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## Introduction

I had a memorable library day trying to find an answer to a question that is simple to formulate: What is a theoretical value of energy and heat capacity of a classical liquid? I looked through all of the textbooks dedicated to liquids, as well as statistical physics and condensed matter textbooks, in the Rayleigh Library at the Cavendish Laboratory in Cambridge, UK. To my surprise, they had either very little or nothing to say about the matter. I then took a short walk to Cambridge University Library and did a thorough search there. This returned the same result.

My surprise quickly grew closer to astonishment, for two reasons. First, heat capacity is one of the central properties in physics. Constant-volume heat capacity is the temperature derivative of the system energy, the foremost property in physics including statistical physics. Heat capacity informs us about the system's degrees of freedom and regimes in which the system is in, classical or quantum. It is also a common indicator of phase transitions, their types and so on. Understanding the energy and heat capacity of solids and gases is a central and fundamental part of theories of these two phases. Thermodynamic properties such as energy and heat capacity are also related to important kinetic and transport properties, such as thermal conductivity. Not having this understanding in liquids, the third basic state of matter, is a glaring gap in our theories. This is especially so in view of the enormous progress made in condensed matter research in the last century.

The second reason for my surprise was that the textbooks did not mention the absence of a discussion of liquid heat capacity as an issue. It is harder to solve a problem if we don't know it exists.

Around the same time, I met Professor Granato from the University of Illinois who shared my observations. He notes [2] that nothing is said about liquid specific heat in standard introductory textbooks, and there is little or nothing in advanced texts, adding that there is little general awareness of what the basic experimental facts to be explained are. This was reflected in his teaching: Granato recalls how he enjoyed teaching theories of the specific heat of gases and solids but lived in

constant fear that a student might ask “How about liquids?”. That question was never asked over many years of teaching involving about 10,000 students. Granato attributes this to an issue with our teaching practice, that is, that unsolved problems in physics are not sufficiently covered.

The available textbooks are mostly concerned with liquid structure and dynamics. They do not discuss most basic thermodynamic properties, such as liquid energy and heat capacity, or explain whether the absence of this discussion is related to a fundamental theoretical problem. Textbooks in which we might expect to find this discussion but don't include those dedicated to liquids [6, 9–22] and related systems [23–28], advanced condensed matter texts [29–33] and statistical physics textbooks [3, 5, 34–41].<sup>1</sup>

This list has a notable outlier: the *Statistical Physics* textbook by Landau and Lifshitz [3]. Landau and Lifshitz discuss the general thermodynamic properties of liquids and explain why they *cannot* be calculated, contrary to solids and gases. This explanation is quoted in the present book's preface, together with a related quote from Pitaevskii that discusses the absence of a small parameter in liquids. The absence of a small parameter implies that we can't use well-known tools such as quadratic forms based on the harmonic expansion in solids and perturbation theory in gases in order to understand liquids theoretically. Other authors have made similar observations, which we will encounter throughout this book. For example, Tabor says that “the liquid state raises a number of very difficult theoretical problems” [6].

As set out by Landau, Lifshitz and Pitaevskii, the liquid problem is formidable. It could explain why liquid energy and heat capacity are not discussed in textbooks, although in my experience, an experience shared by Granato, the lack of these discussions may be related to the low awareness of which experimental facts need to be explained, let alone of the fundamental problem of liquid theory.

The problem of liquids was well recognised in the area of molecular modelling and molecular dynamics simulations. It is interesting that a classic textbook on molecular dynamics simulations is entitled *Computer Simulation of Liquids* [42]. This method can simulate solids, gases or any other system in which an inter-atomic interaction is known, yet the textbook title focuses on liquids. As the book's authors explain, an important motivation for such computer simulations was the need to understand liquids, because they are not amenable to a theoretical understanding using approximate perturbative approaches or virial expansions. The authors note that, for some liquid properties, it may not even be clear how to begin constructing an approximate theory in a reasonable way. Computer modelling was seen as a way to help fix this problem.

<sup>1</sup> I will discuss two books by D. Wallace and J. Proctor separately.

In view of the enormous progress made in condensed matter research, it is perhaps striking to realise that we do not have a basic understanding of liquids as the third state of matter and certainly not on a par with solids and gases. This was one of the reasons I decided to look into this problem.

As its title suggests, this book follows the path from excitations in liquids to their thermodynamic properties. This general path is well established in statistical physics: an interacting system has collective excitations, or collective modes. Thermodynamic properties are then calculated on the basis of these collective excitations. The solid state theory is a celebrated case in which the solid energy is calculated on the basis of phonons in the Einstein or Debye model, with all of the important consequences that follow. In liquids, this path was largely unexplored in the past (with an exception of liquid helium, for which the quantum nature of the system, perhaps surprisingly, simplifies the theory). Until fairly recently, collective excitations in liquids were not understood well enough, and it was unclear if and how they could be related to liquid thermodynamics on the basis of a quantitative theory.

As is often the case, a difficult problem needs to be addressed from different perspectives, and the first aim of this book is to synthesise the results coming from three different lines of enquiry: experimentation, theory and molecular modelling. Some of these results are fairly new, while others date back nearly two centuries. I will show that liquids have a long and extraordinary history of research, but this history has been fragmented and sometimes undervalued.

When considered from a longer term perspective, the history of collective excitations in liquids reveals a fascinating story that involves physics luminaries and includes milestone contributions from Maxwell in 1867, followed by Frenkel and Landau. A separate and largely unknown line of enquiry aiming to connect phonons in liquids and liquid thermodynamics involved the work of Sommerfeld, published in 1913, one year after the Debye's paper on the heat capacity of solids. This line of enquiry was later developed by Brillouin and by Wannier and Piroué. When we get to the equation written (but not solved) by Frenkel to describe collective excitations in liquids, we will see that this equation was introduced by Kirchhoff in 1857 and discussed by Heaviside and Poincaré.

The second and most technical aim of this book is to connect excitations in liquids to their thermodynamic properties. In the process, a distinct liquid story will emerge, and this will achieve the third aim of this book: to put real liquids and an understanding of their experimental properties in to the spotlight. Tabor calls liquids the "neglected step-child of physical scientists" and "Cinderella of modern physics" compared with solids and gases [6]. Although this observation was made nearly 30 years ago, Tabor would have reached the same conclusion today with regard to liquid thermodynamics on the basis of more recent textbooks (listed

earlier). The third aim of this book is therefore to make liquids a full family member on a par with the other two states of matter, if not more sophisticated and refined due to the ability of liquids to combine oscillatory solid-like and diffusive gas-like components of particle motion. We will see how these two components endow the phase space for collective excitations in liquids with an important property: its ability to change with temperature.

The focus of this book is on understanding real liquids and their experimental properties, rather than on model systems. This importantly differentiates this book from others.

The experimental properties include specific heat as an important indicator of the degrees of freedom in the system and a quantity that can be directly measured experimentally and compared with theory. I start, in Chapter 2, with a brief account of the experimental data that we will be mostly concerned with. It will quickly become apparent that the common models used to understand liquids, such as the van der Waals and hard-sphere models, are irrelevant for understanding the specific heat of real liquids, bringing about the realisation that something quite different is needed. I will then recall our current understanding of collective modes in solids and gases and how these modes underly the theory of their thermodynamic properties in Chapters 3 and 4. An important observation here is that quadratic forms greatly simplify theoretical description. We particularly appreciate this simplification when we deal with liquids where we don't have them.

The small parameter problem discussed by Landau, Lifshitz and Pitaevskii does not necessarily mean that liquids cannot be understood in some other way. However, in Chapter 5, we will see that a head-on first-principles description of liquids, which we use in the solid state theory, is exponentially complex and therefore intractable.

An alternative approach to liquids is based on an integral involving interactions and correlation functions, and I review this approach in Chapter 6. This will show that earlier liquid theories and the solid state theory diverged in their fundamental approaches. Early theories considered that the goal of the statistical theory of liquids was to provide a relation between liquid thermodynamic properties and the liquid structure and intermolecular interactions. Working towards this goal involved ascertaining the analytical models for structure and interactions in liquids. Developing these models then became the essence of earlier liquid theories. I will review the general problems involved in this approach, including the inevitable problems set out by Landau, Lifshitz and Pitaevskii in the this book's preface. I will then highlight that these problems are absent in the solid state theory because this theory does not operate in terms of correlation functions and interactions and is based on phonons instead. This makes the solid state theory tractable, physically transparent and predictive. One of the main aims of this book is to show that liquids can be understood using a similar theory based on phonons.

In Chapter 7, I will show how Frenkel's ideas broke new ground for understanding liquids. This notably involves the concept of liquid relaxation time and its implications for liquid dynamics and collective excitations. This resulted in several important predictions, including the propagation of solidlike transverse waves in liquids at high frequency. The main difference between liquids and solid glasses was thought to be resistance to shear stress; however, Frenkel proposed that this was not the case: liquids too can support shear stress, albeit at a high frequency. Frenkel also proposed that the liquid–glass transition is a continuous, rather than a discontinuous, process. As we will see in Chapter 16, this continues to be the topic of current glass transition research.

In Chapter 8, I will discuss the equation governing liquid transverse modes that Frenkel wrote but, surprisingly, did not solve. Once simplified, this equation becomes the “telegraph equation” discussed by Kirchhoff, Heaviside and Poincaré. Surprisingly, in view of its wide use, the telegraph equation was not fully explored in terms of the different dispersion relations it supports. I will show how the solution gives rise to an important property of collective transverse modes in liquids: these modes exist above the threshold wavevector only and correspond to *gapped* momentum states. In terms of propagating waves, the gap also exists in the frequency domain. The gap increases with temperature, and this brings about the key property of liquids: the volume of the phase space available to collective excitations *reduces* with temperature. This is in striking difference from solids, for which this phase space is fixed. I will discuss the evidence for this reduction of the phase space on the basis of experimental and modelling data.

I will highlight that the hydrodynamic description was historically adopted as a starting point of discussing liquids and their viscoelastic properties. In this approach, hydrodynamic equations are modified to account for a solid-like response. I will show that this is related to our subjective perception rather than liquid physics and that both hydrodynamic and solid-like elastic theories are equally legitimate starting points of liquid description, both resulting in the telegraph equation. In this sense, liquids have a symmetry of their description where by the “elastoviscosity” term is as justified as the commonly used term “viscoelasticity” to discuss liquid properties.

As mentioned earlier in this chapter, widely used molecular dynamics simulations were stimulated by the need to understand liquids. This was because liquids were not thought to be amenable to theory. In Chapter 9, I will review the molecular dynamics simulations method and focus on two sets of molecular dynamics data related to the main topic of this book: thermodynamic properties and constant-volume specific heat ( $c_v$ ) in particular, as well as collective excitations.

Armed with preceding results, I will discuss the calculation of liquid energy and specific heat on the basis of propagating phonons in Chapter 10. I will demonstrate the advantage of this approach over that based on inter-atomic potentials

and correlation functions. Theoretical results will be compared to a wide range of experimental data, universally showing the decrease of the liquid specific heat with temperature. This decrease is related to the reduction of the volume of the phase space available for collective excitations due to the progressively smaller number of transverse phonons at high temperature. I will also discuss independent verifications of this theory.

In Chapter 11, I will examine the relation between collective excitations in quantum liquid  $^4\text{He}$  and its specific heat as discussed by Landau and Migdal. I will also discuss  $^3\text{He}$ , for which, differently from other systems, low-temperature thermodynamic properties are governed by localised quasi-particles rather than collective modes.

In Chapter 12, I will recall Tabor's discussion of what constitutes the *sui generis* approach to liquids. In the light of preceding results and our current understanding, the key to *sui generis* in liquids is to observe that these are systems in a *mixed* dynamical state involving both oscillations and the diffusion of particles, in contrast with pure dynamical states in gases and solids where by particle motion is purely diffusive and oscillatory. The balance between oscillatory and diffusive motion shifts with temperature (pressure), representing the sophistication of liquids compared with solids and gases. This shift is related to the variation of the volume of phase space available to collective excitations mentioned earlier. This, in turn, provides the key to understanding liquid thermodynamics and the universal decrease of liquid specific heat with temperature, in particular.

In Chapter 13, I will review the history of research aiming to link liquid thermodynamic properties to liquid collective excitations. Involving physics luminaries, this history dates back over a century. Quite remarkably, the first attempt at the theory of liquid thermodynamics based on phonons was done by Sommerfeld only one year after the Debye theory of solids and six years after Einstein's theory were published. Whereas the Debye theory has become part of every textbook in which solids are mentioned, we had to wait for about a century until we started understanding phonons in liquids well enough to be able to connect them to liquid thermodynamic properties. Sommerfeld's line of enquiry was taken up by Brillouin, who reconciled his theory of liquids and experimental data by making a fascinating proposal that liquids may consist of small crystallites. Wannier and Piroué later expanded on this work, as did other authors.

I will follow the link between excitations in liquids and their thermodynamics in a wide range of pressures and temperatures on the phase diagram, from high-temperature supercritical fluids through subcritical liquids to low-temperature viscous systems approaching the glass transition. In Chapter 14, I will examine the reduction of the phase space available to collective excitations above the critical point. Above the Frenkel line corresponding to the disappearance of the

oscillatory component of particle motion and two transverse modes, this reduction is due to the progressive disappearance of the remaining longitudinal mode. In view of the increasing deployment of supercritical fluids in environmental, cleaning and extracting applications, this discussion is of environmental and industrial relevance, as Chapter 14 will show.

The phase space available to collective excitations depends on the Frenkel hopping frequency, which, in turn, depends on viscosity. The temperature dependence of viscosity shows universal minima, and the minima themselves are related to the dynamical crossover of particle dynamics discussed in Chapter 14. This leads us to Chapter 15, where I will show that the viscosity *minimum* is a universal quantity for each liquid and is fixed by fundamental physical constants, an interesting result considering that viscosity is strongly system and temperature dependent. I will show how this provides an answer to the question asked by Purcell and considered by Weisskopf in the 1970s, namely “Why does viscosity never drop below a certain value comparable to that of water?”.

The minimal viscosity turns out to depend on  $\hbar$  and hence be a quantum property. This has immediate consequences for water viscosity and essential processes in living organisms and cells. Water and life appear to be well attuned to the degree of quantumness of the physical world and other fundamental physical constants. This adds another layer to the anthropic principle.

Considering another extreme of large viscosity at low temperature brings us to the realm of viscous liquids, as discussed in Chapter 16. Here, the link between excitations and system thermodynamics becomes fairly simple because the reduction of the phase space available to collective excitations can be safely ignored. As a result, liquid energy and specific heat to a very good approximation are given by  $3N$  phonons as in solids. Together with the dynamical disappearance of the viscous response at the glass transition temperature, this explains the observed jump of liquid specific heat at the glass transition temperature, which logarithmically increases with the quench rate.

In Chapter 17, I will discuss Mott’s recollection of the Frenkel work. Mott says that Frenkel was interested in real systems and what is really happening in those systems. This prompts a discussion of what we aim to achieve through a physical theory and what this theory should do.

The final two chapters, Chapters 18 and 19, explore how the insights we gained from the liquid theory can be used in other areas. Chapter 18 discusses how spin glasses can be understood on the basis of spin waves as is done in the theory of ferromagnets and anti-ferromagnets and similarly to how structural glasses are understood on the basis of phonons. In Chapter 19, I discuss the problem of strongly coupled field theories and make an analogy with strongly interacting liquids.

I have not discussed all of the sources I have consulted in this book. The selection of topics was helpfully aided and narrowed down by the guiding principle I used in writing this book. This principle is based on a well-established approach in physics where by an interacting system is fundamentally understood on the basis of its excitations [3, 5]. I have also taken a cautious attitude towards proposals that have not yet shown themselves to be well founded or constructive (I briefly touch upon this issue in Chapter 17). I may have missed subtle or more important points, and for this reason I recommend that an inquisitive reader consult references for details and look elsewhere. This is particularly so given that this book includes the results of my own group and collaborators. However, where I have really made a difference is in writing this overview as more than a collection of ideas, concepts and models related to liquids. By focusing on collective excitations in liquids and basic liquid properties, I have shown that earlier and more recent research and ideas physically link to each other and in ways not previously considered.

I end several chapters with questions and proposals for future research to either complement the already existing results or pursue a new line of enquiry.