Comment on “Explaining the specific heat of liquids based on instantaneous normal modes”

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In a recent paper (Phys. Rev. E 104, 014103 (2021)) M. Baggioli and A. Zaccone formulate a theoretical description of the specific heat of liquids by using Debye’s expression for the specific heat of solids and inserting a density of states (DOS) which they claim to represent the instantaneous-normal-mode (INM) spectrum of a liquid. However, the quantum-mechanical procedure of Debye cannot be used for a classical liquid and the authors’ formula for the INM spectrum does not represent the known INM spectra of simple liquids. Furthermore, the derivation of this formula from their model equation of motion is mathematically in error. Finally experimental test of the theory for the specific heat of liquids is performed by fitting the data of supercritical fluids. To our opinion, these and a lot of other inconsistencies render this work not suitable for studying the specific heat of liquids.

Baggioli and Zaccone (BZ) present in a recent paper [1] a treatise on the specific heat of liquids. They claim that this would be a fundamental new theory for the specific heat of liquids. The authors end with the statement: “To summarize, the above theory provides a definitive answer to the mystery of liquid specific heat and ideally completes the agenda of the kinetic theory of matter, set over 100 yr ago by Debye, Einstein, Planck, and co-workers.”

By contrast, on the hand, the specific heat of liquids is not a mystery, on the other hand, the paper turns out to contain so many elementary scientific and mathematical inconsistencies and errors, that it does not appear to be of any value for studying the specific heat of liquids.

BZ (i) formulate a Debye-like quantum theory, in which they treat the instantaneous-normal (INM) modes, which are the eigenmodes of the Hessian of a simulated classical liquid [2, 3] as bosons in an interacting quantum liquid, referring, among others, to papers on quantum chromodynamics [4]. They repeatedly claim that there would be no satisfactory theory for the specific heat of liquid available yet, ignoring the existing literature on the thermodynamics of simple liquids [5-7]. What BZ have done, boils down to (ii) inserting an expression for the density of states for the INM modes, derived by BZ previously [8], into Debye’s expression for the quantum specific heat of a solid. They (iii) claim to have good agreement with specific heat data on simple liquids.

(i) It is well known that quantum effects are not relevant to most liquids (the exceptions are the helium liquids), because in the liquid state the thermal de-Broglie wavelength \( \lambda = \frac{h}{mk_B T} \) is much smaller than the diameter of the liquid particles. Here \( h \) and \( k_B \) are Planck’s and Boltzmann’s constants, \( m \) is the particle mass, and \( T \) is the temperature.

BZ motivate their quantum approach by discussing a weakly interacting Bose gas with elementary excitations of energy \( H[\omega_q] \), where they obviously identify the frequencies \( \omega_q \) with those appearing in Eq. (2) (see below), the modulus of the square-root of the eigenvalues of the instantaneous Hessian matrix of a classical liquid. The dispersion \( \omega_q \) is not specified. As mentioned above, BZ invoke papers on unstable (massive) bosons in quantum chromodynamics as justification of their identification.

For classical liquids and gases, the partition function factorizes into a factor arising from integrating over the kinetic energy and the configurational factor arising from integrating over the potential energy (configuration integral). This means (as is well known [5]), that the dynamics of a classical liquid does not enter into its thermodynamic properties.

For simple liquids in an \( (N,V,T) \) system, the energy equation of states is given by the sum of the ideal and the excess term

\[
\frac{1}{N} U(N,V,T) = \frac{1}{N} \left( U^{id} + U^{ex} \right) \\
= \frac{3}{2} k_B T + 2 \pi \rho(T) \int d^3 r \phi(r) g(r,T)
\]  

(1)

and the specific heat per particle \( c_V(T) = c^{id}_V + c^{ex}_V \) is just the derivative with respect to the temperature \( T \). Here
\( \phi(r) \) is the pairwise potential and \( g(r, T) \) the radial pair distribution function, for which well-established thermodynamic theories exist, notably thermodynamic perturbation theory [4]. For example, Rosenfeld and Tarazona [5] (not cited in [1]) use density-functional theory and thermodynamic perturbation theory to come up with an expression of the excess internal energy \( U^{ex} \) and the corresponding specific heat \( c_v^{ex} \), which depend on the temperature \( T \) via a power law \( U^{ex} \propto T^{3/5}, c_v^{ex} \propto T^{-2/5} \), which stems from the singularity induced by the presence of the atomic hard cores. It has been demonstrated that this equation of state and the corresponding free-energy functional describe the thermodynamics of liquids rather well, in particular the temperature dependence of the specific heat [7, 6].

Conclusion: At variance with the claims of BZ, a quantum description of simple liquid is not adequate, and a well-established thermodynamic theory for classical liquids, including the specific heat, is available.

\( (i) \) We turn now to the BZ formula for the density of states of the instantaneous-normal modes of a simulated model for a classical liquid. In the INM literature it had been customary to represent the INM spectrum, i.e. the normalized histogram \( \rho(\lambda) \) of eigenvalues \( \lambda_i = \omega_i^2 \) of the Hessian matrix of the potential energy of a liquid at a certain time instant, as

\[
g(\omega) = \begin{cases} 
2\omega \rho(\lambda) & \text{for} \quad \lambda = \omega^2 \geq 0, \\
2|\omega| \rho(\lambda) & \text{for} \quad \lambda = \omega^2 < 0, 
\end{cases}
\]

where the absolute sign \( | \ldots | \) refers to that of a complex number, and the unstable part of the spectrum is plotted along the negative \( \omega \) axis. At very high frequencies \( g(\omega) \) can be taken to represent something like the density of states for vibrations, which are known to exist at such frequencies. At low and negative values of \( \lambda \) the modes represent unstable configurations. BZ acknowledge this and design a model for the DOS, motivated by a Langevin-type equation (see below) [1, 8]

\[
g(\omega) \propto \sum_i \frac{\omega \Gamma_i}{\omega^2 + \Gamma_i^2} \tag{3}
\]

According to this equation BZ [8] claimed that the function \( g(|\omega|) \) would be proportional to \( |\omega| \) for small \( \lambda \). This would mean that \( \rho(\lambda) \) would be constant in this regime. However it is known since long time [9, 10] and has recently been explained [11], that \( \rho(\lambda) \) is strongly peaked at small values of \( \lambda \), i.e. far from being constant. \( \rho(\lambda) \) is also not universal, as claimed by BZ [8], but depends strongly on temperature [11]. Furthermore, BZ claim to have derived expression (3) from a Langevin equation (strange enough without fluctuating forces) for the local velocities \( v_i \) with damping coefficients \( \Gamma_i \)

\[
\frac{d}{dt} v_i = -\Gamma_i v_i \tag{4}
\]

The vibrational DOS, however, has to be calculated from the imaginary part of the Green’s function for the displacements \( \mathbf{u}_i \) with \( v_i = \frac{d}{dt} \mathbf{u}_i \). For model [1] this Green’s function takes the form

\[
G_{ii}(\omega) = \frac{1}{-i\omega-i\omega+\Gamma_i} \tag{5}
\]

Taking the imaginary part we arrive at

\[
g(\omega) \propto \sum_i 2\omega \text{Im}\{G_{ii}(\omega)\} \tag{6}
\]

\[
\propto \sum_i \frac{\Gamma_i}{\omega^2 + \Gamma_i^2},
\]

which is at variance with BZ’ expression (3), where obviously a factor \( 1/\omega \) is missing. Certainly this, together with the inadequateness of [8] to describe simulated INM spectra [11], invalidates all reasoning in Refs. [1] and [8].

\( (iii) \) Let us now look at the comparison with experiment. BZ modified their formula of Ref. [8] as follows:

\[
g(\omega) \propto \frac{\omega}{\omega^2 + \Gamma_0^2} e^{-\omega^2/\omega_B^2}, \tag{7}
\]

replacing Debye’s cutoff with a soft Gaussian. They assumed that the damping constant obeys an Arrhenius temperature law \( \Gamma = \Gamma_0 e^{-\epsilon/k_B T} \), where \( \epsilon \) is the Lennard-Jones depth parameter and \( \Gamma_0 \) is a prefactor.

Fits with inserting \( g(\omega) \) according to Eq. (7) into Debye’s formula for the specific heat have been performed for the inert gases neon, argon, krypton and xenon, as well as nitrogen. BZ took values for the Debye frequency from literature of solid rare gases and \( N_2 \), together with known values for the Lennard-Jones parameter \( \epsilon \) and took the prefactor \( \Gamma_0 \) as fit parameter.

In Fig. 1 we report the data from Fig. 2 of BZ, and we add arrows indicating the appropriate values of the
critical temperatures for the investigated materials. We observe that the data fitted by BZ with formula \(7\) are predominantly in the \textit{supercritical} states, i.e. the liquid theory has been tested against supercritical fluids. So BZ use a quantum theory and values of the Debye frequency of solids to fit supercritical gases, not liquids, and take this as evidence for the descriptive power of a theory for a liquid.

There are more elementary inconsistencies in Ref. \[1\], e.g. calling the specific heat law for a free one-atomic gas \(c_V^d = \frac{3}{2} k_B\) the \textit{Dulong-petit law}. As is well known, the latter holds for a solid and gives the double value due to the additional presence of the harmonic vibrational degrees of freedom.

We conclude that both publications of BZ, Ref. \[1\] and Ref. \[8\] are not helpful for understanding the dynamics and thermodynamics of simple liquids.

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