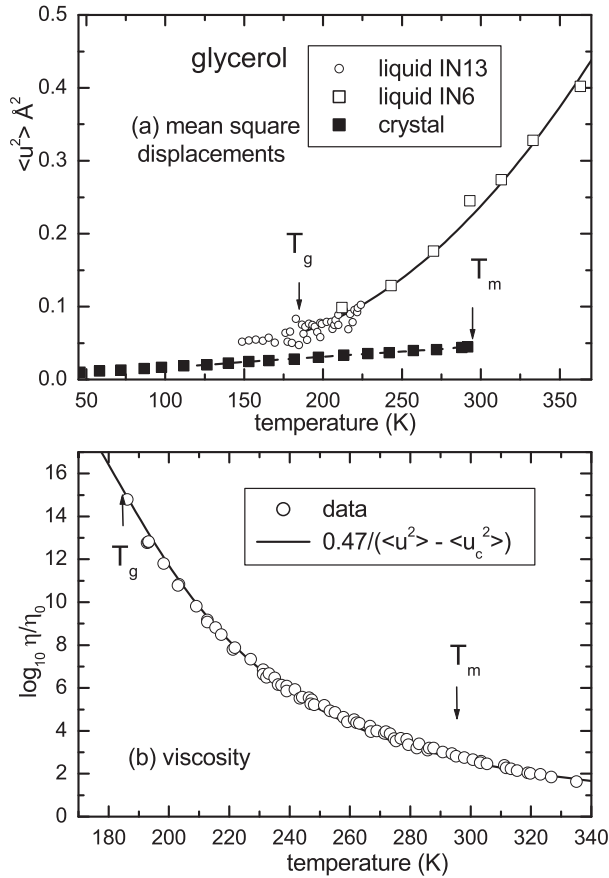


FIG. 4. (a) The mean square displacements in crystalline [34] and liquid [16,35] glycerol. The lines are the corresponding fits. (b) Proportionality of the logarithm of the viscosity [36]  $\eta / \eta_0 = 1.6$  mPas to the inverse difference between liquid and crystalline mean square displacements (the continuous line).

compare the slope). The slope of our values is only half of the nonlinear dielectric ones.

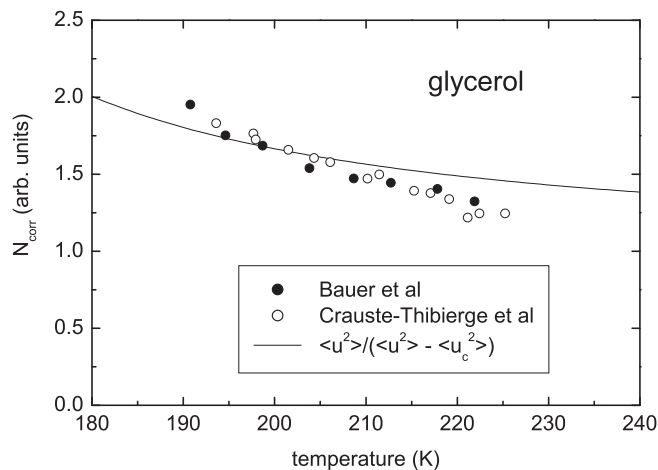


FIG. 5. Comparison of the number  $N_{\text{corr}}$  of atoms in a cooperatively rearranging region obtained from nonlinear dielectric measurements [9,10] with those obtained by our method. Note that one does not have absolute values and can only compare the slope.

Searching for an explanation, one notes that both results agree if the nonlinear dielectric technique does not measure  $N_{\text{corr}}$  alone, but rather the barrier height itself, together with its anharmonic changes. This was, in fact, the (rather simple and convincing) explanation of the first publication on the nonlinear dielectric effect in glycerol [43], which has been confirmed more directly by a recent study [44]. This explanation is further supported by the proportionality of the supposed  $N_{\text{corr}}$  to the effective flow barrier in all four measured substances [10]; in none of them appears any influence of the anharmonicity.

The alternative is to postulate a flow energy barrier which does not feel the influence of the anharmonicity, which we find difficult to believe. In a sample with a normal thermal expansion such as glycerol, the anharmonicity of the interatomic potential must be expected to lower a configurational energy barrier.

If the nonlinear dielectric method [9,10,43,44] does indeed measure the full effective flow barrier, the method proposed here is at present the only one able to determine the two influences on the fragility separately.

#### IV. DISCUSSION AND SUMMARY

In Sec. II, the comparison between two different methods for the determination of the anharmonic part of the fragility showed that the anharmonicity coefficients from mean square displacement measurements are decidedly smaller than the ones determined from ultrasonic shear modulus measurements and contradict the hypothesis of a pure anharmonic origin of the fragility.

In the examples of Sec. II, the shear modulus anharmonicity coefficient always agreed with the mean square displacement one if both were measured at the same frequency. This is a bit surprising because the Debye approximation leading to Eq. (3), the relation between  $G$  and  $T / \langle u^2 \rangle$ , does by no means stand on firm theoretical grounds, not even if one considers only vibrations and no relaxation. In fact, the validity or nonvalidity of the Debye approximation at the boson peak is another controversial topic in the field, with no conclusive theoretical answer so far [45–47]. Therefore, one cannot exclude the possibility that the mean square displacement anharmonicity coefficients are, in principle, different from the shear modulus ones.

But the backscattering measurements [16] show unequivocally that the relaxations have higher anharmonicity coefficients than the vibrations, a fact which is also extracted from the frequency dependence of the shear modulus in polybutadiene [28–30]. From these results and from the good agreement of the mean square displacement anharmonicity coefficient with Brillouin values in glycerol and  $B_2O_3$ , one would believe that the two methods do indeed determine the same anharmonicity coefficient, provided that they are measured on the same time scale.

One can understand the large anharmonicity of the secondary relaxations in terms of the asymmetry model [48], which is able to explain the large asymmetry of about  $4 k_B T_g$  between the two minima of secondary relaxations found in a key experiment on aging [49]. The asymmetry model postulates relaxational jumps of a central core of  $N$  atoms into

a different local structure with a distorted shape and attributes the large asymmetry to the elastic misfit. For a constant density of possible stable structures in the six-dimensional distortion space, the probability density for a given asymmetry  $\Delta$  of the two minima is

$$p(\Delta) = \frac{c_N}{N^3} \frac{\Delta^2}{(G\nu)^3} e^{-\Delta/kT}, \quad (10)$$

where  $c_N$  is a constant. Assuming that the mean square displacement of a jump into a new structure does not depend on  $\Delta$ , the integration over the asymmetry yields a proportionality of the mean square displacement to  $T^3/G^3$ . If  $G$  has the anharmonicity coefficient  $I_G$ , the resulting relaxation anharmonicity coefficient will then be  $3I_G + 2$ , more than a factor of three higher. Since the relevant  $G$  is the one of the average lifetime of the structural variants of the core, this mechanism is, in principle, able to explain the dramatic increase of the anharmonicity coefficient towards lower frequency.

In any case, the picosecond anharmonicity of a neutron time-of-flight measurement is the relevant one for the flow barrier because the passage of the barrier occurs within a picosecond, with not enough time to lower the barrier by any relaxation processes. For an exact description of the frequency dependence of the anharmonicity coefficients in the relaxational range, more dedicated experimental investigations and a more complete survey of existing experimental evidence will be necessary.

An even stronger reservation holds for the main point of Sec. III, aimed at showing that the relation in selenium between the viscosity and the mean square displacements of liquid and crystal, given by Eq. (7), is also valid in other glass formers. The example of orthoterphenyl suffers from a resolution which is too good to supply the picosecond mean square displacements which should be really compared to the viscosity. In the example of glycerol, the crystalline mean square displacements have only been calculated and

not measured. So also here, more dedicated measurements to check the hypothesis would be highly desirable.

But in spite of these reservations, the evidence described in the present paper shows convincingly that the fragility is not due to a single mechanism. The considerations in Sec. II show clearly that the anharmonicity is too weak to explain more than half of the fragility in most glass formers (though strong enough to rule out the explanation in terms of the cooperativity alone [9–11]). The rest must be left to another mechanism, for which the cooperativity evidenced from numerical work [12–14] is the logical candidate.

To conclude, the heavily studied fragility of undercooled liquids is due to two physical mechanisms, the Adam-Gibbs mechanism of an increasing number of atoms in a cooperatively rearranging region and the anharmonicity of the interatomic potential. On the basis of this concept, one finds a physical explanation for the proportionality of the logarithm of the viscosity ratio  $\eta/\eta_0$  ( $\eta_0$  high temperature viscosity) to the inverse of the difference of the picosecond mean square displacements of liquid and crystal. The explanation provides a physical basis for the Vogel-Fulcher law. The liquid mean square displacement shows a stronger curvature with temperature than the crystalline one, corroborating the finding of others that there is no real divergence of the viscosity at a finite Kauzmann temperature. A measurement of the two mean square displacements in the coexistence region of liquid and crystal allows one to determine the temperature (or pressure) dependence of the volume of the cooperatively rearranging region, an alternative to other newly developed methods to study dynamic length scales in real glass formers. At present, it is the only method able to measure the two influences on the fragility separately.

#### ACKNOWLEDGMENTS

M.A.R. acknowledges financial support by the Spanish MINECO (Project No. FIS2011-23488).

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