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Isochoric specific heat in the Dual Model of Liquids.

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Abstract.

We continue in this paper to illustrate the implications of the Dual Model of Liquids (DML) by deriving the expression for the isochoric specific heat as function of the collective degrees of freedom available at a given temperature and analyzing its dependence on temperature.

Two main tasks will be accomplished. First, we show that the expression obtained for the isochoric specific heat in the DML is in line with the experimental results. Second, the expression will be compared with the analogous one obtained in another theoretical dual model of the liquid state, the Phonon Theory of Liquid Thermodynamics. This comparison will allow to get interesting insights about the number of collective degrees of freedom available in a liquid and on the value of the isobaric thermal expansion coefficient, two quantities that are related to each other in this framework.

Keywords: Liquid model, Phonons in liquids, Instantaneous Normal Modes, Mesoscopic model of liquids; Phonon – particle interaction; Specific heat.

1. Introduction

In a previous paper [1] the Dual Model of Liquids (DML) has been introduced. It is a mesoscopic model that assumes a liquid be a system made up of molecules arranged in solid-like dynamic structures in continuous rearrangement, swimming in an ocean of amorphous liquid. These solid-like aggregates, that we like to call *liquid particles*, interact with *lattice particles*, the phonons, present in liquids and responsible for the propagation of elastic and thermal energy. As consequence of the interactions, the dynamic solid-like aggregates of molecules and the phonons exchange energy and momentum with each other. This interaction is described in Figure 1, where the two elementary events at the base of the DML are represented. In events of type (a), an energetic wave-packet (throughout this paper we will use the terms wave-packets, phonons, collective excitations, interchangeably) interact with a solid-like structure, the *liquid particle*, transferring to it energy and momentum. Events of type (b) are just the opposite, a wave-packet interact with a *liquid particle* and emerges from the interaction with increased energy. The two events are commuted one into the other by time reversal. These interactions are proposed in the DML as the basis of the Onsager Reversibility Principle [2-3]; furthermore, they are responsible for the propagation of momentum, energy and mass in a liquid, and in this framework thermal energy is seen as a form of elastic energy [1].

The elementary interaction is subdivided in two parts. Taking for instance event (a), the first part is that in which the *lattice particle* (the wave-packet) collides with the *liquid particle* and transfers to it momentum and energy, a fraction of which being transformed in kinetic energy of the *liquid particle*, and the remaining in potential energy of its internal DoF. This first part lasts $\langle \tau_p \rangle$ and the particle travels by $\langle \Lambda_p \rangle$, at the end of which the second part begins, the *liquid particle* relaxes and the energy is returned to the thermal pool through a *lattice particle*, alike in a *tunnel* effect. This second part lasts $\langle \tau_R \rangle$, during which the particle travels by $\langle \Lambda_R \rangle$. Figure 2 is a close-up of the first event, that lasting τ_p, of the wave-packet ↔ *liquid particle* interaction shown in Figure 1a. $\langle \Lambda_{wp} \rangle$ is the size of the wave-packet and $\langle d_p \rangle$ that of the *liquid particle* [1] (here and in the rest of the paper, the two brackets $\langle \ \rangle$ indicate the average over a statistical ensemble of the quantity inside them).

Starting from this considerations and applying a simple kinetic model we have calculated, among others, the expressions for several macroscopic quantities in terms of elementary parameters. Examples are the thermal conductivity, the thermal diffusivity, the specific heat, etc.. The order of magnitude of the particle and wave-packet mean free paths and in particular of the relaxation times involved in their interactions, have also been calculated [1].

The internal energy associated to the pool of wave-packets, q_T^{wp}, is represented in the DML as a fraction of the total one, q_T, namely:

$$1. \qquad q_T^{wp} = mq_T = m\int_0^T \rho C_V \, d\theta = \mathcal{N}^{wp} \langle \varepsilon^{wp} \rangle$$

The classical expression for q_T, where ρ is the medium density and C_V the isochoric specific heat per unit mass, is now multiplied by m; besides, $\mathcal{N}^{wp}$ is the number of wave-packets per unit of volume[1] and $\langle \varepsilon^{wp} \rangle$ their average energy. The dynamics described above occurs at high frequencies and involves only the DoF of the lattice; the parameter m that we have introduced accounts for the

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[1] $\mathcal{N}^{wp}$ is the average density of the wave-packets statistical distribution. As such $\mathcal{N}^{wp}$ is represented by a Bose-Einstein distribution function

ratio between the number of collective DoF surviving at temperature T, and the total number of available DoF. We will return on the meaning and values of m in the course of the paper, for now it is relevant to note that $0 \leq m \leq 1$.

Figure 1a shows that the energy acquired by the liquid particle is given back to the pool of elastic excitation a $\langle \Lambda \rangle = \langle \Lambda_p \rangle + \langle \Lambda_R \rangle$ step forward and a $\langle \tau \rangle = \langle \tau_p \rangle + \langle \tau_R \rangle$ time lapse later, alike in a *tunnel effect*, as pointed out before, $\langle \tau \rangle$ assuming also the role of a relaxation time [1]. One of the immediate consequences of this model is that thermal (and elastic) energy spread in liquids is naturally described by a propagation equation, such as the Cattaneo equation, rather than by a diffusion equation, such as the Fourier [4], the delay time introduced into the propagation equation being physically interpreted as the time taken by the thermal energy to reappear in a different place, or by the *icebergs* to move from a place to the next, as in Figure 1.

Very interestingly, in the last few years several papers have appeared on international journals devoted to the liquid modelling, in particular the “Phonon theory of Liquid Thermodynamics” (PLT) [5-15], the theory of dissipative systems with k-gap [16-17] and a theory of specific heat derived by means of an analytical form of the Vibrational Density of States of liquids based on the existence of Instantaneous Normal Modes [18-19].

The PLT, like the DML, is a theoretical model that assumes liquids as dual systems. In the PLT the energy content of a liquid is described by a solid-like Hamiltonian, modified to account for the presence in liquids of anharmonic DoF. One of the main achievements of the PLT is that the Hamiltonian provides an expression for the isochoric specific heat C_V covering the solid, glassy, liquid, gas and quantum liquids states of matter. Two expressions are obtained for the specific heat, one in harmonic approximation, the other including the anharmonic contributions to the pool of energy. The theoretical expressions arrived at have been confirmed experimentally in 21 different liquids. Moreover, PLT has also provided a theoretical interpretation of the elastic, visco-elastic and viscous behaviour response of matter to external disturbances as due to the value of the product[2] $\nu\tau$, where ν is the frequency of the excitation of the DoF, and τ the relaxation time as defined above. It depends on whether ν is larger, comparable or smaller than $1/\tau$, respectively [1,5-15].

Microscopically, the gap in k-space in liquids can be related to a finite propagation length of shear waves; indeed the gap in momentum space in liquids emerges only in the transverse spectrum, while the longitudinal one remains gapless. One needs two essential ingredients for the k-gap to emerge in the wave spectrum. First, we need a wave-like component enabling wave propagation;

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[2] This product is normally reported as $\omega\tau$ by many authors instead of $\nu\tau$. It is clear that there is no ambiguity among the two definitions.

this is represented in the DML by the wave packets. Second, we need a dissipative effect, the process that disrupts the wave continuity and dissipates it over a certain distance, thus destroying waves with long wavelengths and giving origin to the gap in k-space. This last is obviously represented by the “wave packet – liquid particle” interaction, that is the source of dissipation, and works displacing the wave packets from one place, where it is absorbed by the liquid particle, to another, where it returns to the system’ energy pool, alike a tunnel effect. If $\langle\tau\rangle$ introduced above is the time during which the shear stress relaxes, then $\langle\Lambda\rangle=\langle v_s\rangle\cdot\langle\tau\rangle$ gives the shear wave propagation length (or liquid elasticity length) [1].

The solution for the fundamental law of Density of States (DoS) in liquids [18] has allowed to calculate an expression for the specific heat of liquids based on the Instantaneous Normal Modes (INMs) [19], a concept extended from solids to liquids in view of the experimental evidence that INMs dominate the low- and intermediate-frequency ranges of the DoS in liquids.

The paper is organized as follows. In Section 2 the expression for the isochoric specific heat C_V in the frame of reference of the DML is obtained as function of the number of collective DoF available at a given temperature, m. Then C_V is compared with the analogous expression arrived at in the (PLT) [5-15] and their similarities, insights and the implications are discussed, in particular, about the limiting values of the collective DoF, and on that of the isobaric thermal expansion coefficient of the liquid, α, two quantities that are related to each other in this framework. In Section 3 the DML is shortly summarized and compared with the PLT. Finally in the last Section some further consequences and comparisons even between the two theories are discussed.

2. Isochoric specific heat in DML and PLT models: similarities and insights.

Scope of this Section is first to calculate the expression for the isochoric specific heat obtained in the DML, and then to compare it with that of the PLT. The same physical quantity is indeed obtained with two different approaches, namely a thermodynamic approach for the PLT and a mesoscopic-statistical approach for the DML. Consequently the comparison between the two expressions could shed light on some parameters adopted in their derivation. This is actually the case for m, used in the DML approach, and for α, used in the PLT model. For both these quantities, some limits are deduced from the comparison of the two expressions for C_V.

The first step to accomplish the task is to calculate the specific heat in the frame of DML [1]. Let us return then to Eq.(1), which can be re-written as follows:

$$2.\qquad q_T^{wp}=mq_T=\mathcal{N}^{wp}\langle\varepsilon^{wp}\rangle=m^*\rho C_V T$$

where the quantity $m^* = m\dfrac{\int_0^T \rho C_V\, d\theta}{\rho C_V T}$ depends on the nature of the liquid, and has been introduced for the sake of simplifying the expression. q_T^{wp} in Eqs. (1) and (2) allows for calculating the phonon specific heat contribution C_V^{DML} to the total one, C_V :

$$3. \quad \begin{cases} \rho C_V^{DML} = \dfrac{\partial q_T^{wp}}{\partial T} = \dfrac{\partial}{\partial T}(m q_T) = q_T \dfrac{dm}{dT} + m\dfrac{\partial q_T}{\partial T} = q_T \dfrac{dm}{dT} + m\rho C_V = \\ \qquad = m\rho C_V \left[\dfrac{q_T}{m\rho C_V}\dfrac{dm}{dT} + 1 \right] = m\rho C_V \left[\dfrac{m^*}{m^2}\dfrac{dm}{dT} T + 1 \right] \end{cases}$$

Let’s evaluate now the quantity in square brackets at the last member. Because

$$4. \quad \rho C_V^{DML} = \frac{\partial q_T^{wp}}{\partial T} \geq 0,$$

and $0 \leq m \leq 1$, this implies that $\left[\dfrac{m^*}{m^2}\dfrac{dm}{dT} T + 1 \right] \geq 0$. As for the temperature dependence of m, the basis for the reasoning is the experimental evidence of the presence in liquids of transversal modes [20-36] actives for the propagation of elastic energy by means of shear waves working as in the solid phase. These modes however persist in the liquid phase as long as solid-like structures survive. Experiments have shown that the two transversal modes disappear when the system approaches the critical point, where only the longitudinal collective modes survive accounting for the compression and expansion waves responsible for hydrodynamic modes propagation. This topic has been extensively discussed elsewhere [1], here it is important to have in mind that the number of collective DoF defined by m decreases with temperature, so that $\dfrac{dm}{dT} < 0$. Consequently, $\dfrac{m^*}{m^2}\dfrac{dm}{dT} T \geq -1$, and this defines the lower limit for $\dfrac{m^*}{m^2}\dfrac{dm}{dT} T$. As for the upper limit, because of the fact that $\dfrac{dm}{dT} < 0$ and $\left[\dfrac{m^*}{m^2}\dfrac{dm}{dT} T + 1 \right] \geq 0$, we get for the maximum value $\dfrac{m^*}{m^2}\dfrac{dm}{dT} T \leq 0$. Definitively we may conclude that

$$5. \quad 0 \leq \left[\frac{m^*}{m^2}\frac{dm}{dT} T + 1 \right] \leq 1$$

and finally

$$6. \quad C_V^{DML} \leq C_V$$

as one would have expected.

One of the most important results of the PLT is that of having provided for the first time an expression for the isochoric specific heat C_V for liquids that was shown to be valid for the solid, glassy, liquid, gas and quantum liquids states of matter [5-15]. To get this expression the Authors proposed a solid-like Hamiltonian of the system in which only harmonic terms are included because of the harmonic character of the interactions in a solid lattice. In order to tailoring the Hamiltonian for the liquid structure, it has been modified to account also for inelastic interactions, thus including the anharmonic contributions to the pool of energy. The theoretical expressions arrived at for C_V have been confirmed experimentally in 21 different liquids. Without entering into the details of the calculations, it is enough for our purposes to quote the expressions for the specific heat as obtained from the PLT accounting for both harmonic C_V^H and anharmonic C_V^A contributions, namely:

7. $$C_V^H = \frac{1}{N}\left(\frac{\partial q_T{}^H}{\partial T}\right)_V = 3-\left(\frac{\tau_D G_\infty}{\eta}\right)^3 + \frac{3T}{2\eta}\left(\frac{\tau_D G_\infty}{\eta}\right)^3 \frac{d\eta}{dT};$$

8. $$C_V^A = \frac{1}{N}\left(\frac{\partial q_T{}^A}{\partial T}\right)_V = 3\alpha T - \alpha T\left(\frac{\tau_D G_\infty}{\eta}\right)^3 + \frac{3\alpha T^2}{2\eta}\left(\frac{\tau_D G_\infty}{\eta}\right)^3 \frac{d\eta}{dT} = \alpha T C_V^H$$

from which we get:

9. $$C_V^{PLT} = C_V^H + C_V^A = C_V^H\left(1+\alpha T\right)$$

In Eqs.(7) through (9) indexes '*H*' and '*A*' stay for harmonic and anharmonic respectively, while q_T is the total heat content of the liquid defined in Eq.(1). The remaining terms have the same meanings as those quoted in [5,7], i.e. α is the coefficient of isobaric thermal expansion of the liquid, η its viscosity, τ_D the Debye vibration period and G_∞ the instantaneous shear modulus. Scope of the present section is to compare the expression given by Eq.(9), for the total specific heat C_V^{PLT} due to collective oscillations (phonons) as calculated in the PLT, with the corresponding one calculated in the DML frame of reference, C_V^{DML}, obtained from Eq. (3) [1]:

10. $$C_V^{DML} = mC_V\left[\frac{m^*}{m^2}\frac{dm}{dT}T+1\right].$$

As pointed out before, here C_V is the total specific heat of the liquid. This last definition should not surprise the reader; indeed, notwithstanding in the DML the exchange of energy and momentum is due to the presence of collective oscillations, this picture nevertheless modifies gradually as temperature increases. If at the triple point quite all the energy is supposed to be propagated by means of phonons and wave-packets, as the temperature increases the solid phase gives progressively way to dynamic *icebergs* swimming in an ocean of amorphous liquid; the number and size of *icebergs* decrease and the amount of amorphous liquid increases, to the point where it reaches the pure liquid, at the Frenkel line. Thus at the triple point one has $m \cong 1$, while m decreases progressively to zero at the Frenkel line, so that $\frac{dm}{dT} < 0$. The result at the mesoscopic scale is that the energy propagation by means of wave-packets becomes less and less important as the temperature increases. This is in line with Eq.(6). Ultimately, we may assume that in a liquid the total specific heat C_V is contributed as:

$$\text{11.}\qquad C_V = C_V^M + C_V^H + C_V^A = C_V^M + C_V^{DML} = C_V^M + C_V^H\left(1+\alpha T\right),$$

where with C_V^M we have indicated the classical contribution due to molecular interactions, and the last two members have been obtained using Eq.(9).

We are now ready to accomplish the task by comparing Eqs.(9) and (10) among them:

$$\text{12.}\qquad C_V^{DML} \equiv C_V^{PLT} \Rightarrow mC_{\mathrm{V}}\left[\frac{m^*}{m^2}\frac{dm}{dT}T + 1\right] = C_V^H\left(1+\alpha T\right)$$

We start by deriving the expression for $\frac{dm}{dT}$ taking into account that $\frac{dm}{dT} < 0$:

$$\text{13.}\qquad \frac{dm}{dT} = \frac{C_V^H\left(1+\alpha T - m\right) - m\left(C_{\mathrm{V}} - C_V^H\right)}{C_{\mathrm{V}}\frac{m^*}{m}T} < 0$$

Because the quantities at the denominator are all positive defined, the above relation reduces to discussing the algebraic sign of the numerator. Two possibilities may be considered, namely:

$$\text{14.}\qquad \begin{array}{l} A)\;\; C_V^H\left(1+\alpha T - m\right) < 0 \\ B)\;\; \begin{cases} a)\;\; C_V^H\left(1+\alpha T - m\right) > 0 \\ b)\;\; C_V^H\left(1+\alpha T - m\right) < m\left(C_{\mathrm{V}} - C_V^H\right) \end{cases} \end{array}$$

The case A) is however not acceptable because by definition $0 \le m \le 1$; therefore we will discuss case B) only. Because C_V^H is a positive defined quantity, we have

$$\text{15.}\qquad \begin{cases} a)\;\; 1+\alpha T - m > 0 \\ b)\;\; 1+\alpha T - m < m\left(\frac{C_{\mathrm{V}}}{C_V^H} - 1\right) \end{cases}$$

from which we easily get

$$\text{16.}\qquad \begin{cases} a)\;\; 1+\alpha T > m \\ b)\;\; 1+\alpha T < m\frac{C_{\mathrm{V}}}{C_V^H} \end{cases}$$

Eq.(16) allows us to identify specific limits for the parameter m:

17. $\frac{C_V^H}{C_V}(1+\alpha T) < m < (1+\alpha T)$

We then see that the parameter m is strictly linked to α. In the general case in which $\alpha > 0$, Eq.(17) becomes:

18. $\frac{C_V^H}{C_V}(1+\alpha T) < m < 1, \ \alpha > 0$

while the lower limit goes to zero as C_V^H. This conclusion is in line with the hypothesis of the DML. In fact, at high temperature icebergs melt and disappear from the liquid, and with them also the collective DoF contributing to C_V^H.

There are however very few cases in nature where $\alpha < 0$, as for instance the water in the temperature range $(0 < T < 4)°C$ at atmospheric pressure. In these cases the assumption introduced in Eq.(18) cannot be adopted.

There are other interesting insights that can be deduced from Eq.(16-b). Remembering that it is valid for $\frac{dm}{dT} < 0$, an upper limit can be deduced for α, namely:

19. $\alpha < \frac{1}{T}\left(m\frac{C_V}{C_V^H} - 1\right); \ \frac{dm}{dT} < 0$

Because usually it is also $\alpha > 0$, we get the following relation holding for the specific heat:

20. $C_V^H < mC_V$

which represents in turn an upper limit for C_V^H, providing the maximum thermal energy that can be stored into harmonic DoF of icebergs. Incidentally, this is in line also with the limits imposed to the total specific heat C_V^{DML} [see Eqs.(10) and (12) and the related validity range]. Compiling Eqs.(12) and (20), we get the following expression for the lower limit of α

21. $\alpha > \frac{m^*}{m^2}\frac{dm}{dT}$

where the second member is a negative quantity. Thus, also in the very few cases in which $\alpha < 0$, there is a minimum value for α as function of the number of collective excitations present in the liquid. The complete range holding for α is obtained compiling Eqs.(19) and (21):

22. $\frac{m^*}{m^2}\frac{dm}{dT} < \alpha < \frac{1}{T}\left(m\frac{C_V}{C_V^H} - 1\right).$

3. Dual Model of Liquids comparison with other recent liquid modelling: the same scenario seen from different perspectives.

The liquid state was initially dealt with as a sort of extension of the gaseous one, this mainly because of its property of flowing like gases, of the lacking of the capability of transmitting shear stresses, and of adapting to the shapes of their containers. However, this approach has never allowed to go very far in the formulation of theories that were able to provide a fairly general picture of the physical quantities characterizing the liquid state. Let us take for instance the specific heat, for which strong theoretical basis exist for gaseous and solid states, but not for the liquid one.

The alternative approach, to consider the liquid state in the same way as that of a solid, has illustrious predecessors, such as Debye [37-38], Brillouin [39-40], and Frenkel [41]. However, they too have never gone so far as to provide a model that went beyond an intuitive description, this probably because of the lack of experimental evidences that could guide and/or validate it. Nevertheless, recent measurements have given credit again to the ideas of Frenkel and Brillouin. At low frequencies, i.e. large wavelengths, it is not possible to "see" the mesoscopic structure of liquids. The entire liquid oscillates, compressing and expanding under the effect of pressure waves, which travel at the speed of sound. When one investigates the behaviour of a liquid at very high frequencies, and therefore at small wavelengths, it is discovered that it has a mesoscopic structure organized by means of solid-like dynamic aggregates, although ephemeral, that are identified here in a picturesque and imaginative way with the *icebergs*, elsewhere simply called pseudo-crystalline structures (see for instance [20-36]).

The first experimental evidence, although indirect, that on short time- and length-scale liquids are organized by means of solid-like local structures with a pseudo-periodicity, came in 1996 [27], when Ruocco and Sette measured by IXS experiments, therefore at high frequency, in liquid water at ambient conditions, the propagation speed of elastic waves, and found it equal to 3200 m/s, i.e. more than double that known at traditional frequencies, 1500 m/s, and very close to that of solid water, 4000 m/s. Starting from the results of experiments performed on various liquids with INS and IXS techniques, [20-36], the idea that pseudo-crystalline structures “exist and persist” in liquids on short time- and length-scales has gradually consolidated, their size and number depending on the liquid temperature (and pressure). The presence of these ephemeral dynamical structures can obviously be deduced only when high frequency measurements are carried out, typical of INS and IXS techniques, the wavelengths of the radiation involved being small enough to interfere with them. In the DML these pseudo-crystalline structures within which elastic energy is propagated by means of (quasi) harmonic waves (phonons), interact with the rest of the (amorphous) liquid through anharmonic interactions, represented by wave-packets, which arise at their border.

Ultimately, a quasi-elastic propagation within icebergs is transmitted to the amorphous matrix in the form of anharmonic wave-packets, and vice-versa. Unlike in crystalline solids, the anharmonicity allows a non-infinitesimal duration of the interactions, with consequent transport not only of energy but also of momentum, and furthermore exchange of energy with the internal DoF of the icebergs. Figure 3 shows the process described above.

How is the liquid state organized in the DML and how does it evolve? At the Triple Point the solid structure is not everywhere and abruptly lost. The liquid state resembles an ocean where pieces of solid, in continuous rearrangement, continue to exist and participate in the propagation of energy and momentum. Being solid-like, they are also able to transmit shear stresses and not only longitudinal compressions and expansions of the medium. As the temperature rises, the fusion is not instantaneous, the solid phase giving progressively way to solid-like dynamic structures in continuous evolution (the *icebergs*) swimming in an ocean of amorphous liquid; the number and size of the solid-like structures decrease more and more and the amount of amorphous liquid increases, to the point where it reaches the pure liquid, at the Frenkel line. On the other hand, it would not be surprising if the transition from the solid to the liquid phase took place over a wide range of temperature and pressure rather than over a restricted interval around the triple point.

This vision of liquids is not entirely new; from the historically point of view, besides the pioneering ideas of Debye and Brillouin, Frenkel proposed that liquids were constituted by a very large number of randomly oriented crystals of submicroscopic size, those he defined *cybotactic groups*[3]. The concept of relaxation time was early introduced by Maxwell in the liquid dynamics as a phenomenological concept related to the visco-elastic nature of liquid [42]. Frenkel, trying to compile a solid-like vision of liquids with their peculiarity of flowing, recovered the concept of relaxation time giving it a microscopic interpretation as "*the average time between particle jumps at one point in space in a liquid*" [41]. Its inverse, $\nu_F = 1/\tau_F$, is the frequency of occurrence of particle jumps. In the Frenkel model the way of distinguishing a liquid from a solid or a gas goes around the value of the relaxation time τ_F. If, at a given temperature, the characteristic time t of a perturbation propagating in the liquid is much shorter than τ_F (or the frequency f much larger than ν_F), over the time interval t the medium is seen by the perturbation as a solid, because the particles have not enough time to rearrange. The dynamic response is that of a free recoil of the liquid particle after the collision with the probe. Incidentally, this figure matches the interdependence between the relaxation time and the excitation frequency introduced in the *Introduction*.

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[3] In his book [41] Frenkel actually affirms that this idea was introduced by Stewart around 30's; Stewart proposed to denote such submicroscopic crystals, consisting of few tens of molecules, at most, by the term "*cybotactic group*" (or regions), and assumed them to be connected with each other by thin layers of the wholly amorphous phase.

The value obtained experimentally for the speed of sound in liquid water [25-27,32] proves that, in the range of momentum exchange examined and during the time lapse of the relaxation time, water behaves as a rigid network of molecules, and intermolecular forces are the same as in ice. Indeed the energy of the acoustic wave generated after the collision of the probe with the target particle of the medium, increases from the viscous to the elastic regime, i.e. upon frequency increase, due to the decrease of the acoustic dissipation. The same trend holds for the speed of sound, which manifests a positive dispersion vs frequency (PSD), while the opposite is true for the viscosity. Consequently, fingerprints of relaxation phenomena typical of collective dynamics can be found by examining the trend of the liquid physical parameters with frequency [22]. Surprisingly, and this is the demonstration of their ingenious intuitions, this conclusion is exactly the same that Brillouin and Frenkel had reached in their pioneering works [39-41], which anticipated what has been experimentally assessed on the structure of liquids only a century later.

The presence of relaxation time is a distinguishing aspect of liquids vs gases; in the latter every collision is independent from any other, and every collision is equal to the previous and successive ones. The heat motion in liquids close to the crystallization point has the same character as in solids, consisting of oscillations of molecules around their equilibrium positions. The positions of atoms in liquids are of course not permanent but temporary. After performing a number of oscillations around a given position, the atom can jump to another equilibrium position, far δ from the previous, where δ is of the same order of magnitude as the average distance among molecules in that liquid. This step-by-step wandering, lasting a time τ_F, is a sort of self diffusion motion, leading to a gradual mixing up of all the atoms [see for instance 43,44]. It must proceed much faster in liquids than in solids, and must have a simpler character because of the absence of definite lattice sites. Figure 3 illustrates the scenario. The relaxation time τ_F has two intrinsic limits [see for instance 5,6,15,23]. The upper limit is at low temperatures, anyway above the crystallization point, to leave the atoms the possibility to jump between two equilibrium positions. This limit corresponds to time intervals $\tau_F \approx 10^2 \div 10^3 s$ typical of the glass transition. The lower limit corresponds, at high temperature, to the minimum value of the Debye vibration period, $\tau_F = \tau_D = 1/\nu_D \approx 0.1 ps$, and the time interval between two successive jumps, the relaxation time, becomes comparable with the shortest vibration period. Thus one way of distinguishing a liquid from a solid or a gas goes around the values of the relaxation time τ_F. If, at a given temperature, the characteristic time t of a perturbation propagating in the liquid is much shorter than τ_F (or the frequency f much larger than ν_F), over the time interval t the medium is seen by the perturbation as a solid, the particles have no time to rearrange. The dynamic response is that of a free recoil of the liquid particle after the elastic collision with the probe (neutron or X-ray photon). The emerging spectrum is that of a solid being determined by the classical Maxwell-Boltzmann distribution [24], while the speed of sound is much higher. This case is that of “fast sound”, whose velocity for water of $\approx 3200 m/s$ obtained experimentally [25-27,32] is very close to the sound velocity found in crystalline ice Ih, of ≈ 4000 m/s, confirming that, in the explored range of temperature, water is in the viscoelastic regime, i.e. they combine viscous and solid-like elastic properties, as early suggested by Maxwell [42] and subsequently by Frenkel [41]. In this configuration the medium supports one longitudinal mode and two transversal modes. At time significantly longer than t the opposite is true, the system is seen as a viscous medium and it supports only one longitudinal mode. More precisely, liquids support 2 transversal and 1 longitudinal modes at low temperature; as far as the temperature increases approaching the liquid-to-gas transition, the capability of supporting shear stresses is lost, and only the longitudinal mode survives (however, the fact that flat waves are not intrinsic excitations in disordered media like liquids, inevitably leads to mixing longitudinal and transverse excitations, unlike in crystals, these type of excitations being not orthogonal). This limit provides the border line between purely diffusive motions and vibratory, or oscillatory, motions.

What described above is equivalent to assert that liquids and solids differ only quantitatively and not qualitatively [10], the border line being the frequency ν_F, or the relaxation time τ_F, as guessed by Frenkel [41]. This concept, i.e. that the distinction between liquids and solids is quantitative rather than qualitative, was introduced for the first time by Eckart [45-46] in his famous papers on the theory of “anelastic fluid”. Eckart demonstrated also that the propagation velocity of isentropic longitudinal waves is a complex number because it depends on frequency. He also faced in his model the problem of the relaxation times occurring in the dissipative processes. He ignored all the possible causes of dissipation except the collision process (as in the DML), that results in the viscous forces, and considered the type of dissipative process that is characteristic of anelastic media, either solid and liquid. This process depends on the fact that the anelastic variations of strain can occur independently of changes in density.

If, on one side, the presence in liquids of relaxation times distinguishes them from gases, on the other the thermal unrest in liquids has the same character as in solids, consisting of oscillations of molecules around their equilibrium positions. As in solids, a liquid particle may oscillate along with 3 preferred directions, one longitudinal (L) and two transversal (T). At low temperatures therefore liquids manifest also the capability of reacting to shear stresses, this behaviour being explained by the presence of the *icebergs*. Because of the progressive disappearance of *icebergs*, the capability of liquids to react to shear stresses by means of transversal DoF, is progressively lost as it approaches the Frenkel line. This is in line with the structural cross-over existing in liquids [8,23]. Consequently, the number m of lattice collective DoF available in a liquid, introduced in Eq.(1), decreases as the temperature increases, $dm/dT < 0$. Indeed, at low temperature energy and momentum in liquids are propagated also by means of transversal DoF, because the propagation mechanism involves a structural relaxation of the pseudo-crystalline structure. As the temperature increases this property is progressively lost and energy and momentum are propagated only by means of longitudinal DoF, because only collisional mechanisms are involved. Therefore, at low temperature m approaches unity, while it decreases by increasing the temperature because the number of lattice collective DoF decreases with increasing T, $0 \le m \le 1$ (at the Frenkel line only the longitudinal DoF survive). This is a fundamental point of the DML. It is worth noting that, apart the hypothesis of the mesoscopic organizations of liquids by means of dynamic *icebergs*, this figure matches that of the PLT, DML representing its mesoscopic counterpart. The above argument related to the variation with temperature (and pressure) of the number of DoF is supported also by measurements [20-36].

A very interesting insight has emerged from the comparison with recent developments in theoretical models on systems exhibiting k-gaps [16]. Baggioli et al. [16] very ingenuously used a two-fields Lagrangian to describe from the theoretical point of view systems with k-gap constituted by two mutually interacting sub-systems (that we identify with the wave-packets and the liquid particles in the DML). They used a two-scalar fields, ϕ_1 and ϕ_2, to represent velocities or displacements, from which build up the Lagrangian, instead of a single scalar field. Without entering into the details of the mathematical formalism, that is out of the scope here, what matters is that the equations of motion for the two scalar fields decouple; the development of the Lagrangian leads to two separate Cattaneo-like equations for both ϕ_1 and ϕ_2[4]:

$$\begin{cases} \phi_1 = \phi_0 \exp\left(-\dfrac{t}{2\langle\tau\rangle}\right)\cos(kx-\omega t) \\ \phi_2 = \phi_0 \exp\left(\dfrac{t}{2\langle\tau\rangle}\right)\cos(kx-\omega t) \end{cases} \tag{23}$$

The solution for such a system shows many interesting key-points, the more relevant for our purposes are:

1) the interaction potential is an oscillating function (see Figure 5 in [16]), that is the two scalar fields, and therefore the two interacting sub-systems, exchange energy among them: ϕ_1 and ϕ_2

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[4] Indeed, Frenkel [41] already deduced a Cattaneo-like propagation equation introducing into the Navier-Stokes equation the contribution due to the shear in a liquid (although he did not solve the equation he arrived at).

reduce and grow over time $\langle \tau \rangle$, respectively. This process is not dissimilar from phonon scattering in crystals due to defects or anharmonicity where a plane-wave phonon (ϕ_1) decays into other phonons (represented by ϕ_2) [16] and acquires a finite lifetime $\langle \tau \rangle$ as a result.

2) Being the total scalar field the product of ϕ_1 and ϕ_2, the total energy of the composite system does not have exponential terms depending on time due to their cancellation; consequently the total energy is a constant of motion.

3) The motion described by the solutions of the two scalar fields, or by the function represented in Figure 5 in [16], is a typical dissipative hydrodynamic motion. If the anharmonic interaction described by the Lagrangian (i.e. the wave packet – liquid particle interaction in DML) has a double-well (or multi-well) form, the field can move from one minimum to another (tunnel effect) in addition to oscillating in a single well.

4) This motion is analogous to diffusive particle jumps in the liquid and represents a possible origin for the viscosity. The motion is indeed a sort of hopping motion of the field, via thermal activation or tunnelling, between different wells with frequency $\nu_F = 1/\tau_F$. It is worth noticing that the dissipation concerns the propagation of plane waves in the anharmonic field described by the two scalar fields of the Lagrangian. The dissipation varies as $\nu_F = 1/\tau_F$: large $\langle \tau \rangle$ corresponds to rare transitions of the field between different potential minima.

A distinct effect of dissipation is related to a situation where the energy of the system is not changed overall, but the propagation range of a collective mode (e.g. phonon) acquires a finite range. No dissipation takes place when a plane wave propagates in a crystal where the wave is an eigenstate. However, a plane wave dissipates in systems with structural and dynamical disorder, such as liquids. Particle dynamics in liquids involves both solid-like oscillatory motion at quasi-equilibrium positions and diffusive jumps into neighbouring locations [7,9,15,41,16,47]. The first allows liquids to show a solid-like parameters when experimentally investigated over mesoscopic scales, while the jumps enable liquids to flow and associate them with viscosity. However, describing this dynamics needs consideration of a non-linear interaction allowing for both oscillation and jumps activated over potential barrier of the inter-particle potential. This problem does not originate in solids and gases. The smallness of atomic displacements in solids and the weakness of interactions in gases simplify their theoretical description, as already pointed out above. Liquids do not have those simplifying features: they combine large displacements with strong interactions (*liquids do not have small parameters*). For this reason, liquids are believed to be not described by theoretical tools at the same level as gases and solids [48].

There are interesting features that associate the presence of k-gaps in liquids with the fast sound or positive sound dispersion (PSD), the increase with frequency of the measured speed of sound over its hydrodynamic value. As first noted by Frenkel, a non-zero shear modulus of liquids implies that the propagation velocity crosses over from its hydrodynamic value $v = \sqrt{B/\rho}$ to the solid-like elastic value $v = \sqrt{(B + 4/3G)/\rho}$, where B and G are bulk and shear moduli, respectively. According to the above, shear modes become propagating at high k values, implying PSD at these k points. This further implies that PSD should disappear with temperature starting from small k because the k-gap increases with temperature [16].

The positions of atoms, or better, of *liquid particles* in fluids are of course not permanent as in solids but temporary. This is explained by the fact that the kinetic energy, E_p^k, of a *liquid particle* is comparable with the potential energy, Ψ_p, that kept it to a definite lattice point. Unlike in solids, where obviously $\Psi_p >> E_p^k$, or in gases, where the opposite holds, $\Psi_p << E_p^k$, in liquids the intermediate situations is true, $\Psi_p \approx E_p^k$. This step-by-step wandering, totally lasting a time τ_F for each jump, must proceed much faster in liquids than in solids, and must have a simpler character because of the absence of definite lattice sites.

The arrangement of liquid molecules on mesoscopic scale along with local lattices justifies the experimental value found for the speed of sound in water (and in other liquids) close to that of the corresponding solid form [20-33,35-36]. Liquid molecules are bounded to the local dynamic lattice, the *iceberg*; as far as thermal perturbations propagate inside an *iceberg*, they behave as in solids. When perturbations cross the boundary between two such local lattices, inertial effects develop, giving rise to momentum transport, as in the Frenkel model. The interactions are accompanied by propagation of elastic energy in forms of wave-packets because of the anharmonicity of the potential field [1]. The anharmonic character of the collisions generated at the border between two nearest-neighbour *icebergs* makes the interaction time non negligible, thus allowing also momentum transport. This gives origin to the displacement of *icebergs* and consequently to their diffusion. When wave-packets propagate in the amorphous phase, the speed of sound decreases and the same happens for the other liquid parameters. Incidentally this figure provides a qualitative explanation of the Positive Sound Dispersion (PSD) observed in liquids at high frequencies.

It is clear from above that what we usually mean as a “liquid” is not a liquid at all in the DML, but a mixture of solid-like dynamic structures and an amorphous, i.e. liquid phase in its common sense. As consequence, any liquid parameter whose magnitude is experimentally measured at temperatures and pressures where a usual liquid phase exists, is actually a pondered average of a solid/liquid value, in particular at those frequencies where the duality [1,5,7-8,10-15] of liquids phase emerges.

It is very interesting even to compare the DML with the PLT. The PLT describes the liquid from a statistical-thermodynamic point of view, therefore it cannot provide a direct answer on “why” the liquid particles oscillate. DML instead faces the problem from the opposite, mesoscopic point of view, starting from the elementary wave packet $\leftrightarrow$*liquid particle* collision that gives rise to the harmonic and anharmonic contributions present even in the PLT. DML provides and analyzes the microscopic elementary mechanism by which elastic and thermal energy, as well as momentum, are exchanged between *liquid particles* and lattice particles (phonons) and show that this scenario is in agreement with that of the PLT. One of the junction points between the two approaches, PLT and DML, is the relaxation times involved in the elementary interactions. Because of the thermodynamic-statistical nature of the theory, PLT from its side is only able to provide an indication of the variation range of the relaxation time through the value of the product $\nu\tau$. On the other side, DML is a mesoscopic model and analyzes the intimate mechanism of interaction of liquid particles with lattice modes; this provides both the answer to the question of “why” liquid particles oscillate, and a way for calculating the order of magnitude of τ in ordinary liquids [1]. We have shown [1] that the attained value of τ and of the product $\nu\tau$ are in the range foreseen on thermodynamic statistical basis from PLT. The relaxation time is one of the key-points of both models, and because the only common argument of PLT and DML is the assumption that thermal energy in liquids is transported by means of collective lattice excitations, both harmonic and anharmonic, the mutual agreement shows that both of them look at the model of liquid state in the same way, although from different observation points.

Another similitude of PLT and DML is the presence of harmonic and anharmonic contributions to the pool of energy. From the statistical-thermodynamic point of view, this fact is accounted for in the PLT by considering both contributions into the Hamiltonian of a liquid, giving rise in turn to the expression for the specific heat (the Hamiltonian adopted in the PLT has however many other interesting consequences, which anyway are not discussed here being out of the specific topic of the present paper). On the other side, harmonic and anharmonic oscillations are believed in the DML responsible for the propagation of energy and momentum within a liquid. In fact, energy is supposed to propagate inside the solid-like aggregates by means of harmonic oscillations. *Liquid particles* communicate among them and with the disordered liquid by means of anharmonic wave-packets, capable as such to exchange not only energy but also momentum. In such a way the macroscopic phenomena of diffusion (and thermal diffusion) may be easily interpreted in the DML.

The duality of liquids, supposed by both DML and PLT, however, does not exclude of course classical mechanisms of intermolecular interactions, as we will see in the Section **Error! Reference source not found.** when discussing the similarities of the isochoric specific heat expressions and their implications. The propagation of energy in a condensed medium through inter-molecular interactions on one side, or interactions between wave packets and pseudo-crystalline structures on the other, may be supposed working simultaneously and uniformly at the mesoscopic level. Which of the two prevails over the other depends on the thermodynamic conditions of the system. In a solid only the phononic part will be present. When the solid melts, the molecules begin to arrange in local solid-like lattices, phononic propagation gradually leaves way for propagation through molecular interactions, until the former completely disappears when the gaseous state is reached, only the molecular one remaining. While in solids there are always three modes of vibration, two transversal and one longitudinal, in liquids the transverse modes will be active only for frequencies higher than ω_F, $\omega > \omega_F = \frac{2\pi}{\tau_F}$, where τ_F is the relaxation time. In other words, on interaction times lower than the relaxation time, liquids behave as solids, while for times longer than τ_F, liquids lose the ability to support transversal ways, as in the classical approach.

An alternative – or rather complementary - expression for the liquid specific heat has emerged from another model recently proposed by Baggioli and Zaccone [19]. Starting from the solution they found for the Vibrational DoS in liquids [18], they have obtained an expression for C_V due to the only contribution of the experimentally proven presence in liquids of INMs, and neglecting the contribution of the “traditional” normal modes, on which the PLT is on the contrary based. INMs are indeed not normal modes in the traditional meaning, but rather pure imagery modes due to the anharmonic interaction potential typical of liquids. As such, they are absent in solids. Their comparison with the expressions for C_V provided by DML and PLT is not straightforward.

4. Further discussion and conclusions.

The hypotheses behind the DML, duly described in [1] and to which the reader is referred to for an in-depth study, are actually two, and both have an experimental background. The first is that experiments performed with the IXS and INS techniques [20-36] have made it possible to highlight that the mesoscopic structure of liquids is characterized by the (ephemeral) presence of solid-like, pseudo-crystalline structures, whose size being of a few molecular diameters and mass of few molecules, within which the elastic waves propagate as in the corresponding solid phase. The number and size of these structures varies with the temperature and pressure of the liquid. The

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second hypothesis is a direct consequence of the first. It consists in the assumption that elastic energy and momentum in liquids propagate by means of collective oscillations, or wave-packets, in a similar way as in crystalline solids. The perturbation propagates inside the solid-like structure by means of (quasi) harmonic waves; when it crosses the boundary, they leave way to anharmonic wave-packets, responsible for the propagation among solid-like structures and with the surrounding amorphous liquid phase. This scheme and the DML may be obtained by gathering together the early pictures of liquids of Debye [37-38] Brillouin [39-40] and Frenkel [41] in the light even of what is known today from the high frequency scattering experiments. In fact, as result of the interaction described in Figure 1, being the *icebergs* in continuous rearrangement, molecules continuously move from an *iceberg* to the nearest neighbour and *icebergs* too jump in the liquid from one site to the nearest-neighbour one, as hypothesized by Frenkel for the cybotactic groups introduced in [41].

Here in this paper and also elsewhere [1] we have largely discussed and commented the intimate similitude and differences of the DML and PLT models, in particular they are both dual models of liquids, both consider the presence of harmonic and anharmonic oscillations, give a pivotal role to relaxation times, etc.. All these arguments bring to the obvious conclusion that the two models show an evident visual identity: in the liquid state both harmonic modes, typical of the solid state, and anharmonic modes, typical of non-crystalline structures, are simultaneously present. The comparison of the two expressions for the specific heats provides interesting information about the degree of excitation of vibratory modes in liquids. Besides, we have also pointed out the central role of relaxation times in both models; in particular, their role has the consequence, among others, that heat propagation in liquids is described by a propagation (Cattaneo) equation instead of a diffusive equation [4].

As outlined above, and duly discussed in [1], key point of the DML is that the liquid is composed of two systems, the *liquid particles* and the *lattice particles*; they interact among them through a harmonic potential inside the iceberg, and through an anharmonic potential outside. The presence of k-gap reinforces this point and also the fact that not only longitudinal but also transversal modes are allowed in liquids. As far as the system is in thermodynamic equilibrium, the same holds for the two subsystems; when however a non-equilibrium state is imposed, even the two populations reach two distinct equilibria. The anharmonic character of the interaction allows the two populations to exchange among them not only energy but also momentum. This is another key point of the model, because the interaction represents a mechanism through which energy is dissipated. A possible application of the DML is indeed that of providing an elementary mechanism to explain the viscosity, that is a dissipative phenomenon present in liquids [49]. In a physical model for viscosity of liquids the exchange of momentum and energy among the two subsystems –

liquid particles and *lattice particles* - should be indeed accounted for, for instance by a suitable modification of the Navier-Stokes equation by using a two-fields Lagrangian. Another interesting topic to be investigated is the transition from inviscid liquid to gas.

If the elementary wave-packet $\leftrightarrow$ *liquid-particle* interactions would be perfectly elastic, all the energy (and momentum) lost by the wave-packet in an event such that of Figure 1a would be acquired by the *particle* and converted into kinetic energy, only the translational DoF being involved in the scattering process. Nevertheless, being the interaction anharmonic, not only it is not instantaneous, the momentum exchanged between wave-packet and *particle* is proportional to the duration of the interaction, $\langle \tau_p \rangle$ (i.e. to the time-length of the wave-packet) but also the energy lost by a wave-packet in an event of type a) of Figure 1 is only partially converted into kinetic energy of the *particle*. The remaining part is converted into internal molecular energy, exciting the corresponding DoF. This is an important point of the model, which introduces the exchange of energy with the internal vibratory DoF of the molecular cluster in a phononic model of liquid. It is possible to define an *"effective heat capacity"* C_{eff} for the total heat absorbed by (or given to) a *liquid particle*, taking into account the two branches of DoF. C_{eff} results to be a complex quantity whose real part is the static contribution pertaining to external translational DoF, while the imaginary part depends on that pertaining to the internal vibratory (quantized) DoF, on the frequency and on the relaxation time [50]. The pool of energy stored into the cluster will be released after a time lag $\langle \tau_R \rangle$. Depending on the OoM of such time interval, the events of Figure 1 can be considered elastic, quasi-elastic or inelastic [1,5,15,23].

One of the peculiarities of the interactions between wave packets and liquid particles is to work as a tunnel effect, by moving quantities of energy from one place to another in a well-defined time interval, the relaxation time, during which it is kept out of the heat current. The role of relaxation times is important in all the situations in which transport phenomena are influenced by a delay occurring in the microscopic transport processes. One of these cases is that of the heat transport in non stationary conditions, where such delays have a relevant role in the correct identification of the physical process and of the related mathematical equations describing the heat propagation in condensed media. It is well known indeed that in non stationary conditions a Cattaneo-like hyperbolic equation should be used to describe the heat propagation instead of a Fourier-like parabolic one to describe the heat diffusion.

Some final remarks are in order about the comparison of the expression for the isochoric specific heats deduced from PLT and DML. This comparison has provided very interesting information about the physical limits of the parameter m and the coefficient of isobaric thermal expansion α. An additional relation is also deduced for the ratio between the harmonic contribution to the specific heat, C_V^H, with respect to the total specific heat of the liquid. Besides the intrinsic information, unfortunately presently not supported by experimental confirmation, all the attained expressions and limits are internally consistent with the model, and with other limits provided on different basis. Having found limiting values for these quantities stimulates our reasoning on the fact that other Authors [51-55] have identified limiting values albeit for different physical quantities. However an answer to such comparison is still premature, although not absurd in principle.

Yet still today there are many questions on the nature of liquids that are still unanswered, as well a deficit of experiments. Performing experiments at the onset of a temperature gradient may allow to investigate how liquid parameters evolve from equilibrium to non equilibrium conditions. It could be possible for instance to investigate the evolution of correlations lengths, sound velocity, thermal conductivity, etc.. Also very interesting could be the investigation of whether and how a temperature gradient affects the viscous coupling between two liquids. Such experiments could be performed, for instance, by applying a temperature gradient to a stabilised isothermal liquid, provided that the average temperature of the system remains unchanged and preventing the convection instability, and performing light scattering experiments until a stationary temperature gradient is reached, i.e. during the transient, exactly the situation that is normally avoided in all the experiments. An alternative way to heat a small volume of liquid could be that on hitting the liquid with a focalised high power laser beam.

A second type of experiments could be aimed at investigating the glassy and liquid-to-solid transitions. Starting from a stationary temperature gradient, both temperatures could be lowered, thus lowering also the average temperature until the liquid solidifies. Light scattering experiments performed during the non stationary phase should allow to investigate the dynamics of the system when the glassy and liquid-to-solid transitions are crossed. In particular, the local domains should be oriented following the external temperature gradient, thus allowing the increase of the correlation lengths, of sound velocity, of thermal conductivity, etc., along the preferential direction of the external temperature gradient. A difference between the same parameters when measured along the direction of the temperature gradient with respect to those measured along a different direction should be evident from the experimental data collected. This technique could in some way introduce a sort of anisotropy into the liquid matrix, becoming the solid phase anisotropic.

In all the above experimental setups one could fruitfully exploit the characteristics of a special environment such a microgravity laboratory on orbiting platforms, where the above measurements could be pursuit without the disturbing, and often overwhelming effects due to the presence of the Earth’s gravity.

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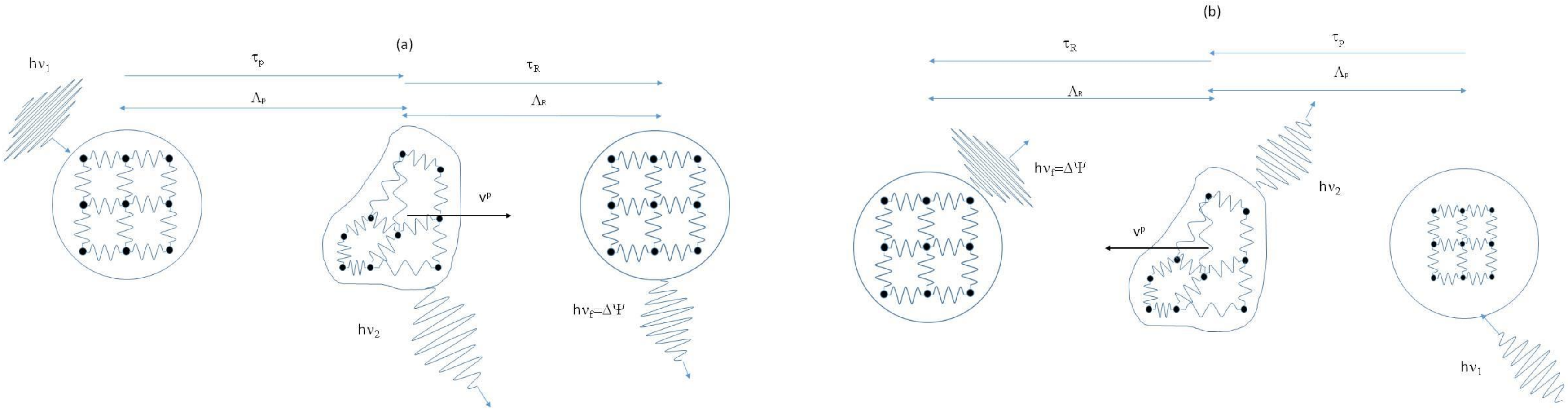
6. *Figures*

Figure 1



$$\Delta\varepsilon^{wp} = h\langle\nu_1\rangle - h\langle\nu_2\rangle = \Delta E_k^p + \Delta\Psi^p = f^{th}\cdot\langle\Lambda_p\rangle$$

$$\Delta p^{wp} = f^{th}\cdot\langle\tau_p\rangle$$

Figure 1. Schematic representation of inelastic collisions between wave-packets and liquid particles. The event represented in (a), in which an energetic wave-packet transfers energy and momentum to a liquid particle, is commuted upon time reversal into the one represented in (b), where a liquid particle transfers energy and momentum to a wave-packet. The particle changes velocity and the frequency of wave-packet is shifted by the amount $(\nu_2 - \nu_1)$. Due to its time symmetry, we assume this mechanism is the equivalent of Onsager' reciprocity law at microscopic level [1-3].

In a pure isothermal liquid energy and momentum exchanged among the icebergs are statistically equivalent, and no net effects are produced. Events of type a) will alternate with events of type b), to keep the balance of the two energy pools unaltered. Besides, the macroscopic equilibrium will ensure also the mesoscopic equilibrium; events (a) and (b) will be equally probable along any direction, to have a zero average over time and space. On the contrary, if a symmetry breaking is introduced, as for instance a temperature or a concentration gradient, one type of event will prevail over the other along a preferential direction.

(Re-drawn after Peluso, F., [1])

Figure 2

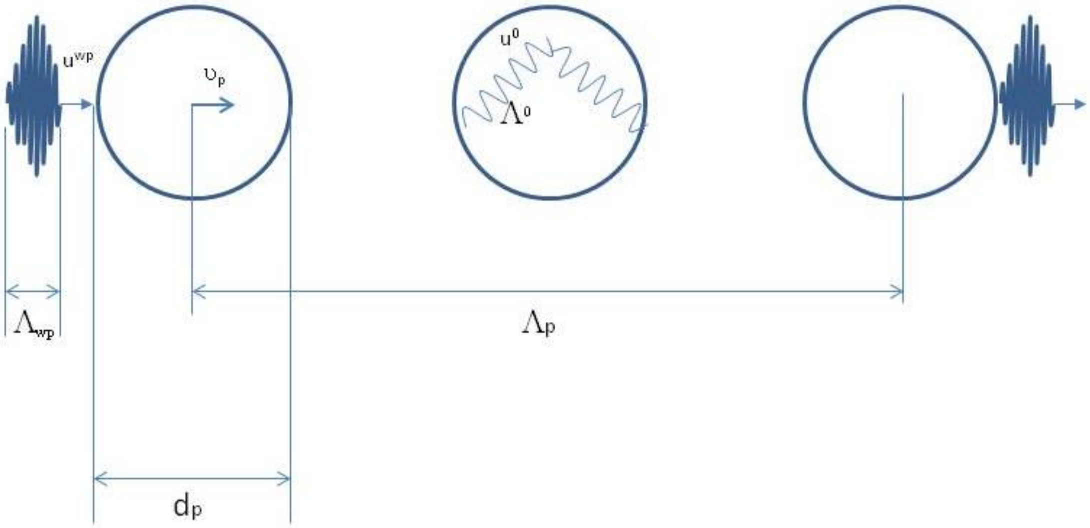


Figure 2. Close-up of the first part of the wave-packet – particle interaction shown in Figure 1a, during which the phonon transfers energy and momentum to the liquid particle. Λ_{wp} is the extension of the wave-packet, and d_p that of the liquid particle. Once τ_p has elapsed and the liquid particle has travelled by Λ_p, the particle relaxes the energy stored into internal DoF; then it travels by Λ_R during τ_R (not shown in the figure above).

(Re-drawn after Peluso, F., [1])

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Figure 3

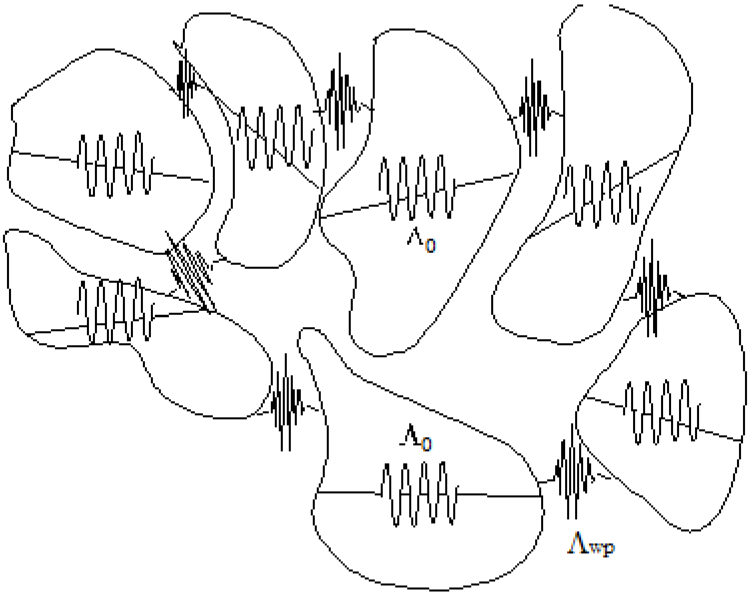

Figure 3. Icebergs of solid lattice fluctuating and interacting within the liquid global system at equilibrium. As far as elastic (thermal) perturbations propagate within an iceberg, they behave as in solids. Propagation velocity has then the values typical as those of the solid lattice, as found by Ruocco et al. [27] of about 3200 m/s for the case of water. Average sizes of icebergs $\langle \Lambda_0 \rangle$ have been found of some nanometers. When perturbations cross the boundary between two icebergs, f^{th} develops and energy and momentum are transmitted from one to the nearest-neighbour iceberg. This pictorial model of liquids at mesoscopic scale, on which the DML is based, reflects also what may be deduced from experiments performed with IXS techniques, able to observe liquids at such scale-lengths.

In a solution solute particles may be considered as icebergs having elastic impedance different from that of the solvent. Energy and momentum exchanged between the two types of icebergs produce a net effect resulting in the diffusion of the solute along the concentration gradient. If a temperature gradient is imposed externally, the net effect will depend on the prevailing flux of wave packets, which will give rise to thermal diffusion of one species with respect to the other.

(Re-drawn after Peluso, F., [1]).