Reply to "Comment on 'Explaining the specific heat of liquids based on instantaneous normal modes'"

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We reply to the Comment by Schirmacher *et al.* [Phys. Rev. E, **106**, 066101 (2022)]. We disagree that the heat capacity of liquids is not a mystery since a widely accepted theoretical derivation based on simple physical assumptions is still missing. We also disagree about the lack of evidence for a linear in frequency scaling of the liquid density of states, which is indeed reported in uncountable simulations and recently also in experiments. We emphasize that our theoretical derivation does not assume any Debye density of states. We agree that such an assumption would be incorrect. Finally, we remark that the Bose-Einstein distribution naturally tends to the Boltzmann distribution in the classical limit, which makes our results valid also for classical liquids. We hope that this scientific exchange will bring more attention to the description of the vibrational density of states and thermodynamics of liquids, which still present many open puzzles.

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In their Comment [1] to our paper [2] Schirmacher, Bryk and Ruocco (SBR) claim that:

(1) "*The heat capacity of liquids is not a mystery and the authors ignore the existing literature and existing models.*"

(2) "*The authors' formula for the instantaneous-normal-mode (INM) spectrum does not represent the known INM spectra of simple liquids.*"

(3) "*The derivation of this formula from their model equation of motion is mathematically in error.*"

(4) "*The experimental test of the theory for the specific heat of liquids is performed by fitting the data of supercritical fluids.*"

(5) "*The quantum-mechanical procedure of Debye cannot be used for a classical liquid.*"

Here, we reply point by point to their statements.

(1) *The problem of the heat capacity of liquids and literature.* We do agree with SBR that [3] should have been cited in our work and we apologize to the authors of Ref. [3] for this oversight. We do not agree with SBR that the problem of the heat capacity of liquids is solved. In particular, we believe that, despite numerous interesting works (e.g., [4]), the fundamental underlying reason behind the decrease in the heat capacity of liquids as a function of temperature (in contrast with the increase in solids) has not been identified yet, and that our analysis could provide a new twist to this story.

(2) *The DOS of liquids.* The "*well known INM spectra of simple liquids*" exhibit a universal linear-in-frequency scaling at low frequency, which is equivalent to saying that $\rho(\lambda = 0) \neq 0$, where $\rho(\lambda)$ is the eigenvalue's density. This is our working assumption, which is corroborated by uncountable older simulations works (e.g., Ref. [5]), discussed in all the main reviews on the topic (e.g., Ref. [6]) and derived in several theoretical models (e.g., Refs. [7,8]). More recently, our formula for the density of states (DOS) of liquids proposed in Ref. [9] has been also confirmed experimentally with great detail using inelastic neutron-scattering experiments in Ref. [10].

(3) *Formula for the vibrational spectrum.* This point of the Comment does not refer to the paper under scrutiny [2], but rather to another paper of ours published in a different journal [9] from which the formula for the DOS is taken. SBR claim that our result is incorrect because, in our computation, the Green's function for the velocity field, rather than that for the displacement field, was used in the derivation of the DOS. In our opinion, this is incorrect because the displacement field is not a well-defined quantity in liquids since the reference configuration changes quickly with time, and there is no static equilibrium configuration around which to expand. On the other hand, our approach of starting from a Langevin-type dissipative equation of motion and consistently writing the Green's function in terms of velocities, provides a consistent description of INMs as "unstable bosons" in liquids in agreement with the original ideas of Ref. [9].

(4) *Test of the theory.* As SBR show themselves in their Fig. 1, our fits cover a large part of the phase diagram (indeed the same as in Ref. [11]) both in the liquid and in the supercritical fluid phases. The fact that our simple formula fits well also the supercritical regime is an interesting observation, which deserves further exploration, rather than being a shortcoming of our analysis.

(5) *Physical assumptions.* SBR claim that we use Debye theory to compute the heat capacity of a liquid. The density

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of states $g(\omega)$ used in our computations is not the one of Debye theory, $g(\omega) \sim \omega^2$ (in three spatial dimensions), which would give rise to a low-temperature heat capacity $c_v \sim T^3$ (in three spatial dimensions) in contradiction with all the results presented in our Reply and all experimental data on liquids. Additionally, SBR claim that the use of the Bose-Einstein distribution (as performed in the Einstein model of solids) is not correct since most of liquids in Nature are classical. The Bose-Einstein distribution as is well known correctly recovers the classical limit at high-temperatures (intended as temperatures larger than the Debye temperature T_D). Indeed, taking the high temperature limit of our formula, one obtains

$$c_v \to k_B \int g(\omega) d\omega, \tag{1}$$

which is exactly the manifestation that each mode contributes k_B to the heat capacity as a classical harmonic oscillator, which, according to equipartition, will yield $\frac{3}{2}k_B$, upon proper normalization, in the asymptotic limit. This shows that our formula correctly recovers the classical limit, in contradiction with what claimed by SBR.

Furthermore, one could ask whether INMs in liquids can be described as bosons. As argued in our previous work [9], not all bosons in Nature are harmonically "stable" particles. There exist important examples of "unstable bosons," where the imaginary part (linewidth) of dispersion relation is overwhelming the real (stable) part. We argued this to be the case of INMs, which, accordingly, can be legitimately described as bosons following the Bose-Einstein statistics (just like W and Z bosons in particle physics, among famous examples of unstable bosons). Although this is a bold assumption, we believe that it should be granted the benefit of doubt and be judged based on its influence on future research and on its ability of steering new results in the field.

Summary. In our Reply, we have addressed all the points in the Comment by SBR and showed that none of them is a valid and well-supported critique to our paper. We are fully aware that our theory is a simple phenomenological model, which needs further investigation and possible completions, e.g., the inclusion of the stable modes contribution, which is of stimulus for future work.

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