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Ten reasons why a thermalized system cannot be described by a many-particle wave function

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ABSTRACT

It is widely believed that the underlying reality behind statistical mechanics is a deterministic and unitary time evolution of a many-particle wave function, even though this is in conflict with the irreversible, stochastic nature of statistical mechanics. The usual attempts to resolve this conflict for instance by appealing to decoherence or eigenstate thermalization are riddled with problems. This paper considers theoretical physics of thermalized systems as it is done in practice and shows that all approaches to thermalized systems presuppose in some form limits to linear superposition and deterministic time evolution. These considerations include, among others, the classical limit, extensivity, the concepts of entropy and equilibrium, and symmetry breaking in phase transitions and quantum measurement. As a conclusion, the paper suggests that the irreversibility and stochasticity of statistical mechanics should be taken as a real property of nature. It follows that a gas of a macroscopic number N of atoms in thermal equilibrium is best represented by a collection of N wave packets of a size of the order of the thermal de Broglie wave length, which behave quantum mechanically below this scale but classically sufficiently far beyond this scale. In particular, these wave packets must localize again after scattering events, which requires stochasticity and indicates a connection to the measurement process.

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1. Introduction

Connecting quantum statistical mechanics (QSM) to many-particle nonrelativistic quantum mechanics (QM) poses severe conceptual problems since quantum mechanics is a deterministic theory for pure quantum states, while statistical mechanics (SM) is based on the concept of probabilities and uses mixed states. Despite of the essential differences between these two types of theories, most publications in the field of the foundations of quantum statistical mechanics (Emch, 2007; Eisert, Friesdorf, & Gogolin, 2015; Gogolin & Eisert, 2016; Linden, Popescu, Short, & Winter, 2010; Reimann & Evstigneev, 2013; Short & Farrelly, 2012) aim at "deriving" the properties of thermalized many-particle systems by starting from the N-particle Schrödinger equation

$$i\hbar\frac{\partial\Psi\left(\vec{x}_1,\ldots,\vec{x}_N,t\right)}{\partial t}=H\Psi\left(\vec{x}_1,\ldots,\vec{x}_N,t\right) \tag{1}$$

with

$$\hat{H}=\sum_{\alpha=1}^{N}\frac{\hat{p}_\alpha^2}{2m_\alpha}+\frac{1}{2}\sum_{\alpha\neq\beta}V\left(\vec{r}_\alpha-\vec{r}_\beta\right). \tag{2}$$

A promising starting point to achieve this goal for isolated systems is the eigenstate thermalization hypothesis (Deutsch, 1991; Srednicki, 1994), which is based on the idea that the finite-energy eigenfunctions of interacting many-particle systems are "random" in a suitable sense, such that the expectation values of thermodynamic observables calculated with these eigenfunctions are identical to the expectation values obtained from statistical mechanics. A more comprehensive research agenda treats thermalized systems as open systems that are embedded in a larger environment. The combined system consisting of the considered system and the environment is taken to be isolated and is modeled by a many-particle Schrödinger equation. Due to the interaction with the environment, which imposes the temperature on the system, the system becomes entangled with the environment. When the trace over the environmental degrees is taken, one obtains the reduced density matrix of the system, and this density

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matrix is that of a mixed state. This mixed state becomes that of quantum statistical mechanics when the non-diagonal elements vanish in the basis of the energy eigenfunctions. This is achieved by making plausible assumptions about the uncorrelatedness of the degrees of freedom of the environment. Similar arguments can be applied to small subvolumes of a large isolated system: due to the interaction with the rest of the system, this subvolume becomes entangled with it, and its reduced density matrix is that of a mixed state. The combined system remains in a pure state and retains all information about the initial state (Popescu, Short, & Winter, 2006).

These promising results, combined with the impressive empirical successes at creating many-particle entanglements and quantum superpositions of mesoscopic objects, lead to the widespread belief that at the microscopic level nature shares the fundamental features of quantum mechanics, including a deterministic, reversible time evolution, linear superposition, and entanglement of all particles that have interacted with each other.

However, this approach brings severe problems with it. The first problem is that of interpreting the mixed state of a thermalized system. While the Schrödinger equation for the combined system is usually interpreted as describing one system (and not an ensemble), the mixed state is taken to represent an ensemble of systems. This problem is analogous to the problem of interpreting the measurement process, where a unitary time evolution according to the Schrödinger equation leads to a mixed state of the observed particle, representing a superposition of all measurement outcomes and not to just one of them, as observed in experiments. Insisting on linear superposition and unitary time evolution leads to interpretations of quantum mechanics such as many worlds (Everett, 1957), consistent histories (Griffiths, 1984), or the relational interpretation (Rovelli, 1996). These interpretations are however difficult to accept for many people, who therefore hold that decoherence theory does not solve the interpretational problems of quantum mechanics, in particular in connection with quantum measurement (Adler, 2003; Ellis, 2014; Schlosshauer, 2005).

Another problem of the said "derivations" of QSM from QM (and in general of decoherence theory) is that of justifying the assumptions required for obtaining a diagonal density matrix for the system. The calculations done to this purpose always include assumptions such as statistical independence and "typicality" that are foreign to a deterministic theory (Drossel, 2015; Kastner, 2014).

The third problem is that the amount of information required in order to specify a many-particle wave function and to calculate its time evolution increases exponentially with the particle number, so that it will forever be practically impossible to test empirically the existence of such wave functions beyond simple systems. Walter Kohn, who won the 1998 chemistry Nobel prize for developing density functional theory, warned us not to take the concept of a wave function too far (Kohn, 1999): "In general the concept of a many-electron wave function $\Psi(r_1, \ldots, r_N)$ for a system of N electrons is not a legitimate scientific concept, when $N > N_0$, where $N_0 \simeq 10^3$. I will use two criteria for defining 'legitimacy': a) That Ψ can be calculated with sufficient accuracy and b) can be recorded with sufficient accuracy".

Due to these problems, the present paper explores a different avenue for connecting SM and QM. Instead of aiming at harmonizing SM and thermodynamics with a deterministic, unitary time evolution on the microscopic level (Callender, 2001), we will argue that SM is not merely empirically adequate but that its stochasticity and irreversibility reflect true features of nature. If this is correct, SM can be used to identify the limits of unitary quantum mechanics. Thus, turning the title of Callender's paper "Taking thermodynamics too seriously" (Callender, 2001) around, this paper is about "taking quantum mechanics too seriously".

In the following section, we will consider the concepts, methods, and calculations used for thermalized many-particle systems. By studying ten different aspects of or approaches to thermalized systems, we will show that they require two important features: stochasticity and a limited spatial extension of the wave function of a particle. If physics shall reflect at least approximately the features of reality and if we are moved to take seriously physical calculations for thermalized systems as they are done in practice, then it seems we ought to conclude that in thermalized many-particle systems there are limits to the extension of a wave function, to its deterministic evolution, to linear superposition, and to entanglement. Accordingly, this paper suggests that the irreversibility and stochasticity of statistical mechanics should be taken seriously as actual properties of nature.

Most of the following is formulated for a simple model system, namely a diluted gas of atoms with short-range interactions, which behaves in very good approximation like an ideal gas.

2. Ten ways in which the physics of thermalized systems limits deterministic, unitary quantum mechanics

2.1. *Molecular dynamics simulations use localized atoms*

Molecular dynamics (MD) simulations are successfully used to characterize the structure and dynamics of systems that consist of many atoms at a finite temperature (Marx & Hutter, 2000; Tuckerman & Martyna, 2000). Such simulations evaluate the motion of atoms and molecules based on the forces between them and describing the system at least in some respects classically. Temperature is taken into account by coupling the system to a "thermostat" that extracts and adds energy in such a way that a Maxwell-Boltzmann distribution of velocities is obtained. The majority of methods use Newton's equations of motion to calculate the motion of the nuclei. In purely classical simulations, molecules are represented as a collection of point masses and charges with restrictions on their relative positions, and forces are effective forces (e.g., van der Waals) obtained from comparison with empirical data or from quantum mechanical calculations. This type of simulations gives very good results for structural relaxation times and concentration profiles in liquids (Klameth & Vogel, 2013), for many biological processes such as transport through pores in biological membranes (Gumbart, Wang, Aksimentiev, Tajkhorshid, & Schulten, 2005), and for protein folding (Karplus & Kuriyan, 2005). When, however, the formation and breaking of bonds, the polarization of atoms or molecules, or excited states shall be taken into account, the quantum mechanical properties of the electrons must be considered, employing ab initio MD simulations. For given positions of the nuclei, the electronic structure of atoms and molecules is calculated using quantum mechanics. The motion of the nuclei is then calculated classically based on the force fields resulting from the electronic structure, and the electronic structure in turn is recalculated based on the changed positions of the nuclei. When quantum mechanical properties of nuclei become important, for instance with proton transfer processes that involve tunnelling, the Feynman path integral formalism of statistical mechanics is used to describe the nuclei. In this formalism, the partition function of one particle is written as $Z(\beta) = \int dx \langle x| e^{-\beta H} |x\rangle$ with the quantum mechanical Hamiltonian $H = T + U$ (with T being here the kinetic energy and not the temperature as in all other equations). This partition function can be rewritten such that it is identical to that of a classical harmonic chain that is closed to form a ring, in the external potential U. The typical size of this ring polymer is of the order of the thermal de Broglie wave length $\lambda_{th} = h/\sqrt{2\pi m k_B T}$. For N particles, this partition function is