Reply to Comment: Disentangling interatomic repulsion and anharmonicity in the viscosity and fragility of glasses [Phys. Rev. B 95, 104203 (2017)]

Johannes Krausser

Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, U.K.

Alexandra Lagogianni

Ruhr Universitaet Bochum, Interdisciplinary Center for Advanced Materials Simulation (ICAMS),
Universitaetsstrasse 150, 44801 Bochum, Germany

Konrad Samwer

I. Physikalisches Institut, Universitaet Goettingen, 37077 Goettingen, Germany

Alessio Zaccone*

Statistical Physics Group, Department of Chemical Engineering and Biotechnology,
University of Cambridge, Philippa Fawcett Drive, CB3 0AS Cambridge, U.K. and
Cavendish Laboratory, University of Cambridge, JJ Thomson Avenue, CB3 0HE Cambridge, U.K.

Abstract: In this Reply to Koperwas and Paluch's Comment to our original article "Disentangling interatomic repulsion and anharmonicity in the viscosity and fragility of glasses" we discuss the differences between physical parameters used in the derivation of the Krausser-Samwer-Zaccone (KSZ) model of viscosity and those used in the justification of the empirical power-density scaling for repulsive power-law fluids. These fundamental differences forbid a direct combination of the two approaches as suggested in Koperwas and Paluch's Comment.

In the preceding comment, Koperwas and Paluch (KP) [1] point out that the Krausser-Samwer-Zaccone (KSZ) model of viscosity of atomic supercooled liquids presented in Ref. [2], and previously in Ref. [3], contains conclusions that cannot be reconciled with the empirical power-density scaling rule for organic supercooled liquids.

The starting point of KP is the isobaric fragility that they obtain from the assumption of power-density scaling, which is the realization that some supercooled liquids present some dynamic observables and thermodynamic quantities which follow the scaling $\sim (V^{-\gamma}T^{-1})$, where γ is the power-density exponent, which, for liquids with purely repulsive inverse power-law (IPL) potential $\sim r^{-n}$, can be related to the power-law n of the intermolecular potential repulsion via $\gamma = n/3$. The density scaling concept is not limited to inverse power potentials, molecular glass formers and polymers, but is also an ingredient of the isomorph theory, based to a large part on simulations of the Lennard-Jones system [4, 5]. From this work, the density scaling exponent is known for the Lennard-Jones potential, with values which depend slightly on temperature and density, but lie between 5.6 and 6.1.

KP then compare the expression for the isobaric fragility obtained from the above power-density scaling

assumptions with the expression for the isobaric fragility obtained within the KSZ model that was proposed for atomic supercooled liquids on the example of an organic liquid.

The KSZ model uses the shoving/cooperative shear model of the glass transition which expresses the viscosity (or relaxation time) as an Arrhenius exponential of the high-frequency shear modulus. The model then employs an atomistic result for the shear modulus at high-frequency based on lattice dynamics (Born-Huang) [6], where the shear modulus is directly proportional to the number of long-lived nearest neighbours in the cage. The latter number can be conservatively estimated by integrating the first peak of the radial distribution function $g(r)$ up to the maximum of the first peak. To keep the result analytical, the KSZ model adopts a power-law approximation of the ascending flank of the first peak of the $g(r)$, with a power-law exponent λ.

Using Boltzmann inversion $V_m/k_BT = -\ln g(r)$ to extract the potential of mean force (PMF) V_m from the $g(r)$, the power-law fit of the $g(r)$ translates into an expression for the PMF, which is given in logarithmic form and where the parameter λ represents the strength of repulsion of the PMF. In this way, the KSZ model provides the shear modulus as a function of λ. Furthermore, the Born-Huang-type expression for the shear modulus is proportional to the atomic density [6], which relates to temperature via the thermal expansion coefficient. Hence the shear modulus is given as a function of

both the repulsion parameter of the PMF, λ, and of the thermal expansion coefficient. Substituting this back in the shoving/cooperate shear model exponential for viscosity, the KSZ equation arises with its characteristic double-exponential dependence of viscosity on temperature, which is modulated by both the interaction parameter λ and the thermal expansion coefficient.

In the KSZ model, the isobaric fragility m follows from taking the second derivative with respect to inverse temperature T_g/T evaluated at T_g of the KSZ equation for the viscosity η of supercooled liquids, $m = \frac{\partial \log_{10} \eta}{\partial (T_g/T)}\big|_{T=T_g}$. KP compare the expression for fragility from the KSZ model [2, 3] with a similar expression they obtained using the power-density scaling rule that has been tested on many *organic* glass-formers.

From this comparison they identify a relationship between the power-density scaling exponent γ and the interaction parameter λ. They find $\gamma = 2 + \lambda$.

KP then consider the case of an organic glass-former, ortho-ter-phenyl (OTP) and assume a value of $\gamma = 4$ deduced from previous collapse of experimental data, using the above assumption of power-density scaling, taken from the literature. Using this $\gamma = 4$ quoted from previous empirical collapse of thermodynamic data, they then claim $\lambda = 2$ in the KSZ model and show that the KSZ equation for the viscosity using this value is not able to fit experimental data. They show that the KSZ equation instead reproduces perfectly the experimental data with $\lambda = 28$. Based on this comparison and the above assumptions, they arrive at the conclusion that the KSZ model is not consistent with the empirical power-density scaling.

We appreciate the effort by KP to establish a connection between the KSZ model and contemporary work on organic glass formers and the empirical power-density scaling assumption. However, unfortunately the analysis of KP of OTP data using the KSZ model is based on comparing apples to oranges. KP pretend that the KSZ model, which was derived and tested on metallic and atomic glasses be applicable (with no changes) to organic glass-formers using the same parameters found from the power-density scaling approach.

One problem in this approach is the identification of the exponents γ, n and λ and their mutual relation. The power-density scaling assumes an inverse-power law potential (IPL), r^{-n}, without any attraction, and shows that $\gamma = n/3$. KP's analysis suggests a relation between the power-law exponent n of the pair potential, which gives $\lambda = n/3 - 2$. This relation is questionable because the parameter n represents the strength of repulsion in the potential of mean force (PMF), which is a different object from the pair potential.

As a matter of fact, the PMF obtained from Boltzmann inversion of the $g(r)$, as is well known from statistical mechanics and liquid theory, is very different from the pair potential, and contains important many-body effects, especially at high densities such as in the supercooled liquid. Only in the low-density limit (basically the ideal gas), the PMF reduces to the pair interaction, as is shown in most textbooks on statistical mechanics or liquid theory (e.g. on page 205 of Ref. [8]).

The above discussion shows that the identification made by KP between the KSZ parameter λ and the power-density scaling parameter γ is questionable and based on the assumption that metallic glasses or simple atomic glass-formers can be treated on the same footing with organic glass-formers which present much more complicated interactions due to irregular molecular shape (steric interactions) and complex hydrogen bonding.

In the absence of a microscopic molecular theory to support the power-density scaling assumption, it is not possible at present to establish a precise one-to-one mapping between the parameters of the empirical power-density scaling assumption and the KSZ theory.

We are glad that KP found instead excellent agreement with a larger value of $\lambda = 28$, which appears reasonable in comparison with values previously obtained for metallic liquids (where $\lambda = 80 - 100$). It is sensible for organic liquids such as OTP to have lower λ values than metals, due to the irregular shape of the OTP molecule (resembling a dumbbell) which introduces a longer decaying repulsion due to local steric effects.

In future work the KSZ model can be adapted to organic glass-formers to include the complexity of the latter, but this requires a deep and serious consideration of the microscopic physics, unlike the superficial and rather careless analysis presented in KP's Comment.

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