

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)] Baggioli and 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 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 the relaxational excitations of a classical liquid. Furthermore, the authors’ formula for the INM spectrum does not represent the known INM spectra of simple liquids, and the derivation of this formula from their model equation of motion is mathematically in error. These and a number of other inconsistencies render their work not very helpful for studying the specific heat of liquids.

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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 following 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 one hand, the specific heat of liquids is not a mystery; on the other hand, the paper turns out to contain a lot of scientific and mathematical inconsistencies and errors.

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 liquids 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 $\lambda = h/[mk_B T]^{1/2}$ 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 $\hbar|\omega_q|$, where they identify the frequencies ω_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 ω_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

$$\begin{aligned} \frac{1}{N}U(N, V, T) &= \frac{1}{N}(U^{id} + U^{ex}) \\ &= \frac{3}{2}k_B T + 2\pi\rho(T) \int d^3\mathbf{r} \phi(r)g(r, T) \quad (1) \end{aligned}$$

and the specific heat per particle $c_V(T) = c_V^{id} + c_V^{ex}$ 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 [5]. For example, Rosenfeld and Tarazona [6] (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 [6,7].

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

(ii) 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

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

where the absolute sign $|\dots|$ refers to that of a complex number and the unstable part of the spectrum is plotted along the negative ω 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 λ the modes represent unstable configurations. BZ acknowledge this and design a model for the density of states (DOS), motivated by a Langevin-type equation (see below) [1,8]

$$g(\omega) \propto \sum_i \frac{\omega\Gamma_i}{\omega^2 + \Gamma_i^2}. \quad (3)$$

According to this equation BZ [8] claimed that the function $g(|\omega|)$ would be proportional to $|\omega|$ for small λ . This would mean that $\rho(\lambda)$ would be constant in this regime. However, it has been known for a long time [9,10] and recently explained [11] that $\rho(\lambda)$ is strongly peaked at small values of λ , 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 \mathbf{v}_i with damping coefficients Γ_i

$$\frac{d}{dt}\mathbf{v}_i = -\Gamma_i\mathbf{v}_i. \quad (4)$$

The vibrational DOS, however, has to be calculated from the imaginary part of the Green's function for the displacements \mathbf{u}_i with $\mathbf{v}_i = \frac{d}{dt}\mathbf{u}_i$. For model (4) this Green's function takes the form

$$G_{ii}(\omega) = \frac{1}{-i\omega - i\omega + \Gamma_i}. \quad (5)$$

Taking the imaginary part we arrive at

$$g(\omega) \propto \sum_i 2\omega \text{Im}\{G_{ii}(\omega)\} \propto \sum_i \frac{\Gamma_i}{\omega^2 + \Gamma_i^2}, \quad (6)$$

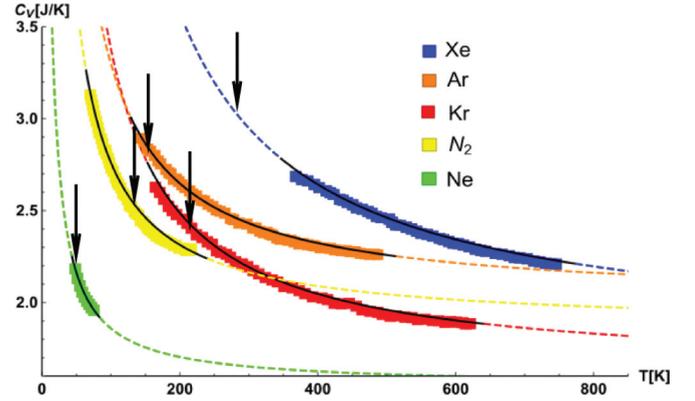


FIG. 1. Specific heat data for some fluid elementary materials, fitted by Baggioni and Zaccane [1] with the DOS of Eq. (7) inserted into the Debye formula. The arrows indicate the liquid-gas critical temperatures T_c : Ne (44 K), Ar (150 K), Kr (210 K), Xe (290 K), and N_2 (126.2 K).

which is at variance with BZ's expression (3), where obviously a factor $1/\omega$ is missing. Certainly this, together with the inadequateness of (3) to describe simulated INM spectra [11], invalidates all reasoning in Ref. [1]. We note here that the *stable* INM spectrum of a one-dimensional low-density liquid has been calculated analytically some time ago by Cavagna, Giardina, and Parisi [12].

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

$$g(\omega) \propto \frac{\omega}{\omega^2 + \Gamma^2} e^{-\omega^2/\omega_D^2}, \quad (7)$$

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 ϵ is the Lennard-Jones depth parameter and Γ_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 the literature of solid rare gases and N_2 , together with known values for the Lennard-Jones parameter ϵ , and took the prefactor Γ_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 *supercritical* states, i.e., the solidlike quantum theory has been tested predominantly against supercritical fluids. Further, BZ use values of the Debye frequency of rare-gas solids.

There is a further elementary inconsistency in Ref. [1]. The authors take the Dulong-Petit law of solids $c_V^{id} = 3k_B$ to be the high-temperature limit of supercritical fluids. The true high-temperature value is given by the temperature derivative of the first term of Eq. (1), i.e., $c_V^{id} = \frac{3}{2}k_B$.

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