

TEMPERATURE IN QUANTUM DYNAMICS

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ABSTRACT. What is the meaning of the thermodynamical temperature in quantum mechanics? What is its role in the classical limit? What can we say about the interplay between quantum and thermal fluctuations? Can we impose a constant-temperature constraint within dynamical simulations of quantum systems as we do in simulations of classical systems? These questions will be reviewed here. In particular, it will be shown how a quantum version of the celebrated Nosé constant-temperature dynamics can be defined within the phase space formulation of quantum mechanics.

1. Introduction

Since the advent of quantum mechanics, unitary time evolution has not been given a satisfactory physical interpretation. In order to interpret it correctly, one should explain why complex numbers are so intertwined with the most fundamental formulations of quantum mechanics [1]. On more practical terms, unitary evolution is a computational problem: It is based on the time propagation of oscillatory quantities, which are called phases. This requires an enormous amount of memory for many-body systems. Moreover, the quantum phase's oscillatory behaviour causes the numerical error to grow very fast with time (the infamous sign-problem of quantum dynamics). In practice, unless a more convenient reformulation of the physical problem of unitary evolution is provided in the future, calculations of quantum dynamics are doomed to be restricted to few-body systems and short time intervals (of course, such a statement does not take into account the possible existence of a quantum computer).

However, unitary evolution is strictly the characteristic of isolated systems (which are just an idealization in nature). Nowadays, it has become widely appreciated that many physical situations should be analyzed in terms of open system dynamics [2] and that both decoherence and dissipation are ubiquitous in open quantum systems. They milden the computational problem with unitary evolution. In the case of a Markovian dynamics, there are already stochastic algorithms which are sufficiently powerful for simulating the dynamics of realistic systems such as optical lattices [3] and Bose-Einstein condensates [4]. Non-Markovian quantum dynamics is a much more difficult problem and, to our knowledge, there is currently no general (or agreed upon) solution, as one could have expected from an analogy with the issues in classical nonequilibrium statistical mechanics [5, 6].

Conceptually, the prototype of an open quantum system is provided by a quantum subsystem in contact with a thermal bath. Can one extend the idea of a thermal bath to calculations of time-dependent properties in quantum mechanics? Is a thermal bath a classical concept only? And if it is a classical concept, how can we treat the consistent coupling of quantum and classical degrees of freedom? Such topics will be reviewed in this paper. Roughly speaking, they all revolve around the definition of a quantum temperature. Here I defend the idea that the temperature is an intrinsically classical concept, which can be defined for a quantum system in a rigorous way only when this is coupled to an external classical bath. When such a philosophy is adopted, it becomes straightforward to extend the method proposed by Nosé [7] for dynamical simulations at constant temperature from the classical to the quantum realm. As a result, open quantum systems, consisting of a quantum subsystem coupled to a classical bath, can be simulated by describing the dynamics of the relevant quantum variables and of a few additional classical degrees of freedom.

This contribution is organized as follows. Section 2 introduces in a very general fashion the problems associated with the meaning of temperature in the quantum realm. Basically, it raises some questions that will remain unanswered here. Nevertheless, such issues are partially the motivation behind the technical work reviewed here. Section 3 sketches the technique (the famous Nosé dynamics) used to implement constant-temperature thermodynamical constraints in classical molecular dynamics simulations [7]. In Section 4 the phase space formulation of quantum mechanics, originally developed by Wigner [8], is summarized. Section 5 reviews how the constant-temperature constraints have been recently introduced in quantum dynamics through the Wigner phase space formulation [9]. In Section 6 it is shown how quantum mechanics can be defined in a partial Wigner representation (Wigner-Heisenberg quantum mechanics). Again, it turns out that the algebraic structure of the theory can be generalized in a way that allows one to introduce the Nosé dynamics of the quantum degrees of freedom represented in phase space [10]. Some final comments and conclusions are given in Section 7.

2. Temperature and quantum fluctuations

As is well-known in classical thermostatics [11], temperature is rigorously defined at thermal equilibrium as a macroscopic intensive parameter:

$$T = \left(\frac{\partial U}{\partial S} \right)_X, \quad (1)$$

where U is the internal energy, S is the entropy, and X stands for all the quantities that are kept constant when performing the partial derivative. Temperature also appears as a parameter of the equilibrium distribution function. For example, in the canonical ensemble one has:

$$\rho_c = Z^{-1} \exp[-\beta H], \quad (2)$$

where H is the Hamiltonian of the system under study, Z is the partition function, and $\beta = 1/k_B T$ is the inverse of the product between the temperature and the Boltzmann constant, k_B . In classical mechanics, temperature can be *estimated* as an average of the

microscopic kinetic energy

$$\left\langle \sum_{i=1}^N \frac{p_i^2}{2m} \right\rangle = \frac{3}{2} N k_B T, \quad (3)$$

where p_i ($i = 1, \dots, N$) are the momenta of N particles of mass m in 3-dimensional space. Equation (3) is also the basis of the equipartition theorem in classical statistical mechanics. Conceptually, it states that the thermodynamical temperature is directly related to a microscopic quantity of the system, viz., the kinetic energy.

In quantum mechanics, temperature is still defined by Eq. (1). Moreover, the meaning associated with the symbols U and S is not modified when one considers quantum effects: Quantum mechanics changes the nature of the microscopic states that are accessible to the system but, once these are specified, the idea of a distribution of properties among such states is purely *classical*. Of course, new concepts arise from the possibility for the system of being in a coherent superposition of states, but we surmise here that they do not involve the temperature. In quantum statistical mechanics, the distribution function must be generalized as a matrix operator, i.e., the density matrix of the system. The temperature appears as a parameter of the density matrix. For example, in the canonical ensemble one has:

$$\hat{\rho}_c = Z^{-1} \exp \left[-\beta \hat{H} \right], \quad (4)$$

where $\hat{H}$ is now a Hamiltonian *operator* while the other symbols keep their meaning (although the partition function is calculated differently with respect to the classical case). The introduction of the density matrix brings with it a host of issues that are worth considering. What is more relevant to the present discussion is that in quantum mechanics the temperature can be estimated as an average of the microscopic kinetic energy *for free particles only*: Equipartition does not hold in general. In a certain sense this means that, once quantum effects become relevant, a microscopic picture of thermal fluctuations is somewhat lost.

The lack of a microscopic interpretation of quantum motion is by all means not restricted to thermal fluctuations. In general, microscopic pictures of quantum phenomena are ambiguous (i.e., they depend on the particular formalism adopted) and they were banned altogether from quantum science by Niels Bohr. Of course, they were reinstated by the intuitive genius of Richard Feynman through his space-time approach and, perhaps, they have always been used in an unspeakable way by many quantum physicists. Probably, the basic source of the problems with microscopic interpretations is that quantum mechanics is intrinsically a statistical theory and the knowledge of the quantum state of the system gives access to average quantities only: Once these are fixed, there is a large freedom in devising various microscopic mechanisms providing the same average properties. Although many agree that the quantum state describes some kind of microscopic motion (or fluctuation), the theory provides only the knowledge of the dynamics of the state: Microscopic dynamical variables are not really addressed by the various formulations of quantum mechanics (perhaps, with the exception of the De Broglie-Bohm theory [12]) and, when they are, it is only as a means to calculate changes in time of average properties. For example, a quantum state in the position representation (usually called wave function) $\psi(x)$ allows

one to calculate the average properties of Hermitian operators $\hat{A}$:

$$\langle \hat{A} \rangle \equiv \int dx \psi^*(x) A(x, x') \psi(x'), \quad (5)$$

where $A(x, x')$ is the position representation of the operator associated with a certain microscopic dynamical quantity. If x represents the coordinate of an objective being (for example, a particle), Eq. (5) expresses the fact that x can vary over the domain of integration. This can be interpreted as a fluctuation of x over the same domain. The quantum state $\psi(x)$ weighs each value of x in a statistical sense and also associates a phase with it (describing the oscillatory motion of the being considered): The phase of the wavefunction represents the oscillatory and coherent nature of the microscopic quantum motion. However, we do not have a clear picture of such microscopic dynamics. As already discussed, the theory of quantum mechanics only provides a recipe for calculating average properties through Eq. (5). The principle of superposition tells that if various quantum states, $\psi_1, \psi_2, \dots, \psi_n$, are accessible to the system, then the total (coherent) state can be taken to be $\psi = \sum_{j=1}^n c_j \psi_j$, where the c_j are complex numerical coefficients in general. This expresses the possibility of a quantum *disorder* (determined by the multiplicity of states accessible) which, rigorously, takes place at $T = 0$. One can introduce a density matrix at $T = 0$ which can be expressed as

$$\rho(x, x') = \sum_{j=1}^n \sum_{k=1}^n c_j c_k^* \psi_j(x) \psi_k^*(x'). \quad (6)$$

Equation (6) expresses the possibility of a coherent (or oscillatory) motion of the system. Since such a motion is described in an average sense only, it is called a quantum fluctuation.

When the temperature is different from zero, another form of disorder appears. Many states, ψ_α , with $\alpha = 1, \dots, n_T$, (providing the same average properties) become accessible to the system. However, such states are to be combined in a partially coherent way: A probability γ_α , such that $\sum_{\alpha=1}^{n_T} \gamma_\alpha = 1$, is associated to each state and a thermal density matrix is introduced:

$$\rho_T(x, x') = \sum_{\alpha=1}^n \gamma_\alpha \psi_\alpha(x) \psi_\alpha^*(x'). \quad (7)$$

Each state ψ_α is coherent but the non-zero temperature leads to the definition of the density matrix following Eq. (7) instead of Eq. (6). Hence, some degree of incoherence is the signature of a non-zero temperature. However, things are not so easy since incoherent and coherent fluctuations are mixed together by Eq. (7) and cannot be disentangled easily. This means that, as far as static average properties are concerned, the distinction between thermal (incoherent) fluctuations and quantum (coherent) fluctuations is somewhat arbitrary. In other words, thermal fluctuations might be considered as coherent fluctuations that have been mixed-up in the formalism so that one is no longer able to recover their dynamical connection, relating the fluctuation at a given instant of time to that at a neighbouring instant. Such a loss of temporal ordering of the representation hinders (but not completely, unless $T \rightarrow \infty$) the coherence itself. However, as it will be discussed in the following, quantum fluctuations are not entirely equal to classical thermal ones.

The classical limit is a very subtle topic in quantum mechanics [13], which is not fully understood yet. In particular, Michael Berry, among others, has often written that the quantum to classical limit ($\hbar \rightarrow 0$) is singular [14]. Hence, it is surprising that the quantum to classical transition can be achieved smoothly by varying the thermodynamical temperature of a system. As a matter of fact, at $T = 0$ ($\beta \rightarrow \infty$) any condensed matter system must show quantum effects in order to accommodate a non-singular entropy S and its derivatives: This is the content of the third principle of thermodynamics [11]. Yet, for $\beta = 0$ ($T \rightarrow \infty$) any system becomes completely classical and all its coherent properties disappear completely. This can be easily appreciated upon looking at the definition of the De Broglie thermal wavelength

$$\lambda = \frac{h}{\sqrt{2\pi m k_B T}} = \sqrt{\frac{h^2 \beta}{2\pi m}}, \quad (8)$$

and verifying its behaviour as $T \rightarrow \infty$: λ (which also gives a measure of quantum delocalization, or space fluctuation, of extended objects) goes to zero when T goes to infinity. From such a perspective, one can conclude that there is no definite boundary between the classical and the quantum world: It is possible to move from one to the other just by changing a macroscopic parameter such the thermodynamic temperature.

Perhaps, the clearest connection between thermal and quantum fluctuation is provided by the path integral approach to quantum statistical mechanics [15]. In this approach the partition function, $Z = \exp[-\beta \hat{H}]$, of a system with a potential energy $V(r)$ and kinetic energy $\hat{p}^2/2m$ can be written as

$$\begin{aligned} \text{Tr} \exp \left[-\beta \left(\frac{\hat{p}^2}{2m} + \hat{V}(r) \right) \right] &= \lim_{P \rightarrow \infty} \left(\frac{mP}{2\pi\beta\hbar^2} \right) \int dr_1 \dots dr_P \\ &\times \exp \left\{ -\beta \sum_{\alpha=1}^P \left[\frac{mP}{2\beta^2\hbar^2} (r_\alpha - r_{\alpha+1})^2 + \frac{V(r_\alpha)}{P} \right] \right\}, \end{aligned} \quad (9)$$

where P is the number of discrete replica of the system configuration, labeled collectively with the coordinate r . The equality in Eq. (9) is strictly valid only for $P \rightarrow \infty$. For any finite P , the path integral expression is just an approximation. However, such an approximation is the basis for developing a very powerful approach to the numerical simulation of time-independent properties of interacting bosonic systems, such as superfluid helium [16]. At the root of path-integral numerical methods one finds the so-called quantum-classical isomorphism [17] entailed by Eq. (9):

$$\begin{array}{ccc} D - \text{dimensional Quantum} & \rightleftharpoons & (D+1) - \text{dimensional Classical} \\ \text{Statistical Mechanics} & & \text{Statistical Mechanics} \end{array} \quad (10)$$

It is easy to realize how this latter statement stems from Eq. (9): As far as time-independent statistical properties are concerned, a single quantum particle, for example, is mapped onto a closed polymer-like ring of particles (called beads or replicas). As a result of this mapping, the statistical mechanics of the quantum particle is isomorphic to the statistical mechanics of the classical-like polymer. When $T \rightarrow \infty$, the harmonic term (arising from the quantum kinetic energy of the single particle) will be so big that all the polymer beads will collapse onto a single point and the system will appear classical. The fact that at finite

T the quantum-classical isomorphism is approximate can be understood by considering not just one single particle but at least two interacting quantum particles. According to Eq. (9) their quantum partition function will be *analogous* to the partition function of two interacting ring polymers. But the word *analogous* must be conveniently emphasized. In fact, the two ring polymers do not interact in a classical way, but each bead on a polymer interacts, through $V(r)$ only, with the homologous bead – identified by the index arising from the discretization of β – on the other polymer. The gyration radius of each isomorphic polymer is related to the De Broglie wave-length of the particle and, as such, it “measures” the quantum delocalization of each particle in space (and time). What is the meaning of all this? In order to get an idea of what is happening in the theory, one should note that upon performing the transformation (an inverse Wick rotation):

$$\beta \rightarrow -\frac{it}{\hbar}, \quad (11)$$

the quantum partition function in Eq. (9) becomes identical to the trace of the real time amplitude. Hence, the discretization of β is analogous to the discretization of real time. Then the path-integral formula (9) expresses the a-causal nature of quantum mechanics: The real time propagator is obtained by summing over all paths of the particle where, because of the quantum kinetic energy, each time configuration r_α at time t_α interacts with the *past* configuration $r_{\alpha-1}$ at time $t_{\alpha-1}$ as well as with the *future* configuration $r_{\alpha+1}$ at time $t_{\alpha+1}$. Quantum coherence and fluctuations are then linked to the time-symmetric nature of the quantum theory [18]. Since β is analogous to a complex time, everything goes as if the precise ordering (and, hence, the coherence) between the different configurations r_α on different polymers (or paths) has been lost so that the a-causal features becomes hidden: It is well known that motion in complex time projects onto the ground state so that the effect of coherent superpositions with excited states is minimized [19]. Hence, one can summarize by saying, in a loose sense, that the thermal fluctuations occurring in a D -dimensional quantum system are analogous, in complex time, to the thermal fluctuations in a $D + 1$ dimensional classical system. Perhaps, a more fundamental connection between quantum and thermal fluctuations is provided by the Unruh effect [20]. It turns out that the inertial (Minkowski) quantum vacuum is equivalent to a thermal bath of particles when seen from an observer who constantly accelerates with respect to it. Such a bath does not display the typical energy spectrum of free particles but it has excitation quanta known as Rindler particles. Its temperature is related to the acceleration of the non-inertial observer. The Unruh effect clearly shows that the particle’s existence is not covariant but depends on the state of motion of the observer. This supports the idea that the fields, not the particles, must be considered as the fundamental entities in physics. The Unruh effect also establishes an equivalence between ground state (vacuum) quantum fluctuations and the thermal disorder of a free field with a slightly distorted energy spectrum.

It is the author’s opinion that the topics reviewed in this section are not fully understood yet. They all impinge on the role of the temperature in the quantum theory. In the next section, we shall review a more technical approach to treat the more specialized problem of describing quantum fluctuations at constant temperature in time-dependent situations.

3. Thermal fluctuations in classical Molecular Dynamics

In order to generate thermal fluctuations within a classical Hamiltonian theory, one needs to couple the system of interest with a thermal bath, i.e., a macroscopic system with an infinite number of degrees of freedom. In other words, one has to resort to open-system dynamics. Under somewhat drastic approximations, such as the Markovian assumption, the degrees of freedom of the bath can be integrated out (projected) and one thus obtains the master equations or the generalized Langevin equations for the relevant degrees of freedom [5, 6].

Within Molecular Dynamics simulation, one can represent thermal fluctuations by means of a non-Hamiltonian theory [21] and just two additional degrees of freedom (or a few more). This is achieved with the celebrated Nosé dynamics [7]. A modern way of sketching the classical Nosé dynamics is provided by the introduction of the so-called Nosé Hamiltonian:

$$\begin{aligned} H^N &= \frac{p^2}{2m} + V(r) + \frac{p_\eta^2}{2m_\eta} + gk_B T \eta \\ &= H + \frac{p_\eta^2}{2m_\eta} + gk_B T \eta, \end{aligned} \quad (12)$$

where k_B is the Boltzmann constant, T is the thermodynamical temperature of the desired canonical ensemble, (r, p) are the phase space coordinates (positions and momenta, respectively) of the physical particles with mass m , (η, p_η) are the two additional Nosé degrees of freedom with inertial “mass” m_η , and g is the number of the physical degrees of freedom in configuration space. The equations of motion can be introduced upon defining the extended phase space point as $x = (r, \eta, p, p_\eta)$ and the antisymmetric matrix [22]

$$\mathcal{B}^N = \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & -p \\ 0 & -1 & p & 0 \end{bmatrix} \quad (13)$$

as

$$\dot{x}_i = \sum_{j,k} \frac{\partial x_i}{\partial x_k} \mathcal{B}_{kj}^N \frac{\partial H_W^N}{\partial x_j} = \{x_i, H_W\}_{\mathcal{B}^N}, \quad (14)$$

where the second equality on the right and side defines the non-Hamiltonian Nosé bracket. When written explicitly, the Nosé equations read:

$$\begin{aligned} \dot{r} &= \frac{p}{m} \\ \dot{p} &= -\nabla V - p \frac{p_\eta}{m_\eta} \\ \dot{\eta} &= \frac{p_\eta}{m_\eta} \\ \dot{p}_\eta &= \frac{p_\eta^2}{m} - 3Nk_B T. \end{aligned} \quad (15)$$

They admit the phase space compressibility κ^N

$$\kappa^N = \sum_i \frac{\partial \dot{x}_i}{\partial x_i} = -3N \frac{p_\eta}{m_\eta} = \beta \frac{d}{dt} H_T, \quad (16)$$

where

$$H_T = \frac{p^2}{2m} + V(r) + \frac{p_\eta^2}{2m_\eta} \quad (17)$$

and we assumed $g = 3N$.

The classical equilibrium statistical mechanics entailed by Nosé dynamics can be addressed by considering the stationary Liouville equation for the distribution function in the extended phase space f_e^N [23]. Such a function obeys the equation

$$\left[\kappa^N + \sum_{i,j} \mathcal{B}_{ij} \frac{\partial H^N}{\partial x_j} \frac{\vec{\partial}}{\partial x_i} \right] f_e^N = 0, \quad (18)$$

and it is written explicitly as

$$f_e^N \propto \exp[-\beta H_T] \delta(E - H^N). \quad (19)$$

Hence, thermal averages in the extended Nosé phase space of physical variables *alone* are written as

$$\begin{aligned} \langle a(r, p) \rangle_N &\propto \int dr dp d\eta dp_\eta a(r, p) f_e^N \\ &= \int dr dp d\eta dp_\eta a(r, p) \exp[-\beta H_T] \delta(E - H^N). \end{aligned} \quad (20)$$

Upon considering the integral $\int d\eta \delta(E - H^N)$ and the identity

$$\delta(\phi(\eta)) = \sum_{\eta_0} \delta(\eta - \eta_0) \left[\frac{d\phi}{d\eta}(\eta_0) \right]^{-1}, \quad (21)$$

which is valid for any differentiable function $\phi = \phi(\eta)$, one obtains

$$\langle a(r, p) \rangle_N = \mathcal{N} \int dr dp a(r, p) \exp[-\beta H] = \langle a(r, p) \rangle_{\text{can}}. \quad (22)$$

Equation (22) shows that one can calculate, by means of the Nosé dynamics, classical averages in the canonical ensemble. In practice, the dynamics must be ergodic. We know that this condition is not fulfilled for stiff harmonic systems. However, for all practical purposes, it seems that Nosé-Hoover chains give a satisfactory solution to the ergodicity problem [24], a chain being a sequence of Nosé variables thermostating each other in order to drive the fluctuation of the one directly coupled to the relevant degrees of freedom.

4. Wigner's quantum statistical mechanics

In the standard formulation of quantum statistical mechanics, dynamical variables are represented by operators on functional spaces (for example, $\hat{H}$, $\hat{L}$, ...), and statistical properties are addressed by the density matrix operator [13]:

$$\hat{\rho} = \sum_k \gamma_k |\Psi^{(k)}\rangle \langle \Psi^{(k)}|, \quad (23)$$

obeying the Heisenberg equation of motion which, when written in matrix form [10], reads

$$i\hbar \frac{\partial \hat{\rho}}{\partial t} = [\hat{H}, \hat{\rho}] = \begin{bmatrix} \hat{H} & \hat{\rho} \end{bmatrix} \cdot \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix} \cdot \begin{bmatrix} \hat{H} \\ \hat{\rho} \end{bmatrix}. \quad (24)$$

Quantum averages are then calculated as

$$\langle \hat{A} \rangle_{(t)} = \text{Tr} \left(\hat{\rho}(t) \hat{A} \right). \quad (25)$$

Almost surprisingly, quantum effects do not require one to renounce to phase space and ordinary functions as the main mathematical objects of the theory. On the contrary, operator quantum mechanics can be exactly represented in phase space, by using ordinary functions, in an infinite number of ways [25]. The first and, perhaps, the simplest mapping of this sort was provided by Wigner [8] who introduced the function [26, 27]:

$$\begin{aligned} f_W(r, p) &\equiv \frac{1}{(2\pi\hbar)^N} \int d^N r' e^{(i/\hbar)p \cdot r'} \hat{\rho} \left(r - \frac{r'}{2}, r + \frac{r'}{2} \right) \\ &= \frac{1}{(2\pi\hbar)^N} \mathcal{W} \{ \hat{\rho} \}. \end{aligned} \quad (26)$$

Operators can also be Wigner-transformed in order to obtain their phase space representation:

$$\chi_W(r, p) \equiv \int d^N r' e^{(i/\hbar)p \cdot r'} \hat{\chi} \left(r - \frac{r'}{2}, r + \frac{r'}{2} \right) = \mathcal{W} \{ \hat{\chi} \}. \quad (27)$$

In such a way, the so-called Wigner's formulation of quantum mechanics is obtained. Quantum averages can then be calculated in phase space as

$$\text{Tr} (\hat{\rho}(t) \hat{\chi}) \equiv \int d^N r d^N p f_W(r, p, t) \chi_W(r, p). \quad (28)$$

The equation governing the time evolution of the Wigner function can be obtained by considering Wigner's transform of the product of operators [28]

$$\mathcal{W} \{ \hat{\chi}_1 \times \hat{\chi}_2 \} = \hat{\chi}_1 \exp \left[\frac{i\hbar}{2} \overleftarrow{\partial}_i \mathcal{B}_{ij}^c \overrightarrow{\partial}_j \right] \hat{\chi}_2. \quad (29)$$

With the above result, the Moyal bracket is introduced upon taking the Wigner transform of the quantum commutator

$$\begin{aligned} \{ \chi_{1,W}(r, p), \chi_{2,W}(r, p) \}_M &\equiv \mathcal{W} \{ [\hat{\chi}_1, \hat{\chi}_2] \} = \mathcal{W} \{ \hat{\chi}_1 \hat{\chi}_2 - \hat{\chi}_2 \hat{\chi}_1 \} \\ &= \hat{\chi}_1 \exp \left[\frac{i\hbar}{2} \overleftarrow{\partial}_i \mathcal{B}_{ij}^c \overrightarrow{\partial}_j \right] \hat{\chi}_2 - \hat{\chi}_2 \exp \left[\frac{i\hbar}{2} \overleftarrow{\partial}_i \mathcal{B}_{ij}^c \overrightarrow{\partial}_j \right] \hat{\chi}_1. \end{aligned} \quad (30)$$

Hence, the Wigner-Moyal equation of motion is obtained upon Wigner-transforming the Heisenberg equation of motion for the density matrix

$$\begin{aligned} \partial_t f_W(r, p, t) &= -\frac{i}{\hbar} \{ H_W, f_W(t) \}_M \\ &= -\frac{i}{\hbar} \overrightarrow{\mathcal{M}} f_W(t). \end{aligned} \quad (31)$$

Moyal bracket enters the definition of quantum averages according to

$$\begin{aligned}\langle \hat{\chi} \rangle &= \int dx \chi_W(x) \exp \left[-\frac{it}{\hbar} \vec{\mathcal{M}} \right] f_W(x) \\ &= \int dx \chi_W(x) \exp \left[\frac{it}{\hbar} \overleftarrow{\mathcal{M}} \right] f_W(x),\end{aligned}\quad (32)$$

where Moyal's propagator has been defined as

$$\vec{\mathcal{M}} \equiv H_W \left(e^{\frac{i\hbar}{2} \overleftarrow{\partial}_i \mathcal{B}_{ij}^c \overrightarrow{\partial}_j} - e^{-\frac{i\hbar}{2} \overleftarrow{\partial}_i \mathcal{B}_{ij}^c \overrightarrow{\partial}_j} \right). \quad (33)$$

The two lines in Eq. (32) define the Schrödinger and Heisenberg dynamical picture in phase space, respectively, depending on whether the Wigner function or the dynamical variable evolves in time. Equation (31) can be equivalently rewritten as

$$\partial_t f_W = (\partial_i H_W) \mathcal{B}_{ij}^c \overrightarrow{\partial}_j f_W + \sum_{n=3,5,7,\dots} \frac{1}{n!} \left(\frac{i\hbar}{2} \right)^{n-1} H_W \left(\overleftarrow{\partial}_i \mathcal{B}_{ij}^c \overrightarrow{\partial}_j \right)^n f_W, \quad (34)$$

in which case it is known as the Wigner-Liouville equation. Wigner originally showed that Eq. (34) can be used to calculate quantum corrections to thermodynamical equilibrium [8].

5. Nosé dynamics in quantum phase space

The antisymmetric matrix structure of Eq. (30) can be exploited in order to generalize the Moyal bracket. In particular, upon defining the special antisymmetric tensor field in quantum phase space

$$\mathcal{B}_{ij} = \mathcal{B}_{ij}[f_W(x); \xi_n(x), t], \quad (35)$$

a generalized Moyal bracket can be introduced as

$$\{H_W, f_W\}_{\mathcal{M}, \mathcal{B}} = H_W e^{\frac{i\hbar}{2} \overleftarrow{\partial}_i \mathcal{B}_{ij} \overrightarrow{\partial}_j} f_W - f_W e^{\frac{i\hbar}{2} \overleftarrow{\partial}_i \mathcal{B}_{ij} \overrightarrow{\partial}_j} H_W. \quad (36)$$

The antisymmetric tensor field can be postulated in order to define a special dynamics in quantum phase space: Non-linear effects, non-equilibrium evolution, a deterministic approach to open-system dynamics and other possibilities yet to be explored. $\mathcal{B}_{ij}$ was used in Ref. [9] to introduce thermal fluctuations in the quantum evolution. This will be reviewed here.

A Nosé-Moyal operator can be defined adopting the antisymmetric matrix given in Eq. (13) and extending Wigner's phase space upon including two additional degrees of freedom (the Nosé coordinates):

$$\vec{\mathcal{M}}^N \equiv H_W^N \left(e^{\frac{i\hbar}{2} \overleftarrow{\partial}_i \mathcal{B}_{ij}^N \overrightarrow{\partial}_j} - e^{-\frac{i\hbar}{2} \overleftarrow{\partial}_i \mathcal{B}_{ij}^N \overrightarrow{\partial}_j} \right). \quad (37)$$

The dynamical variables can be propagated in time as

$$\chi_{NW}(t) = \exp \left[\frac{it}{\hbar} \vec{\mathcal{M}}^N \right] \chi_{NW}(0). \quad (38)$$

At variance with the standard Wigner case, one obtains an adjoint Moyal operator

$$\vec{\mathcal{M}}^{N,\dagger} \equiv H_W^N \left\{ e^{\frac{i\hbar}{2} \left(\overleftarrow{\partial}_i \mathcal{B}_{ij}^N \overrightarrow{\partial}_j + \overleftarrow{\partial}_i (\partial_j \mathcal{B}_{ij}^N) \right)} - e^{-\frac{i\hbar}{2} \left(\overleftarrow{\partial}_i \mathcal{B}_{ij}^N \overrightarrow{\partial}_j + \overleftarrow{\partial}_i (\partial_j \mathcal{B}_{ij}^N) \right)} \right\}. \quad (39)$$

The adjoint dynamics for the Nosé-Wigner function will be defined by

$$f_{NW}(t) = \exp \left[-\frac{it}{\hbar} \overrightarrow{\mathcal{M}}^{N,\dagger} \right] f_{NW}(0) . \quad (40)$$

The stationary Nosé-Wigner function, $f_{NW,e}$, is the solution of the following equation:

$$-(iL^N + \kappa^N) f_{NW,e} = \sum_{n=3,5,7,\dots} \frac{1}{n!} \left(\frac{i\hbar}{2} \right)^{n-1} H_W^N \left[\overleftarrow{\partial}_i \mathcal{B}_{ij}^N \overrightarrow{\partial}_j + \overleftarrow{\partial}_i (\partial_j \mathcal{B}_{ij}^N) \right]^n f_{NW,e} , \quad (41)$$

where

$$iL^N = \mathcal{B}_{ij}^N (\partial_j H_W^N) \overrightarrow{\partial}_i \quad (42)$$

is the Nosé-Liouville operator. As Wigner originally showed, a solution of Eq. (41) can be found as a power series in $\hbar$:

$$\begin{aligned} f_{NW,e} &= \sum_{n=0,2,4,\dots} \hbar^n f_{NW,e}^{(n)} \\ &= f_{NW,e}^{(0)} \left[1 + \sum_{n=2,4,\dots} \hbar^n \tilde{f}_{NW,e}^{(n)} \right] . \end{aligned} \quad (43)$$

The zero order solution is simply the classical Nosé distribution function in the extended phase space:

$$f_{NW,e}^{(0)} \propto \delta(H_W^N) \exp \left[-\int \kappa^N dt \right] . \quad (44)$$

5.1. Quantum-classical approximation. The variables η and p_η are fictitious and have the unique function of simulating the thermal bath. Accordingly, one can disregard quantum effects in their time evolution. This amounts to take a quantum-classical limit of the equations of motion for the Nosé-Wigner dynamics. The formalism admits the small expansion parameter $\sqrt{m/m_\eta} \ll 1$; hence, one can adopt the route to the quantum-classical limit proposed in Ref. [29]. In the following we shall also consider that one is actually interested in the averages of functions of the physical phase space $a(r, p)$, so that, when averaging over p_η , linear terms in p_η in the stationary equation disappear, because of the form of the zero-order solution of the stationary equation. In the quantum-classical limit Eq. (41) becomes:

$$\sum_{n=3,5,7,\dots} \frac{1}{n!} \left(\frac{i\hbar}{2} \right)^{n-1} V(r) \left[\overleftarrow{\partial}_r \cdot \overrightarrow{\partial}_p \right]^n f_{NW,e} = -(iL_N - \kappa^N) f_{NW,e} . \quad (45)$$

Solutions of Eq. (45) provide the stationary quantum-classical Nosé-Wigner function. The solution of the above equation is identical to that given by Wigner for the canonical ensemble. For example, the second order correction term is

$$f_{NW,e}^{(2)}(r, p) = f_{NW,e}^{(0)}(r, p) \left[-\frac{\hbar^2}{24} \frac{\partial^2 V(r)}{\partial r^2} \left[3 \frac{\beta^2}{m} + \beta^3 \frac{p^2}{m^2} \right] - \frac{\hbar^2}{24} \frac{\beta^3}{m} \left(\frac{\partial V(r)}{\partial r} \right)^2 \right] . \quad (46)$$

Within a quantum-classical Nosé-Wigner dynamics, the coupling of the system to a thermal bath is simulated in a deterministic way by means of the Nosé variables (η, p_η) . No additional complexity is added by using Nosé-Hoover chains [24] and, with suitable adjustments, the theory can also describe this more general case. In principle, the Nosé-Wigner dynamics provides an alternative approach to open quantum system evolution that is usually addressed by means of master equations. Moreover, by analogy with classical Molecular Dynamics calculations, the quantum Nosé-Wigner dynamics can be likely used to describe quantum open systems in nonmarkovian as well as nonequilibrium situations.

To summarize what we have said before, the quantum Nosé-Wigner dynamics has been defined upon starting from the Wigner's formulation of quantum mechanics after generalizing the Moyal bracket in a suitable way. A quantum-classical approximation has been taken in order to obtain an expression of the stationary Nosé-Wigner function. In this picture the classical thermostat is directly coupled to the quantum subsystem in phase space. Can this formalism be applied to the case of quantum spins? In the next section, we shall review the changes that are needed for dealing with quantum spins.

6. Nosé dynamics in the Wigner-Heisenberg representation

When one desires to study the coupling of quantum spins to a classical thermal bath, it is convenient to take an alternative route. One can start from the Heisenberg formulation of quantum mechanics and perform a partial Wigner transformation over the degrees of freedom of the bath [29]. This way, the so-called Wigner-Heisenberg representation of quantum mechanics is obtained [30]. For harmonic baths, a linear approximation of the Wigner-Heisenberg bracket is exact. One can then generalize the Wigner-Heisenberg bracket, upon exploiting its matrix structure, and introduce the quantum Nosé dynamics [10, 31]. In this case, the thermostat can be coupled to the quantum subsystem through buffer classical degrees of freedom. This formalism is sketched in the following.

Partial Wigner transforms of the density matrix

$$\hat{\rho}_W(R, P) = \frac{1}{(2\pi\hbar)^{3N}} \int dz e^{iP \cdot z/\hbar} \langle R - \frac{z}{2} | \hat{\rho} | R + \frac{z}{2} \rangle, \quad (47)$$

and of an arbitrary operator $\hat{\chi}$

$$\hat{\chi}_W(R, P) = \int dz e^{iP \cdot z/\hbar} \langle R - \frac{z}{2} | \hat{\chi} | R + \frac{z}{2} \rangle \quad (48)$$

can be defined as in Eqs. (47) and (48). Using the above definitions, one can take the partial Wigner transform of the Von Neumann equation (24). This gives rise to the Wigner-Heisenberg form of the equation of motion

$$\begin{aligned} \frac{\partial \hat{\rho}_W(R, P)}{\partial t} = & -\frac{i}{\hbar} \left\{ \hat{H}_W \exp \left[\frac{i\hbar}{2} \overleftarrow{\partial}_i \mathcal{B}_{ij}^c \overrightarrow{\partial}_j \right] \hat{\rho}_W(R, P) \right. \\ & \left. - \hat{\rho}_W(R, P) \exp \left[\frac{i\hbar}{2} \overleftarrow{\partial}_i \mathcal{B}_{ij}^c \overrightarrow{\partial}_j \right] \hat{H}_W \right\}. \end{aligned} \quad (49)$$

A linear approximation of such an equation, i.e.:

$$\begin{aligned} \frac{\partial \hat{\rho}_W(R, P)}{\partial t} = & -\frac{i}{\hbar} \left\{ \hat{H}_W \left[1 + \frac{i\hbar}{2} \overleftarrow{\partial}_i \mathcal{B}_{ij}^c \overrightarrow{\partial}_j \right] \hat{\rho}_W(R, P) \right. \\ & \left. - \hat{\rho}_W(R, P) \left[1 + \frac{i\hbar}{2} \overleftarrow{\partial}_i \mathcal{B}_{ij}^c \overrightarrow{\partial}_j \right] \hat{H}_W \right\}, \end{aligned} \quad (50)$$

turns out to be exact for harmonic baths.

The structure of Eqs. (49) and (50) is suited to accommodate the Nosé Wigner-Heisenberg dynamics [10, 31]. To this end, one needs to introduce a Nosé Wigner-Heisenberg Hamiltonian:

$$\hat{H}_W^N = \hat{H}_s + \hat{H}_b(R, P) + \hat{H}_c(R) + \frac{p_\eta^2}{2m_\eta} + Nk_B T \eta, \quad (51)$$

where the sum $\hat{H}_s + \hat{H}_b(R, P) + \hat{H}_c(R)$ describes the partially Wigner-transformed Hamiltonian of the physical system, while the remaining terms describe the energy of the Nosé variables. The dynamics of the Wigner-Heisenberg operators can be defined by means of the generalized bracket:

$$\dot{\chi} = \begin{bmatrix} \hat{H}_W^N & \hat{\chi} \end{bmatrix} \begin{bmatrix} 0 & e^{\frac{i\hbar}{2} \overleftarrow{\partial}_k \mathcal{B}_{km}^N \overrightarrow{\partial}_m} \\ -e^{\frac{i\hbar}{2} \overleftarrow{\partial}_k \mathcal{B}_{km}^N \overrightarrow{\partial}_m} & 0 \end{bmatrix} \cdot \begin{bmatrix} \hat{H}_W^N \\ \hat{\chi} \end{bmatrix}, \quad (52)$$

where the antisymmetric tensor field $\mathcal{B}^N$ has been defined in Eq. (13). Such a formalism was successfully adopted in [31] to study numerically the open-system dynamics of a quantum spin coupled to a Ohmic bath of oscillators. This is the celebrated spin-boson model, whose Hamiltonian in the Wigner-Heisenberg representation reads:

$$\hat{H}_W = -\hbar\Omega\hat{\sigma}_x - \sum_{J=1}^N c_J R_J \hat{\sigma}_z + \sum_{J=1}^N \left(\frac{P_J^2}{2M_J} + \frac{1}{2} M_J \omega_J^2 R_J^2 \right). \quad (53)$$

It turns out that at least 200 harmonic oscillators are needed to correctly represent the effect of the bath in agreement with linear response theory [32]. The results obtained in Ref. [31] show that, at least for the values of the parameters use in the numerical calculations, the thermostated spin-boson Model defined by the extended Hamiltonian

$$\hat{H}_W^N = -\hbar\Omega\hat{\sigma}_x - c_1 R_1 \hat{\sigma}_z + \left(\frac{P_1^2}{2M_1} + \frac{1}{2} M_1 \omega_1^2 R_1^2 \right) + \frac{p_\eta^2}{2m_\eta} + k_B T \eta, \quad (54)$$

and by the dynamics given in (52) provides an optimal behavior with just one oscillator [33].

7. Conclusions

In this review we have considered the role of temperature in quantum mechanics. This role still remains partially mysterious because of issues such as the interplay between thermal and quantum fluctuations, the classical limit, the quantum-classical isomorphism, and the Unruh effect, which, in the author's opinion, have not been thoroughly understood yet. Nevertheless, taking a practical attitude, one can extend the classical definition of the temperature to the phase space formulation of quantum mechanics. To this end, we have

reviewed the generalization of brackets in the Wigner and Wigner-Heisenberg representations of quantum mechanics. By means of such generalized brackets, the Nosé dynamics has been defined in quantum phase space as well. In principle, this provides a *deterministic approach* to the quantum dynamics of open systems which promises to be an interesting and rewarding line of research.

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