Statistical Mechanics for the Liquid State

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By

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Foreword

Statistical mechanics is the name used for the discipline devoted to studying systems composed of a large number of particles in order to calculate their macroscopic properties including energy, pressure, entropy... It deals as such with both *equilibrium systems* whose particles are either independent or strongly interacting and *non-equilibrium systems*. In most cases, two different approaches are used to develop a theory of the equilibrium properties of liquids based on the principles of statistical mechanics: (i) the systematic cluster expansion formalism applied to fluids at a density as high as one-third of normal liquid densities, and (ii) the integro-differential equations formalism determining the relationship between the distribution functions and the effective pair interactions. The discussion of the non-equilibrium phenomena have also made significant headway with the sophisticated calculations of the Chapman-Enskog solution for the Boltzmann equation and, more recently, with the linear response theory that provides the transport coefficients in terms of correlations among fluctuations.

Statistical mechanics is a relatively new science that developed in the mid nineteenth century with the scientific works of Clausius, Maxwell and Boltzmann. Clausius laid the foundation of the theory of gases in 1857. Two years later, Maxwell established the law of velocity distribution of molecules in gases. In 1872, Boltzmann went through a harsh period against the supporters of the theory of energy and changed the law of the Maxwell velocity distribution by taking the external fields into account.

The basic grounding in statistical mechanics was actually provided by Gibbs [1] in a book entitled *The principles of statistical mechanics* which almost went unnoticed when it was published in 1902. In this work, Gibbs justified for any system containing interacting particles

the results obtained by Maxwell and Boltzmann by following a different path than what the predecessors had used and offering more rigorous mathematical and logical consistency based on the *concept of ensemble*. Gibbs' distribution is based exclusively on assuming the canonical ensemble to derive the laws of distribution, and makes no use of empirical results about the nature of the intermolecular forces. Any new statistical theory is inspired in some way by Gibbs distribution, and it is not an overstatement to say that it holds the same position as Newton's equation in classical mechanics or Maxwell's equations in electromagnetism.

In 1907, a milestone was passed when Einstein combined the ideas of statistical mechanics and quantum mechanics to explain the specific heat of solids at low temperature. Shortly later, von Neumann established rigorously the link between statistical mechanics and quantum mechanics. Nevertheless, when realizing that the Maxwell-Boltzmann distribution is a limiting case of the Bose-Einstein and Fermi-Dirac distributions, the scope of statistical mechanics has been widely extended. It would be difficult to compile a full list of fields where statistical mechanics identified applications. Statistical mechanics is used in a wide range of fields including radiation (Planck, Bose, Einstein...), Brownian motion (Brown, Einstein, Smoluchowski...), electronic theory of metals (Drude, Sommerfeld, Lorentz...), magnetism (Langevin, Brillouin, Weiss...), specific heat (Einstein, Debye...), semiconductors (Bardeen, Schockley...), superconductivity (Cooper, Schrieffer, Josephson...), superfluidity (Landau...), astrophysics (Fowler, Chandrasekhar...), phase transitions (Domb, Fisher, Wilson...), polymers (Kuhn, Flory...), dense fluids (Kirkwood, Yvon, Green...), etc.

The purpose of this book is primarily to examine and study the structural and thermodynamic properties of dense fluids and their transport properties. It is important to note that the statistical mechanics of dense fluids is divided into two parts. The first one investigates the *equilibrium systems* and makes it possible to calculate their thermodynamic properties and static structure. The second one focuses on the *out-of-equilibrium systems* and open the way to studying individual and collective motions of particles together with determining their transport properties. Regarding the equilibrium systems, there are two distinct ways to calculate the thermodynamic properties. The first one - based on knowledge on the *partition function* - is elegant but it applies to diluted fluids and is the only path to investigate the thermodynamic properties. The second way rest on the use

of *spatial correlation functions*. In addition to the fact that they give access to the thermodynamic properties of dense fluids, they are likely to extract the static structure provided that the interactions between particles are reduced to a sum of pair potentials. Over and beyond that fact, they fall under a more general theory involving the *spatial and temporal correlation functions* that make it possible to calculate the atomic transport properties such as the coefficients of diffusion, viscosity or thermal conductivity.

The aim of this publication is mainly to try and pinpoint what there is behind the seemingly anarchistic proliferation of phenomena observable in liquid state together with the sequence of causes and effects and, where appropriate, identify the general principles and underlying rules governing them. To facilitate the understanding of the microscopic theory of liquids, the tests made often refer to specific cases calling for only easy reasoning and concepts whose aim is not to display the mathematical rigour of the theory, but rather to the implementation of the models under consideration. Nevertheless, numerous details of the calculations are produced to exempt the reader from repeating the demonstrations.

And last but not least, let me express my thanks and gratitude to my colleagues and graduate students for numerous discussions and helpful comments. When writing this book, the purpose was to provide a pre-measured dosage of statistical mechanics to make the reading easier and appetizing and raise interest among students for the liquid theory. Many thanks also go to Jean-Pierre Hansen, Ian McLaughlin and Andrei Postnikov, who displayed much patience and solid expertise when reading over the manuscript and suggesting numerous improvements.

1 The basics of classical statistical mechanics

Unlike classical mechanics and quantum mechanics, adapted to systems with a few degrees of freedom, the statistical mechanics makes it possible for us to study systems containing many particles such as gases, dense fluids and solids. In classical mechanics, the past and future history of systems is fully determined when external forces and initial conditions are known. In contrast to this in statistical mechanics, we should be content with admitting that the initial conditions are always subject to uncertainties due to the large amount of data. Therefore, it is impossible to find a rigorous solution to the equations of motion so that the methods of mathematical statistics become indispensable. In other words, the differences between statistical mechanics and classical mechanics lie in having no knowledge of initial conditions.

The statistical analysis is not restricted to systems containing a large number of particles. It can be also used in classical mechanics with numerical simulation methods. For instance, the Monte Carlo method, when tracking the motion of a small number of particles, merges the advantages of classical mechanics and statistical mechanics.

Whereas the molecular behaviour of matter is described by *microscopic laws* involving coordinates and momenta, the *macroscopic laws* of thermodynamics use an appropriate set of physical properties such as volume, pressure, temperature, density... One of the major objectives of statistical mechanics aims specifically at making the link between the laws of mechanics and the laws of thermodynamics. Gibbs was first to develop the general treatment to express the relevant thermodynamic properties of any chemical system in terms of

the microscopic properties of molecules. Formalism is based on the *concept of ensemble* and the *probability density*. Given that the treatment can lead to severe discrepancies when compared with results of experiments (particularly for specific heats), it has been necessary to introduce the ideas of quantum mechanics to remove the shortcomings.

The purpose of this chapter is to offer a brief reminder of classical mechanics and quantum mechanics that play a central role in the development of the statistical mechanics. Then, we present the concept of ensembles and of probability density conveniently introduced by Gibbs through the phase space considerations. Finally, we state the first postulate of statistical mechanics showing correspondence between the time average and the ensemble average in ergodic systems. Nothing is more solid and effective than a theorem whose validity has been carefully tested.

1.1   Classical mechanics and phase space

Newtonian formalism

The classical mechanics is based on Newton's equation :

$$\mathbf{F}_i = m\frac{d^2\mathbf{r}_i}{dt^2}, \tag{1.1}$$

in which $\mathbf{F}_i$ is the force acting on the ith particle of a system that contains N particles, m the mass of the particle and $\mathbf{r}_i$ its radius vector. This equation can describe the motion of the particle and be reduced to three second-order differential equations whose solutions $x_i(t)$, $y_i(t)$ and $z_i(t)$ are determined when the force $\mathbf{F}_i$ and the initial conditions are known.

For example, to study the motion of the linear harmonic oscillator , the differential equation is:

$$m\frac{d^2X}{dt^2} = -kX, \tag{1.2}$$

where $X(= x - x_0)$ represents the elongation proportional to the force $F(= -kX)$. The solution of this differential equation is $X = X_0\cos(\omega t + \varphi)$, where the angular frequency $\omega = \left(\frac{k}{m}\right)^{1/2}$ depends on

the characteristics of the system, while X_0 and φ are two constants of integration determined from the initial conditions. In practice, this corresponds to the oscillatory motion of a frictionless mass m attached to a spring of stiffness k.

In order to compare meaningfully the different formalisms of classical mechanics, we consider the motion of a particle of mass m in a central field. The potential energy is $U(r) = \frac{k}{r}$ and the force deriving from it is $\mathbf{F} = -\mathbf{grad}U = -k\frac{\mathbf{r}}{r^3}$, so that Newton's equation that governs the motion of the particle is:

$$m\frac{d^2\mathbf{r}}{dt^2} = -k\frac{\mathbf{r}}{r^3}. \tag{1.3}$$

If the trajectory is located in the plane (xy), the projections of this vectorial equation are:

$$m\frac{d^2x}{dt^2} = -k\frac{x}{(x^2 + y^2)^{3/2}}, \tag{1.4}$$

$$m\frac{d^2y}{dt^2} = -k\frac{y}{(x^2 + y^2)^{3/2}}. \tag{1.5}$$

The nature of the problem and the form of the equations require the use of polar coordinates (r, θ) to solve the system of differential equations. After making the change of variables $x = r\cos\theta$ and $y = r\sin\theta$, the system of differential equations written above becomes:

$$\left[m(\ddot{r} - r\dot{\theta}^2) + \frac{k}{r^2}\right]\cos\theta - m(r\ddot{\theta} + 2\dot{r}\dot{\theta})\sin\theta = 0, \tag{1.6}$$

$$\left[m(\ddot{r} - r\dot{\theta}^2) + \frac{k}{r^2}\right]\sin\theta + m(r\ddot{\theta} + 2\dot{r}\dot{\theta})\cos\theta = 0. \tag{1.7}$$

To simplify these equations, we perform their sum after multiplying the first equation by $\cos\theta$ and the second one by $\sin\theta$, and then carry out their difference after the first equation has been multiplied by $\sin\theta$ and the second one by $\cos\theta$. This produces the following two equations:

$$m(\ddot{r} - r\dot{\theta}^2) + \frac{k}{r^2} = 0, \tag{1.8}$$

$$m(r\ddot{\theta} + 2\dot{r}\dot{\theta}) = 0. \tag{1.9}$$

The second equation is an exact differential equation that can be integrated immediately into the form:

$$mr^2\dot{\theta} = l. \qquad (1.10)$$

It is obvious that the quantity $mr^2\dot{\theta} = l$ corresponds to the angular momentum of the particle that is a constant of motion. In eliminating $\dot{\theta}$ between equations (1.8) and (1.10), we obtain the radial equation:

$$m\ddot{r} = -\frac{k}{r^2} + \frac{l^2}{mr^3}. \qquad (1.11)$$

It should be noted that the solution $r(t)$ to this differential equation can be expressed - at least at a matter of principle - in terms of the constants k and l. By comparing equations (1.11) and (1.3), we can also notice the presence of the additional term $\frac{l^2}{mr^3}$ in equation (1.11) that can be interpreted as a fictitious force (centrifugal force), which does not result from an external force, but rather arises from the mode of representation adopted. The centrifugal force and Coriolis force appearing in the coordinate systems in rotation are two examples of fictitious forces.

Lagrangian formalism

The motion of a particle – or more generally of a material system – can also be studied with the Lagrange formalism. This approach is used when the variables are angles or complicated functions of conventional coordinates rather than Cartesian coordinates of individual particles. In this formalism, a system of N particles interacting with each other is defined by its $3N$ generalized coordinates q_i, where $i = 1, 2, ..., 3N$. However, before describing the motion of particles, it is appropriate to calculate the following function known as the *Lagrangian* of the system:

$$L(q_1, q_2, ..., q_{3N} \; ; \; \dot{q}_1, \dot{q}_2, ..., \dot{q}_{3N} \; ; \; t) = T - U, \qquad (1.12)$$

depending on *generalized coordinates* q_i, *generalized velocities* $\dot{q}_i$ and, possibly, on the time t. At the right side of equation (1.12), T is the kinetic energy and U the potential energy of the system. The kinetic energy T is a quadratic function of generalized velocities:

$$T = \frac{1}{2} \sum_{k=1}^{N} m_k \dot{q}_k^2, \qquad (1.13)$$

and the potential energy U depends only on generalized coordinates when the system is conservative. Knowing the kinetic and potential energies of the system, the equations of motion can be derived using the Lagrange equations that arise in the following form:

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_i}\right) - \frac{\partial L}{\partial q_i} = 0 \qquad \text{where} \qquad i = 1, 2, ..., 3N. \qquad (1.14)$$

By way of illustration, the equations of motion can be derived within the Lagrangian formalism of the two systems previously treated with the Newtonian formalism . In this case it is unnecessary to calculate the applied forces. For the linear harmonic oscillator , we use the generalized coordinate $q_1 = X$. The kinetic energy is $T = \frac{1}{2}m\dot{X}^2$ and the potential energy is $U = -\int(-kX)dX = \frac{1}{2}kX^2$, so that the Lagrangian is :

$$L(X, \dot{X}) = \frac{1}{2}m\dot{X}^2 - \frac{1}{2}kX^2. \qquad (1.15)$$

As far as the equation of motion is concerned, the Lagrange equation (Eq. 1.14) is written:

$$\frac{d}{dt}(m\dot{X}) + kX = 0, \qquad (1.16)$$

which coincides with equation (1.2).

Now we consider the particle of mass m in a central field. Its potential energy is $U = \frac{k}{r}$ and its kinetic energy $T = \frac{1}{2}mv^2$ is expressed in terms of generalized coordinates $q_1 = r$ and $q_2 = \theta$. As the square of the velocity - in polar coordinates - has the following expression $v^2 = \dot{r}^2 + r^2\dot{\theta}^2$, the corresponding Lagrangian reads :

$$L(r, \theta, \dot{r}, \dot{\theta}) = \frac{1}{2}m(\dot{r}^2 + r^2\dot{\theta}^2) + \frac{k}{r}. \qquad (1.17)$$

In terms of the coordinates r and θ, the use of the Lagrange equations leads directly to :

$$\frac{d}{dt}(m\dot{r}) - mr\dot{\theta}^2 + \frac{k}{r^2} = 0, \qquad (1.18)$$

$$\frac{d}{dt}\left(mr^2\dot{\theta}\right) = 0. \qquad (1.19)$$

These equations coincide with equations (1.10) and (1.11). Contrary to the Newtonian formalism , the knowledge of actual and fictitious

forces is not required. In particular, the centrifugal force $mr\dot{\theta}^2 = \frac{l^2}{mr^3}$ results understandably from the Lagrangian and this is considered as an advantage over the Newtonian formalism in which the presence of fictitious forces makes things more complex when deriving the equations of motion.

Another advantage of the Lagrangian formalism is offering an identification of quantities called *first integrals* and retained during the motion. A first integral of the motion is particularly important when the Lagrangian does not depend explicitly on time. Let us show it by calculating the total derivative of L with respect to time:

$$\frac{dL}{dt} = \sum_i \frac{\partial L}{\partial q_i}\frac{\partial q_i}{\partial t} + \sum_i \frac{\partial L}{\partial \dot{q}_i}\frac{\partial \dot{q}_i}{\partial t} + \frac{\partial L}{\partial t}. \tag{1.20}$$

According to the Lagrange equation, $\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_i}\right) = \frac{\partial L}{\partial q_i}$, and the relation $\frac{\partial q_i}{\partial t} = \dot{q}_i$, equation (1.20) is rewritten:

$$
\begin{aligned}
\frac{dL}{dt} &= \sum_i \left[\dot{q}_i \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_i}\right) + \frac{\partial L}{\partial \dot{q}_i}\frac{\partial \dot{q}_i}{\partial t}\right] + \frac{\partial L}{\partial t}, \\
&= \sum_i \frac{d}{dt}\left(\dot{q}_i \frac{\partial L}{\partial \dot{q}_i}\right) + \frac{\partial L}{\partial t}, \tag{1.21}
\end{aligned}
$$

hence
$$\frac{\partial L}{\partial t} = -\frac{d}{dt}\left(\sum_i \dot{q}_i \frac{\partial L}{\partial \dot{q}_i} - L\right). \tag{1.22}$$

However, if the Lagrangian does not depend explicitly on time ($\frac{\partial L}{\partial t} = 0$), the above equation reduces to:

$$\sum_i \dot{q}_i \frac{\partial L}{\partial \dot{q}_i} - L = H = const. \tag{1.23}$$

The quantity H, being retained when L does not depend explicitly on time, is a very important first integral of analytical mechanics. Similarly and for instance, if the Lagrangian L is independent of a generalized coordinate q_j, the variation of L with respect to $\dot{q}_j$ is a constant, i.e. $\frac{\partial L}{\partial \dot{q}_j} = const$. Following Lagrange's equation (Eq. 1.14), $\frac{\partial L}{\partial q_j} = 0$ is indeed equivalent to $\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_j}\right) = 0$ or $\frac{\partial L}{\partial \dot{q}_j} = const$. Accordingly, each generalized coordinate q_i is associated to its *conjugate momentum* $\frac{\partial L}{\partial \dot{q}_i} = p_i$ whose leads to the Hamiltonian formalism.

Hamiltonian formalism

In the Lagrangian formalism, the independent variables are the generalized coordinates q_i defining the system state at any moment. They are functions of time that are themselves solutions of a system of $3N$ second order differential equations. By contrast, the independent variables in the Hamiltonian formalism are the generalized coordinates q_i and the conjugate momenta $p_i = \frac{\partial L}{\partial \dot{q}_i}$. Replacing $\frac{\partial L}{\partial \dot{q}_i}$ by the conjugate momenta p_i into equation (1.23) does not bring any obvious advantage, except to define a new function H, called the *Hamiltonian* of the system:

$$H(q_i, p_i, t) = \sum_i \dot{q}_i p_i - L, \qquad (1.24)$$

which has the same unit as L, i.e. energy.

The interest in the Hamiltonian is to be a first integral when the Lagrangian does not depend explicitly on time (Eq. 1.23) and to represent, in most cases, the total energy E of the system. For a conservative system, the potential energy $U(= T - L)$ is indeed a function of the generalized coordinates q_i which allows us to write the conjugate momenta as:

$$p_i = \frac{\partial L}{\partial \dot{q}_i} = \frac{\partial (T - U)}{\partial \dot{q}_i} = \frac{\partial T}{\partial \dot{q}_i}. \qquad (1.25)$$

Moreover, considering that the kinetic energy T is a quadratic function of the generalized velocities (Eq. 1.13), we can write:

$$\sum_i \dot{q}_i \frac{\partial T}{\partial \dot{q}_i} = 2T, \qquad (1.26)$$

by virtue of Euler's theorem. Remember that Euler's theorem stipulates that if a function $f(\lambda x_1, \lambda x_2 ... \lambda x_i)$ is a homogeneous polynomial of degree m in x_i, namely:

$$f(\lambda x_1, \lambda x_2, ... \lambda x_i, ...) = \lambda^m f(x_1, x_2, ..., x_i, ...), \qquad (1.27)$$

f is related to its partial derivatives by the equation:

$$\sum_i x_i \frac{\partial f}{\partial x_i} = mf. \qquad (1.28)$$

To demonstrate this, it is just necessary to differentiate equation (1.27) with respect to λ and to write down $\lambda = 1$, as follows:

$$\frac{\partial f}{\partial \lambda x_1}\frac{\partial \lambda x_1}{\partial \lambda} + \frac{\partial f}{\partial \lambda x_2}\frac{\partial \lambda x_2}{\partial \lambda} + \quad \cdots \quad + \frac{\partial f}{\partial \lambda x_i}\frac{\partial \lambda x_i}{\partial \lambda} + \cdots$$
$$= \quad m\lambda^{m-1}f(x_1, x_2, ..., x_i, ...),$$
$$x_1\frac{\partial f}{\partial x_1} + x_2\frac{\partial f}{\partial x_2} + \quad \cdots \quad + x_i\frac{\partial f}{\partial x_i} + \cdots$$
$$= \quad mf(x_1, x_2, ..., x_i, ...). \qquad (1.29)$$

Given that the kinetic energy T is a homogeneous polynomial of degree two of $\dot{q}_i$, this yields equation (1.26). Therefore, by combining equations (1.24), (1.25) and (1.26), the Hamiltonian of a conservative system reduces to the total energy E:

$$H \quad = \quad \sum_i \dot{q}_i\frac{\partial T}{\partial \dot{q}_i} - L,$$
$$= \quad 2T - L = T + U = E. \qquad (1.30)$$

To establish the equations of motion in the Hamiltonian formalism, we must calculate the total differential of the Hamiltonian $H(q_i, p_i, t)$:

$$dH = \sum_i \frac{\partial H}{\partial q_i}dq_i + \sum_i \frac{\partial H}{\partial p_i}dp_i + \frac{\partial H}{\partial t}dt. \qquad (1.31)$$

As the element dH is also given by the differential of equation (1.24), it can be written again under the following form with the help of equation (1.20):

$$dH = \sum_i d\dot{q}_i p_i + \sum_i \dot{q}_i dp_i - \left[\sum_i \frac{\partial L}{\partial q_i}dq_i + \sum_i \frac{\partial L}{\partial \dot{q}_i}d\dot{q}_i + \frac{\partial L}{\partial t}dt\right]. \quad (1.32)$$

By using the Lagrange equations (Eq. 1.14), namely $\frac{\partial L}{\partial q_i} = \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_i}\right)$, and the conjugate momenta ($p_i = \frac{\partial L}{\partial \dot{q}_i}$), the term in square brackets in the above equation transforms into

$$\left[\sum_i \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_i}\right)dq_i + \sum_i \frac{\partial L}{\partial \dot{q}_i}d\dot{q}_i + \frac{\partial L}{\partial t}dt\right] = \sum_i \dot{p}_i dq_i + \sum_i p_i d\dot{q}_i + \frac{\partial L}{\partial t}dt,$$
$$(1.33)$$

and equation (1.32) simplifies to:

$$
\begin{aligned}
dH &= \sum_i d\dot{q}_i p_i + \sum_i \dot{q}_i dp_i - \left[\sum_i \dot{p}_i dq_i + \sum_i p_i \ d\dot{q}_i + \frac{\partial L}{\partial t} dt \right], \\
&= \sum_i \dot{q}_i dp_i - \sum_i \dot{p}_i dq_i - \frac{\partial L}{\partial t} dt.
\end{aligned} \tag{1.34}
$$

Identifying the terms of equations (1.31) and (1.34) yields the Hamilton equations:

$$
\begin{aligned}
\dot{q}_i &= \frac{\partial H}{\partial p_i}, \\
\dot{p}_i &= -\frac{\partial H}{\partial q_i}, \\
\frac{\partial L}{\partial t} &= -\frac{\partial H}{\partial t}.
\end{aligned} \tag{1.35}
$$

The last of these equations shows that if the Lagrangian does not depend explicitly on the time, the Hamiltonian does not depend on it either. As for the two first equations, they constitute the equations of motion in the Hamiltonian formalism. They form a system of $6N$ first order differential equations that require knowledge of $6N$ initial conditions ($3N$ for p and $3N$ for q). They replace the $3N$ second order differential equations in the Lagrangian formalism, which also require $6N$ initial conditions. The Hamilton equations do not represent an improvement relative to the Lagrange equations; their only advantage is to provide an appropriate basis for the development of quantum mechanics and statistical mechanics. In the Hamiltonian formalism, a $6N$ dimensional space, called the *phase space* Γ, is introduced, where a point defined by $3N$ variables q_i and $3N$ variables p_i describes a trajectory that allows us to follow the evolution of the system over time.

To illustrate the method, consider again the linear harmonic oscillator with the Lagrangian (Eq. 1.15) written as :

$$
L(q, \dot{q}) = \frac{1}{2} m \dot{q}^2 - \frac{1}{2} k q^2 . \tag{1.36}
$$

The conjugate momentum is $p = \frac{\partial L}{\partial \dot{q}} = m\dot{q}$ so that the Hamiltonian $H = p\dot{q} - L$ reduces to :

$$
\begin{aligned}
H &= m\dot{q}^2 - \left(\frac{1}{2}m\dot{q}^2 - \frac{1}{2}kq^2\right), \\
&= \frac{1}{2}\frac{p^2}{m} + \frac{1}{2}kq^2 ,
\end{aligned}
\tag{1.37}
$$

and the equations of motion become:

$$
\dot{q} = \frac{\partial H}{\partial p} = \frac{p}{m} ,
\tag{1.38}
$$

$$
\dot{p} = -\frac{\partial H}{\partial q} = -kq .
\tag{1.39}
$$

After having substituted $\dot{p}$ ($= m\ddot{q}$) in the second equation, we can proceed to the integration of the second order differential equation and draw successively q and p as:

$$
q = q_0 \cos(\omega t + \varphi) ,
\tag{1.40}
$$

$$
p = m\dot{q} = -m\omega q_0 \sin(\omega t + \varphi) ,
\tag{1.41}
$$

where $\omega^2 = \frac{k}{m}$. Since the system is conservative, we can also calculate the total energy by equation (1.37):

$$
\begin{aligned}
E &= H = \frac{1}{2}\frac{p^2}{m} + \frac{1}{2}m\omega^2 q^2 \\
&= \frac{1}{2m}\left[-m\omega q_0 \sin(\omega t + \varphi)\right]^2 + \frac{1}{2}m\omega^2 \left[q_0 \cos(\omega t + \varphi)\right]^2 \\
&= \frac{1}{2}m\omega^2 q_0^2 .
\end{aligned}
\tag{1.42}
$$

It should be noted that the evolution of the system can be represented in the phase space in two dimensions by plotting p versus q. Assuming that the phase φ is zero at the initial moment, the expressions of q and p (Eqs. 1.40 and 1.41) reduce in terms of E (Eq. 1.42) as:

$$
q = \frac{1}{\omega}\sqrt{\frac{2E}{m}} \cos \omega t ,
\tag{1.43}
$$

$$
p = -\sqrt{2mE} \sin \omega t .
\tag{1.44}
$$

It is easy to verify that the trajectory in the phase space describes an ellipse moving clockwise.

1.2 Quantum mechanics

Introduction

Classical mechanics is used to determine the motion of a classical particle – or a set of particles – by solving the equations of motion, when the initial positions and initial velocities are known. However, during the 1920s it became apparent that it was impossible to determine precisely and simultaneously the position and velocity of quantum particles: this is known as the *Heisenberg uncertainty principle*. For these particles, the description of classical mechanics does not apply. In particular, the representative point of the dynamic state in the phase space, at a given moment, cannot be pinpointed. Other considerations apply that are the aim of quantum mechanics.

The fundamental concept of quantum mechanics resides in the *wave function* $\psi(\mathbf{q}, t)$, which is defined in terms of generalized coordinates $\mathbf{q} = (q_1, q_2, ..., q_{3N})$ and time t. Strangely, the wave function is a feature that does not refer to the movement of particles but to the probability of finding particles in a given region of space. Thus the elementary probability that the system is, at a given moment, in the region of space limited to $d\mathbf{q}$, bounded by q_1 and $q_1 + dq_1$, q_2 and $q_2 + dq_2$, ... q_{3N} and $q_{3N} + dq_{3N}$ is:

$$\psi^*(\mathbf{q}, t)\psi(\mathbf{q}, t)d\mathbf{q}, \tag{1.45}$$

where $\psi^*(\mathbf{q}, t)$ is the complex conjugate of $\psi(\mathbf{q}, t)$.

The *first postulate* of quantum mechanics states that the square modulus of the wave function $|\psi(\mathbf{q}, t)|^2 = \psi^*(\mathbf{q}, t)\psi(\mathbf{q}, t)$ represents a probability density function. According to mathematical statistics, this means that the wave function satisfies the normalization condition:

$$\int \psi^*(\mathbf{q}, t)\psi(\mathbf{q}, t)d\mathbf{q} = 1. \tag{1.46}$$

This relationship reflects the fact that the particle is found with certainty in the area considered, since the probability is equal to unity. The wave function is not an observable quantity and never enters the final result. It must be regarded only as a mathematical tool used in the calculation of dynamic quantities such as position, momentum, energy...

The *second postulate* of quantum mechanics stipulates that any dynamic quantity L is associated with a linear operator $\hat{L}$. When the dynamic quantity L is involved, the corresponding operator $\hat{L}$ has to be applied to the wave function $\psi(\mathbf{q}, t)$. However, if one is interested only in stationary states of the system (time-independent states), the only observable results of the physical property are the eigenvalues λ of $\hat{L}$ that satisfy the equation:

$$\hat{L}\psi(\mathbf{q}) = \lambda\psi(\mathbf{q}) \tag{1.47}$$

For example, the operator $\hat{x}$ associated with the position variable x is the function x itself. The action of this operator on the wave function $\psi(x)$ is the multiplication of this function by x:

$$\hat{x}\psi(x) = x\psi(x). \tag{1.48}$$

As regards the operator $\hat{p}_x$ associated with the momentum variable $p_x = mv_x$, it is defined by $\hat{p}_x = \frac{\hbar}{i}\frac{\partial}{\partial x}$, where $\hbar(= 1,054.10^{-34}$ J·s) is Planck's constant divided by 2π and i the imaginary number such as $i^2 = -1$. In a one-dimensional problem, the action of the momentum operator on the wave function $\psi(x)$ reduces to the integration of the differential equation:

$$\hat{p}_x\psi(x) = \frac{\hbar}{i}\frac{d\psi(x)}{dx} = p_x\psi(x), \tag{1.49}$$

where the solution is $\psi(x) = A\exp(i\frac{p_x}{\hbar}x)$, with A the integration constant and $\psi(x)$ the wave function associated with the eigenvalue p_x.

When the energy E of the system must be calculated, it is required to apply the associated operator $\hat{H}$ to the wave function $\psi(q)$, i.e.:

$$\hat{H}\psi(\mathbf{q}) = E\psi(\mathbf{q}). \tag{1.50}$$

This relation corresponds to the Schrödinger equation, independent of time, in which the Hamiltonian operator $\hat{H}$ of a particle is expressed as:

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + U(x, y, z), \tag{1.51}$$

where m is the mass of the particle and $\nabla^2 (= \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2})$ the Lapacian. The first term at the right hand side of the above equation

represents the kinetic energy operator and the second term the potential energy. Therefore, the knowledge of the Hamiltonian operator and boundary conditions of the system allows the determination of E and ψ.

Quantum particle in a rectangular box

By way of illustration and to clarify the concept of energy quantization, let us consider the problem of a quantum particle of mass μ in a rectangular box with sides a, b, c. If the particle is not subject to any external force, the potential energy is zero and the Schrödinger equation (Eq. 1.50) reduces to:

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi = E\psi. \tag{1.52}$$

Let us seek a solution for this partial differential equation in the form of a product with three functions, each of them depending on a single variable, namely:

$$\psi(x, y, z) = \psi_1(x)\psi_2(y)\psi_3(z). \tag{1.53}$$

By substituting the expression of the wave function in equation (1.52), we obtain:

$$-\frac{\hbar^2}{2\mu}\left[\psi_2(y)\psi_3(z)\frac{\partial^2\psi_1(x)}{\partial x^2} \quad + \quad \psi_1(x)\psi_3(z)\frac{\partial^2\psi_2(y)}{\partial y^2}\right.$$
$$\left. + \quad \psi_1(x)\psi_2(y)\frac{\partial^2\psi_3(z)}{\partial z^2}\right] \quad = \quad E\psi_1(x)\psi_2(y)\psi_3(z),$$

or

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{\psi_1(x)}\frac{\partial^2\psi_1(x)}{\partial x^2} + \frac{1}{\psi_2(y)}\frac{\partial^2\psi_2(y)}{\partial y^2} + \frac{1}{\psi_3(z)}\frac{\partial^2\psi_3(z)}{\partial z^2}\right] = E. \tag{1.54}$$

As the sum of the three terms in square brackets is constant, we can write down $E = E_1 + E_2 + E_3$ and change the Schrödinger equation into three independent equations:

$$\frac{\partial^2\psi_1(x)}{\partial x^2} = -\frac{2\mu E_1}{\hbar^2}\psi_1(x), \tag{1.55}$$

$$\frac{\partial^2\psi_2(y)}{\partial y^2} = -\frac{2\mu E_2}{\hbar^2}\psi_2(y), \tag{1.56}$$

$$\frac{\partial^2\psi_3(z)}{\partial z^2} = -\frac{2\mu E_3}{\hbar^2}\psi_3(z). \tag{1.57}$$

Solving these equations of the form $\ddot{X} = -k^2 X$ is immediate. The solutions are:

$$
\begin{aligned}
\psi_1(x) &= A \sin k_1 x + A' \cos k_1 x\,, & \text{(1.58)} \\
\psi_2(y) &= B \sin k_2 y + B' \cos k_2 y\,, & \text{(1.59)} \\
\psi_3(z) &= C \sin k_3 z + C' \cos k_3 z\,, & \text{(1.60)}
\end{aligned}
$$

where $k_1 = \sqrt{\frac{2\mu E_1}{\hbar^2}}$, $k_2 = \sqrt{\frac{2\mu E_2}{\hbar^2}}$ and $k_3 = \sqrt{\frac{2\mu E_3}{\hbar^2}}$. Now, to completely determine the solution of the problem, let us consider the boundary conditions imposed by the box walls which are:

$$
\begin{aligned}
\psi(0, y, z) &= \psi(a, y, z) = 0, & \text{(1.61)} \\
\psi(x, 0, z) &= \psi(x, b, z) = 0, & \text{(1.62)} \\
\psi(x, y, 0) &= \psi(x, y, c) = 0. & \text{(1.63)}
\end{aligned}
$$

The first of these boundary conditions requires that

$$
\psi(0, y, z) = \psi_1(0)\psi_2(y)\psi_3(z) = 0 \tag{1.64}
$$

in the x-direction, i.e. $A' = 0$ for all y and z. Likewise there is $B' = C' = 0$ in the directions y and z, Moreover, at $x = a$, the boundary condition reads:

$$
\begin{aligned}
\psi(a, y, z) &= \psi_1(a)\psi_2(y)\psi_3(z) = 0, \\
&= (A \sin k_1 a)(B \sin k_2 y)(C \sin k_3 z) = 0\,, \quad \text{(1.65)}
\end{aligned}
$$

that is to say $k_1 = \frac{l\pi}{a}$ irrespective of y and z. When repeating the calculation procedure in the directions y and z, we find the expressions of the parameters k_1, k_2 and k_3:

$$
\begin{aligned}
k_1 &= \sqrt{\frac{2\mu E_1}{\hbar^2}} = \frac{l\pi}{a}, & \text{(1.66)} \\
k_2 &= \sqrt{\frac{2\mu E_2}{\hbar^2}} = \frac{m\pi}{b}, & \text{(1.67)} \\
k_3 &= \sqrt{\frac{2\mu E_3}{\hbar^2}} = \frac{n\pi}{c}, & \text{(1.68)}
\end{aligned}
$$

where l, m and n are positive integers. Then, these values of k_1, k_2 and k_3 make it possible to calculate the energy $E = E_1 + E_2 + E_3$:

$$
E = \frac{\hbar^2}{2\mu}(k_1^2 + k_2^2 + k_3^2) = \frac{\hbar^2 \pi^2}{2\mu}\left(\frac{l^2}{a^2} + \frac{m^2}{b^2} + \frac{n^2}{c^2}\right), \tag{1.69}
$$

as well as the wave function (Eq. 1.53):

$$\psi(x, y, z) = ABC \left(\sin \frac{l\pi}{a} x\right)\left(\sin \frac{m\pi}{b} y\right)\left(\sin \frac{n\pi}{c} z\right). \qquad (1.70)$$

From then on all we have to do is determining the constant (ABC) by using the normalization condition for the wave function:

$$\iint \psi^*(x, y, z)\psi(x, y, z) dx dy dz = 1, \qquad (1.71)$$

or:

$$(ABC)^2 \int \sin^2\left(\frac{l\pi}{a} x\right) dx \times \int \sin^2\left(\frac{m\pi}{b} y\right) dy \times \int \sin^2\left(\frac{n\pi}{c} z\right) dz = 1. \qquad (1.72)$$

As the three integrals are respectively $\frac{a}{2}$, $\frac{b}{2}$ and $\frac{c}{2}$, the resulting expression for the wave function is:

$$\psi(x, y, z) = \sqrt{\frac{8}{abc}}\left(\sin \frac{l\pi}{a} x\right)\left(\sin \frac{m\pi}{b} y\right)\left(\sin \frac{n\pi}{c} z\right). \qquad (1.73)$$

Degeneracy and density of states

Considering the expression of energy of the particle (Eq. 1.69), we see that it can take a succession of discrete values corresponding to the integers l, m and n. Being characterized by the three *quantum numbers* l, m, n, the energy of the particle is thus quantized. It may be noted in passing that quantification is a consequence of the boundary conditions of the wave function on the box walls and that the energy decreases as the particle mass and the box sizes are increasing, for given quantum numbers.

The fact that many wave functions may possess the same energy is an important aspect of the energy quantization. Assuming that $a = b = c$, the wave function and energy become respectively:

$$\psi(x, y, z) = \sqrt{\frac{8}{a^3}}\left(\sin \frac{l\pi}{a} x\right)\left(\sin \frac{m\pi}{a} y\right)\left(\sin \frac{n\pi}{a} z\right), \quad (1.74)$$

$$E = \frac{\hbar^2 \pi^2}{2\mu a^2}(l^2 + m^2 + n^2). \qquad (1.75)$$

Therefore, for each triplet of values (l, m, n), the permutation of two of them keeps the energy unchanged while giving different wave functions. The energy states are then said to be *degenerate*. For instance, if $l = m = 3$ and $n = 4$, the energy is:

$$E = \frac{\hbar^2 \pi^2}{2\mu a^2} \left[(3)^2 + (3)^2 + (4)^2 \right] , \tag{1.76}$$

and does not vary by permutation of the integers l, m, n. Conversely, after permutation of the integers l, m and n, the wave function takes one of the three following forms:

$$\psi_{3,3,4} = \sqrt{\frac{8}{a^3}} \left(\sin \frac{3\pi}{a} x \right) \left(\sin \frac{3\pi}{a} y \right) \left(\sin \frac{4\pi}{a} z \right), \tag{1.77}$$

$$\psi_{3,4,3} = \sqrt{\frac{8}{a^3}} \left(\sin \frac{3\pi}{a} x \right) \left(\sin \frac{4\pi}{a} y \right) \left(\sin \frac{3\pi}{a} z \right), \tag{1.78}$$

$$\psi_{4,3,3} = \sqrt{\frac{8}{a^3}} \left(\sin \frac{4\pi}{a} x \right) \left(\sin \frac{3\pi}{a} y \right) \left(\sin \frac{3\pi}{a} z \right). \tag{1.79}$$

In this case, the energy is three-fold degenerate. It should be noted that, if the three quantum numbers are equal, there is only one wave function so that the energy is non degenerate.

When the values of integers l, m and n are very high, the intervals between the energy levels become so low that a continuous variation of energy can be admitted. The relative energy difference reduces indeed with equation (1.75) to:

$$\frac{E_{l,m,n+1} - E_{l,m,n}}{E_{l,m,n}} = \frac{\left[l^2 + m^2 + (n+1)^2 \right] - (l^2 + m^2 + n^2)}{l^2 + m^2 + n^2}$$

$$= \frac{2n + 1}{l^2 + m^2 + n^2} \ll 1. \tag{1.80}$$

As a result, the *density of states* defined as the number of states per interval of energy at each energy level is usually evaluated as follows. For this purpose, each energy state, $E_{l,m,n}$, is depicted by a point of coordinates

$$\sqrt{\frac{\hbar^2 \pi^2}{2\mu a^2}} \, l \,, \qquad \sqrt{\frac{\hbar^2 \pi^2}{2\mu a^2}} \, m \,, \qquad \sqrt{\frac{\hbar^2 \pi^2}{2\mu a^2}} \, n \,. \tag{1.81}$$
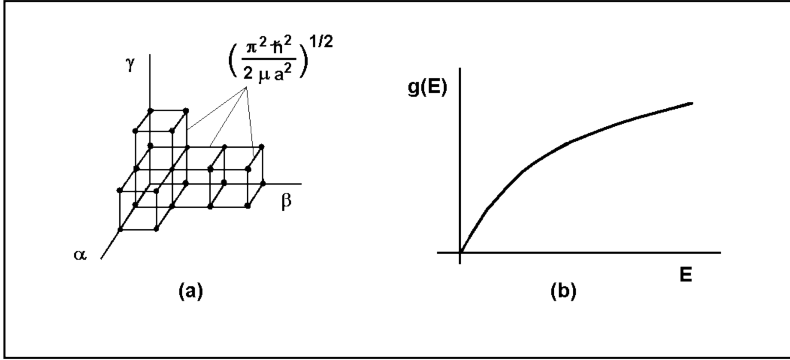
Figure 1.1: (a) Representative points of the energy states in the $\alpha\beta\gamma$ space. (b) Schematic representation of the variation of the density of states versus energy.

in the $(\alpha\beta\gamma)$ Cartesian coordinate system made of elementary cubes of side $\sqrt{\frac{\hbar^2\pi^2}{2\mu a^2}}$ and volume $\left(\frac{\hbar^2\pi^2}{2\mu a^2}\right)^{3/2}$ constituting a cubic lattice (Fig. 1.1).

As each elementary cube has 8 vertices and each vertex is shared by 8 cubes, the volume available for each point (state of energy) is the volume element $\left(\frac{\hbar^2\pi^2}{2\mu a^2}\right)^{3/2}$. It could be noted that the square of the distance ρ from a point of the network to the origin is:

$$\rho^2 = \frac{\hbar^2\pi^2}{2\mu a^2}\left[l^2+m^2+n^2\right] = E_{l,m,n}\,. \qquad (1.82)$$

The higher the values of l, m, n the higher the number of points located on a sphere of equal energy. Therefore the number of energy states in the volume of a spherical ring, between ρ and $\rho+d\rho$, can be obtained by dividing the volume of the spherical ring $4\pi\rho^2 d\rho$ by the volume attributed to each point. As the numbers l, m, n are positive integers, only 1/8 of the spherical ring has to be considered, so that the number of energy states dG in the spherical ring is reduced to

$$dG = \frac{1}{8}\frac{4\pi\rho^2 d\rho}{\left(\frac{\hbar^2\pi^2}{2\mu a^2}\right)^{\frac{3}{2}}} = \frac{\pi}{2}\left(\frac{2\mu a^2}{\hbar^2\pi^2}\right)^{\frac{3}{2}}\rho^2 d\rho\,. \qquad (1.83)$$

When it comes to calculating the density of states $g(E) = \frac{dG}{dE}$ as a function of energy, the variable ρ is substituted by the variable E by using equation (1.82) and by:

$$d\rho = \frac{1}{2E^{1/2}}dE . \tag{1.84}$$

Consequently, the density of states $g(E)$ is expressed as:

$$g(E) = \frac{dG}{dE} = \frac{a^3}{4\pi^2}\left(\frac{2\mu}{\hbar^2}\right)^{\frac{3}{2}}E^{1/2} . \tag{1.85}$$

The density of states is proportional to the square root of energy (Fig. 1.2c), that is to say to the square root of the sum of the squares of quantum numbers. Furthermore, it is an increasing function of the particle mass and box size and has the dimensions of inverse of energy. More importantly, it represents the number of wave functions per unit of energy between E and $E+dE$. For instance, let us calculate the density of states dG in the energy interval $E \pm \Delta E$ with $\Delta E = 0.01E$ for a classical particle (ion) of mass $\mu (= 2 \cdot 10^{-27}$ kg) in a cubic box of side $a = 10^{-2}$ m, at temperature $T = 300$ K. The energy $E \left(= \frac{3}{2}k_B T\right)$, where $k_B = 1.38 \cdot 10^{-23}$ J·K^{-1}, is $E \simeq 6 \cdot 10^{-21}$ J, and the number of energy states is:

$$
\begin{aligned}
dG &= \frac{a^3}{4\pi^2}\left(\frac{2\mu}{\hbar^2}\right)^{\frac{3}{2}}E^{\frac{1}{2}}dE \\
&= \frac{10^{-6}}{4\pi^2}\left[\frac{4 \cdot 10^{-27}}{(1.054 \cdot 10^{-34})^2}\right]^{\frac{3}{2}}(6 \cdot 10^{-21})^{\frac{1}{2}}\frac{6 \cdot 10^{-21}}{100} \simeq 2.5 \cdot 10^{22} . \tag{1.86}
\end{aligned}
$$

As a result, the degeneracy of a classical particle at room temperature is considerable. However, It should be stressed that the degeneracy i of a quantum particle is just slightly lower than that of a classical particle. It is indeed easy to check whether the number of energy states of an electron of mass $\mu = 0.911 \cdot 10^{-30}$ kg at the Fermi temperature of 50000 K and under the same conditions as those of the classical particle is a few hundred times lower. Moreover, if $N \simeq 10^{23}$ particles are considered in the cubic box in place of a unique particle, a calculation more complex than the previous one shows that the number of energy states is $dG \simeq 10^N$, i.e. considerably higher than it would be for a single particle.