

Chaos and Quantum Thermalization

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ABSTRACT: We show that a bounded, isolated quantum system of many particles in a specific initial state will approach thermal equilibrium if the energy eigenfunctions which are superposed to form that state obey *Berry's conjecture*. Berry's conjecture is expected to hold only if the corresponding classical system is chaotic, and essentially states that the energy eigenfunctions behave as if they were gaussian random variables. We review the existing evidence, and show that previously neglected effects substantially strengthen the case for Berry's conjecture. We study a rarefied hard-sphere gas as an explicit example of a many-body system which is known to be classically chaotic, and show that an energy eigenstate which obeys Berry's conjecture predicts a Maxwell-Boltzmann, Bose-Einstein, or Fermi-Dirac distribution for the momentum of each constituent particle, depending on whether the wave functions are taken to be nonsymmetric, completely symmetric, or completely antisymmetric functions of the positions of the particles. We call this phenomenon *eigenstate thermalization*. We show that a generic initial state will approach thermal equilibrium at least as fast as $O(\hbar/\Delta)t^{-1}$, where Δ is the uncertainty in the total energy of the gas. This result holds for an individual initial state; in contrast to the classical theory, no averaging over an ensemble of initial states is needed. We argue that these results constitute a new foundation for quantum statistical mechanics.

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I. INTRODUCTION

Take some helium atoms, put them in one corner of a well insulated box, and let them go. Wait a while, then punch a small hole in the side of the box. As the atoms emerge, one by one, measure their momenta. Make a histogram, plotting the fraction of atoms with magnitude of momentum between p and $p + dp$.

Every physicist knows what the result of this experiment will be. The histogram will be very well approximated by the Maxwell–Boltzmann distribution

$$f_{\text{MB}}(\mathbf{p}, T) = (2\pi mkT)^{-3/2} e^{-\mathbf{p}^2/2mkT} \quad (1.1)$$

multiplied by $4\pi F p^2 dp$, where $F = (\pi/8mkT)^{1/2} p$ is a flux factor. Here m is the mass of a helium atom, k is Boltzmann’s constant, and T is the “temperature,” a number which will depend on how the atoms were originally put into the corner of the box, how much space they occupied, and other details of the initial conditions. The challenge is to derive this result from first principles.

The biggest problem with a theoretical analysis of this particular experiment is the need to treat the hole in the box in a reasonable way. It is much easier to study the following thought experiment instead. Suppose, after preparing the system in its initial state, we are able to measure the momentum of one atom at a specific (but arbitrary) time t . Suppose further that, after having made this measurement, we can empty out the box, and then start it off again with the system in exactly the same initial state. We now do this repeatedly, each time measuring the momentum of one atom after exactly the same amount of time t has passed. We make a histogram of the results.

Let us analyze this experiment, beginning with classical mechanics as the underlying theory. We take the hamiltonian for N atoms to be

$$H = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} + \sum_{i<j} V(|\mathbf{x}_i - \mathbf{x}_j|) , \quad (1.2)$$

where we take $V(r)$ to be a hard-sphere potential:

$$V(r) = \begin{cases} +\infty & \text{for } r < 2a \\ 0 & \text{for } r > 2a . \end{cases} \quad (1.3)$$

We assume perfectly reflecting boundary conditions at the walls of the box. The atoms initially have some definite total energy U . The phase space of this system is known to be fully chaotic, with no invariant tori for any value of U [1]. Thus the motion in phase space on any constant energy surface is ergodic and mixing. (For a review of classical chaos theory, see, e.g., [2–4].)

However, this is entirely irrelevant if we always start out with exactly the same initial state, and always make the measurement after exactly the same amount of time has elapsed. The momentum of the measured atom (assuming that it is always the same atom) is determined exactly by the initial conditions, and so will always be the same. To have any hope of getting a distribution of momenta, we must average over either the initial conditions or the times of measurement or both.

If we keep the initial conditions fixed, ergodicity implies that the system wanders all over the constant energy surface. (This assumes that we have not started the system off at a point located on a periodic orbit; such points form a set of measure zero.) If we divide the constant energy surface into many patches of equal area (and that area is not too small) then after a certain finite time the system will, to a very good approximation, be equally likely to be in any one of these patches at any later time. Conversely, if we permit a range of initial conditions, mixing implies that, if the measurement time is fixed but not too early, the system will once again, to a very good approximation, be equally likely to be in any one of the equal-area patches. The rule that equal-area patches are equally likely is just the usual formulation of the microcanonical ensemble, which after a little work leads to eq. (1.1) for the fraction of atoms with momentum in a range of d^3p around \mathbf{p} , with the temperature T simply given by the ideal gas formula $U = \frac{3}{2}NkT$. In short, if we do a modest average over either the initial conditions or the times of measurement, then classical chaos results in classical thermalization. (For an elementary review of chaos theory as it applies to classical statistical mechanics, see [5].)

On the other hand, if we have a weakly perturbed integrable system (for example, harmonic oscillators with small nonlinear couplings), then according to the Kolmogorov–Arnol’d–Moser theorem [6], its phase space is foliated by invariant tori almost everywhere, and we do not expect it to thermalize. If it is partially integrable, with some invariant tori embedded in an otherwise chaotic phase space, then the system may or may not thermalize, depending on the initial state.

These results from classical mechanics are clear and powerful, and provide a satisfying explanation of statistical behavior in classical systems which exhibit chaos. However, we know that the real world is ultimately described by quantum mechanics, and we should seek the quantum analog of the classical analysis. We would like to know, for example, what property a quantum system must possess, analogous to classical chaos, so that “most” of its initial states thermalize, in the sense discussed above. Furthermore if a quantum system does possess this property (whatever it may be), then we might hope that the inherent uncertainties in quantum mechanics lead to a thermal distribution for the momentum of a single atom, even if we always start with exactly the same initial state, and make the measurement at exactly the same time. If this is true, then quantum mechanics automatically provides the “coarse graining” which is missing [3,7] in the classical theory.

I will argue that the property needed for thermalization of a quantum system is the validity of *Berry’s conjecture* [8–10]. For a quantum gas of hard spheres, Berry’s conjecture

states that each energy eigenfunction appears to be a superposition of plane waves (in the $3N$ dimensional coordinate space) with random phase and gaussian random amplitude, but fixed wavelength. In general, Berry’s conjecture is expected to hold only for systems which exhibit classical chaos in all or at least most of the classical phase space. As already noted, a hard sphere gas meets this condition.

We will see that Berry’s conjecture leads to either Bose–Einstein, Fermi–Dirac, or Maxwell–Boltzmann statistics, depending on whether the wave functions are chosen to be completely symmetric, completely antisymmetric, or nonsymmetric functions of the positions of the N atoms. Furthermore we will find that any nonthermal features of the initial distribution of momenta decay away at least as fast as $O(\hbar/\Delta)t^{-1}$, where \hbar is Planck’s constant and Δ is the uncertainty in the total energy. Thermal behavior thus appears for a very wide range of possible initial states, without assuming that the system interacts with an external heat bath, or any other environmental variables. We also do not need to take any averages over initial states, times of measurement, or hamiltonians, or make any unjustifiable approximations to the quantum equation of motion, such as truncation of the BBGKY hierarchy.

The rest of this paper is organized as follows. In Sect. II, we review Berry’s conjecture for a system of hard spheres in a box. In Sect. III, we show how Berry’s conjecture leads, in the limit of low density and high energy, to a Maxwell–Boltzmann distribution for the momentum of a single atom in the gas, with a temperature that is related to the total energy by the ideal gas law. In this section we treat the atoms as distinguishable, making no assumptions about the symmetry of the wave function of the gas under exchange of individual atoms. In Sect. IV, we evaluate the effects of certain corrections to Berry’s conjecture known as “scars,” and reconsider some of the numerical results on Berry’s conjecture which have appeared in the literature. In Sect. V, we examine time evolution beginning with a nonthermal initial state, and study the approach to equilibrium. In Sect. VI, we consider wave functions which are completely symmetric or antisymmetric under exchange of atoms, and see that these lead to Bose–Einstein or Fermi–Dirac distributions for individual momenta, respectively. Conclusions, speculations, and possible extensions are presented in Sect. VII.

II. BERRY’S CONJECTURE

Consider a system of N hard spheres, each of radius a , in a cubic box with edge length $L+2a$. Call the energy eigenvalues U_α and the corresponding eigenfunctions $\psi_\alpha(\mathbf{X})$, where $\mathbf{X} = (\mathbf{x}_1, \dots, \mathbf{x}_N)$ denotes the $3N$ coordinates, and $\mathbf{P} = (\mathbf{p}_1, \dots, \mathbf{p}_N)$ will denote the $3N$ conjugate momenta. We take the wave functions to be defined on the domain

$$D = \left\{ \mathbf{x}_1, \dots, \mathbf{x}_N \mid -\frac{1}{2}L \leq x_{i1,2,3} \leq +\frac{1}{2}L; |\mathbf{x}_i - \mathbf{x}_j| \geq 2a \right\}, \quad (2.1)$$

with the boundary condition that each $\psi_\alpha(\mathbf{X})$ vanish on the boundary of D . For now we assume that $\psi_\alpha(\mathbf{X})$ has no symmetries under exchange of individual \mathbf{x}_i .

The energy eigenfunctions $\psi_\alpha(\mathbf{X})$ can always be chosen to be everywhere real, and can be written as

$$\psi_\alpha(\mathbf{X}) = \mathcal{N}_\alpha \int d^{3N}P A_\alpha(\mathbf{P}) \delta(\mathbf{P}^2 - 2mU_\alpha) \exp(i\mathbf{P} \cdot \mathbf{X}/\hbar), \quad (2.2)$$

where \mathcal{N}_α is a constant to be determined by the normalization condition

$$\int_D d^{3N}X \psi_\alpha^2(\mathbf{X}) = 1, \quad (2.3)$$

and where $A_\alpha^*(\mathbf{P}) = A_\alpha(-\mathbf{P})$. For this system, Berry's conjecture is equivalent to assuming that $A_\alpha(\mathbf{P})$ can be treated as a gaussian random variable with a two-point correlation function given by

$$\langle A_\alpha(\mathbf{P}) A_\beta(\mathbf{P}') \rangle_{\text{EE}} = \delta_{\alpha\beta} \delta^{3N}(\mathbf{P} + \mathbf{P}') / \delta(\mathbf{P}^2 - \mathbf{P}'^2). \quad (2.4)$$

Here $\delta^{3N}(\mathbf{P})$ is the $3N$ -dimensional Dirac delta function and $\delta(x)$ is the one-dimensional Dirac delta function. The subscript EE stands for "eigenstate ensemble." This is a fictitious ensemble which describes the properties of a typical energy eigenfunction. Individual eigenfunctions behave *as if* they were selected at random from the eigenstate ensemble. Berry's conjecture also asserts that the eigenstate ensemble is gaussian, so that all multi-point correlation functions are given in terms of the two-point correlation function; e.g.,

$$\begin{aligned} \langle A_\alpha(\mathbf{P}_1) A_\beta(\mathbf{P}_2) A_\gamma(\mathbf{P}_3) A_\delta(\mathbf{P}_4) \rangle_{\text{EE}} &= \langle A_\alpha(\mathbf{P}_1) A_\beta(\mathbf{P}_2) \rangle_{\text{EE}} \langle A_\gamma(\mathbf{P}_3) A_\delta(\mathbf{P}_4) \rangle_{\text{EE}} \\ &+ \langle A_\alpha(\mathbf{P}_1) A_\gamma(\mathbf{P}_3) \rangle_{\text{EE}} \langle A_\delta(\mathbf{P}_4) A_\beta(\mathbf{P}_2) \rangle_{\text{EE}} \\ &+ \langle A_\alpha(\mathbf{P}_1) A_\delta(\mathbf{P}_4) \rangle_{\text{EE}} \langle A_\beta(\mathbf{P}_2) A_\gamma(\mathbf{P}_3) \rangle_{\text{EE}}. \end{aligned} \quad (2.5)$$

Of course, each $A_\alpha(\mathbf{P})$ must give back a $\psi_\alpha(\mathbf{X})$ which vanishes on the boundary of D ; this is not a stringent requirement on $A_\alpha(\mathbf{P})$ at high energy, where $\psi_\alpha(\mathbf{X})$ has many wavelengths between any two segments of the boundary. We will say more about the requirement of high energy shortly. Meanwhile, for a more general but less transparent definition of Berry's conjecture, see sect. 4; for related mathematical results, see [11,12].

Berry's conjecture is based on semiclassical reasoning, and is manifestly untrue for systems whose classical phase space is foliated almost everywhere by invariant tori [13]. It has been investigated numerically for simple systems which are fully chaotic classically, such as a single particle in a two-dimensional stadium-shaped box [14–18], or a single particle on a two-dimensional surface with constant negative curvature and periodic boundary conditions [19,20]. In these systems, Berry's conjecture is found to be valid for eigenstates of sufficiently high energy, and its validity has even been suggested as a good *definition* of

chaos in a quantum system [21]. However, an important caveat is the existence of “scars” on some energy eigenfunctions, regions of enhanced value of $\psi_\alpha(\mathbf{X})$ which follow the paths of the most stable classical periodic orbits [14,15]. For now we will ignore the scars, since their presence will not alter any of our conclusions. We will discuss them in more detail in sect. 4. Also, there we will argue that some numerical results which have been interpreted as evidence against Berry’s conjecture actually provide evidence for it.

Even in a system which is fully chaotic classically (like a hard-sphere gas), Berry’s conjecture will certainly not be valid for eigenfunctions which are too low in energy. The low-lying states necessarily have specific structure: the ground state, for example, is nodeless. A rough criterion for the validity of Berry’s conjecture is that the average wavelength of each particle be small enough to “see” the features which produce classical chaos [16]. For the hard-sphere gas, the relevant feature is the nonzero radius a of each particle. Anticipating a bit and defining a temperature T_α for each energy eigenvalue U_α via the ideal gas formula $U_\alpha = \frac{3}{2}NkT_\alpha$, and further defining a “thermal” wavelength $\lambda_\alpha = (2\pi\hbar^2/mkT_\alpha)^{1/2}$, then the criterion for the validity of Berry’s conjecture is $\lambda_\alpha \lesssim a$. Numerically, this becomes $T_\alpha \gtrsim (300/ma^2)$ Kelvin, where a is in angstroms and m is in amu.

It turns out that getting explicit results will also require us to work at low density, $Na^3 \ll L^3$. Combining this with $\lambda_\alpha \lesssim a$, we see that we need to have $N\lambda_\alpha^3 \ll L^3$, a condition which is also required, in quantum statistical mechanics, for the Bose–Einstein and Fermi–Dirac distributions to be well approximated by the Maxwell–Boltzmann distribution.

Let us now consider the eigenfunctions in momentum space:

$$\begin{aligned} \tilde{\psi}_\alpha(\mathbf{P}) &\equiv h^{-3N/2} \int_D d^{3N}X \psi_\alpha(\mathbf{X}) \exp(-i\mathbf{P}\cdot\mathbf{X}/\hbar) \\ &= h^{3N/2} \mathcal{N}_\alpha \int_{-\infty}^{+\infty} d^{3N}K A_\alpha(\mathbf{K}) \delta(\mathbf{K}^2 - 2mU_\alpha) \delta_D^{3N}(\mathbf{K} - \mathbf{P}), \end{aligned} \quad (2.6)$$

where we have defined

$$\delta_D^{3N}(\mathbf{K}) \equiv h^{-3N} \int_D d^{3N}X \exp(i\mathbf{K}\cdot\mathbf{X}/\hbar). \quad (2.7)$$

If the condition needed for Berry’s conjecture is satisfied ($\lambda_\alpha \lesssim a$), *and* we are in the low density regime ($Na^3 \ll L^3$), then we can make the substitutions

$$\begin{aligned} \delta_D^{3N}(0) &\rightarrow (L/h)^{3N}, \\ \delta_D^{3N}(\mathbf{P}) &\rightarrow \delta^{3N}(\mathbf{P}), \\ [\delta_D^{3N}(\mathbf{P})]^2 &\rightarrow (L/h)^{3N} \delta^{3N}(\mathbf{P}). \end{aligned} \quad (2.8)$$

Now using eqs. (2.2), (2.4), (2.6), and (2.8), we find that (for $\lambda_\alpha \lesssim a$ and $Na^3 \ll L^3$),

$$\langle \tilde{\psi}_\alpha^*(\mathbf{P}) \tilde{\psi}_\beta(\mathbf{P}') \rangle_{\text{EE}} = \delta_{\alpha\beta} \mathcal{N}_\alpha^2 h^{3N} \delta(\mathbf{P}^2 - 2mU_\alpha) \delta_D^{3N}(\mathbf{P} - \mathbf{P}'), \quad (2.9)$$

which will play a key role in the next section.

III. EIGENSTATE THERMALIZATION

Let us now put our gas of N hard spheres into some initial state specified by the momentum-space wave function

$$\tilde{\psi}(\mathbf{P}, 0) = \sum_\alpha C_\alpha \tilde{\psi}_\alpha(\mathbf{P}). \quad (3.1)$$

We take the energy eigenfunctions to be orthonormal, and also assume $\tilde{\psi}(\mathbf{P}, 0)$ to be normalized, so that $\sum_\alpha |C_\alpha|^2 = 1$. The expectation value of the energy is then

$$\bar{U} = \sum_\alpha |C_\alpha|^2 U_\alpha, \quad (3.2)$$

and the uncertainty in the energy is Δ , where

$$\Delta^2 = \sum_\alpha |C_\alpha|^2 (U_\alpha - \bar{U})^2. \quad (3.3)$$

We will assume that $\Delta \ll \bar{U}$. The initial wave function will evolve in time according to the Schrodinger equation:

$$\tilde{\psi}(\mathbf{P}, t) = \sum_\alpha C_\alpha \exp(-iU_\alpha t/\hbar) \tilde{\psi}_\alpha(\mathbf{P}). \quad (3.4)$$

Now return to the thought experiment in which the system is repeatedly prepared in the same initial state (specified by the C_α 's), and the momentum of one atom is repeatedly measured after the same elapsed time t . The theoretical prediction for the fraction of atoms with momentum in a range d^3p around \mathbf{p} is $f_{\text{QM}}(\mathbf{p}, t) d^3p$, where

$$\begin{aligned} f_{\text{QM}}(\mathbf{p}_1, t) &= \int d^3p_2 \dots d^3p_N |\tilde{\psi}(\mathbf{P}, t)|^2 \\ &= \sum_{\alpha\beta} C_\alpha^* C_\beta e^{i(U_\alpha - U_\beta)t/\hbar} \int d^3p_2 \dots d^3p_N \tilde{\psi}_\alpha^*(\mathbf{P}) \tilde{\psi}_\beta(\mathbf{P}) \\ &= \sum_{\alpha\beta} C_\alpha^* C_\beta e^{i(U_\alpha - U_\beta)t/\hbar} \Phi_{\alpha\beta}(\mathbf{p}_1). \end{aligned} \quad (3.5)$$

In the last line we have introduced

$$\Phi_{\alpha\beta}(\mathbf{p}_1) \equiv \int d^3p_2 \dots d^3p_N \tilde{\psi}_\alpha^*(\mathbf{P}) \tilde{\psi}_\beta(\mathbf{P}), \quad (3.6)$$

which obeys the normalization condition

$$\int d^3p_1 \Phi_{\alpha\beta}(\mathbf{p}_1) = \delta_{\alpha\beta}. \quad (3.7)$$

If the system thermalizes, then after some time has passed, $f_{\text{QM}}(\mathbf{p}_1, t)$ should be equal to the Maxwell–Boltzmann distribution of eq. (1.1), although (as in the classical case) some modest averaging over either the initial conditions (the C_α ’s) or the times of measurement (the value of t) might first be necessary. Furthermore the temperature \bar{T} should be given at least approximately by the ideal gas law $\bar{U} = \frac{3}{2}Nk\bar{T}$, with a fractional uncertainty of order Δ/\bar{U} .

To practice on a simple example, let us study the case where the initial state is a single energy eigenstate. This is, of course, unphysical: we cannot actually prepare such a state in a time less than $O(\hbar/\delta)$, where δ is the mean energy level spacing near U_α [22]. This is fantastically small in any realistic case [$\delta_\alpha = 1/n_\alpha$, where n_α is given by eq. (4.6)], so that \hbar/δ_α is much longer than the age of the universe. Nevertheless taking the initial state to be an energy eigenstate will turn out to be an instructive exercise.

In this case, eq. (3.5) becomes simply $f_{\text{QM}}(\mathbf{p}_1, t) = \Phi_{\alpha\alpha}(\mathbf{p}_1)$, which is independent of time. We now study the properties of $\Phi_{\alpha\alpha}(\mathbf{p}_1)$ in the eigenstate ensemble introduced in the previous section. Assuming high energy ($\lambda_\alpha \lesssim a$) and low density ($Na^3 \ll L^3$), it follows from eqs. (2.8), (2.9), and (3.6) that

$$\langle \Phi_{\alpha\alpha}(\mathbf{p}_1) \rangle_{\text{EE}} = \mathcal{N}_\alpha^2 L^{3N} \int d^3p_2 \dots d^3p_N \delta(\mathbf{P}^2 - 2mU_\alpha). \quad (3.8)$$

We introduce the useful formula

$$\begin{aligned} I_D(x) &\equiv \int d^D P \delta(\mathbf{P}^2 - x) \\ &= \frac{(\pi x)^{D/2}}{\Gamma(D/2)x}, \end{aligned} \quad (3.9)$$

and use it to fix $\mathcal{N}_\alpha^{-2} = L^{3N} I_{3N}(2mU_\alpha)$ via eq. (3.7). We then find

$$\begin{aligned} \langle \Phi_{\alpha\alpha}(\mathbf{p}_1) \rangle_{\text{EE}} &= \frac{I_{3N-3}(2mU_\alpha - \mathbf{p}_1^2)}{I_{3N}(2mU_\alpha)} \\ &= \frac{\Gamma(3N/2)}{\Gamma((3N-3)/2)} \left(\frac{1}{2\pi m U_\alpha} \right)^{3/2} \left(1 - \frac{\mathbf{p}_1^2}{2mU_\alpha} \right)^{(3N-5)/2}. \end{aligned} \quad (3.10)$$

If we now set $U_\alpha = \frac{3}{2}NkT_\alpha$ and take the large N limit, we get

$$\langle \Phi_{\alpha\alpha}(\mathbf{p}_1) \rangle_{\text{EE}} = (2\pi mkT_\alpha)^{-3/2} e^{-\mathbf{p}_1^2/2mkT_\alpha}, \quad (3.11)$$

which is precisely $f_{\text{MB}}(\mathbf{p}_1, T_\alpha)$.

Let us note first that, given eq. (3.8) as a starting point, eqs. (3.9–11) simply recapitulate a standard derivation of the canonical ensemble from the microcanonical [23].

More importantly, we must study the fluctuations of $\Phi_{\alpha\alpha}(\mathbf{p}_1)$ about its average value in the eigenstate ensemble. We begin by defining

$$[\Delta\Phi_{\alpha\beta}(\mathbf{p}_1)]^2 \equiv \langle |\Phi_{\alpha\beta}(\mathbf{p}_1)|^2 \rangle_{\text{EE}} - |\langle \Phi_{\alpha\beta}(\mathbf{p}_1) \rangle_{\text{EE}}|^2. \quad (3.12)$$

Using eqs. (2.5), (2.8), (2.9), and (3.6), we find

$$\begin{aligned} [\Delta\Phi_{\alpha\beta}(\mathbf{p}_1)]^2 &= \mathcal{N}_\alpha^2 \mathcal{N}_\beta^2 (Lh)^{3N} \int d^3p_2 \dots d^3p_N d^3p'_2 \dots d^3p'_N \\ &\quad \times \delta(\mathbf{P}^2 - 2mU_\alpha) \delta(\mathbf{P}'^2 - 2mU_\beta) \delta_D^{3N}(\mathbf{P} - \mathbf{P}'). \end{aligned} \quad (3.13)$$

Before evaluating eq. (3.13) explicitly, we can see that it will be very small: if we replace $\delta_D^{3N}(\mathbf{P} - \mathbf{P}')$ by its maximum value $(L/h)^{3N}$ everywhere, the right-hand side of eq. (3.13) becomes $\langle \Phi_{\alpha\alpha}(\mathbf{p}_1) \rangle_{\text{EE}} \langle \Phi_{\beta\beta}(\mathbf{p}_1) \rangle_{\text{EE}}$ [cf. eq. (3.8)]. Of course this replacement results in a huge overestimate of $[\Delta\Phi_{\alpha\beta}(\mathbf{p}_1)]^2$, since in fact $\delta_D^{3N}(\mathbf{P} - \mathbf{P}')$ is close to zero almost everywhere. Thus we will have, in particular, $\Delta\Phi_{\alpha\alpha}(\mathbf{p}_1) \ll \langle \Phi_{\alpha\alpha}(\mathbf{p}_1) \rangle_{\text{EE}}$. Furthermore we see why $\Delta\Phi_{\alpha\alpha}(\mathbf{p}_1)$ is so small: $\tilde{\psi}_\alpha(\mathbf{P})$ has fluctuations of order one in the eigenstate ensemble, but these are washed out when we integrate over most of the momenta. (In Sect. IV we will see that the same fate befalls the “scars” mentioned in Sect. II.)

We now turn to the evaluation of eq. (3.13), to find out just how small it is. We will need to know a bit more detail about $\delta_D^{3N}(\mathbf{P} - \mathbf{P}')$ than the substitution rules of eq. (2.8). We therefore approximate it with a gaussian:

$$\delta_D^{3N}(\mathbf{P} - \mathbf{P}') \simeq (L/h)^{3N} \exp[-(\mathbf{P} - \mathbf{P}')^2 L^2 / 4\pi\hbar^2]. \quad (3.14)$$

In the low density regime ($Na^3 \ll L^3$), using eq. (3.14) instead of eq. (2.7) changes the result only by an overall constant of order one. Substituting eq. (3.14) into eq. (3.13), setting $\alpha = \beta$, and taking the large N limit yields

$$\Delta\Phi_{\alpha\alpha}(\mathbf{p}_1) = O(1) N^{1/2} e^{-3N/4} (L/\lambda_\alpha)^{-(3N-6)/2} e^{+\mathbf{p}_1^2/4mkT_\alpha} f_{\text{MB}}(\mathbf{p}_1, T_\alpha). \quad (3.15)$$

Since we have $L \gg \lambda_\alpha$, we see that *the fluctuations in $\Phi_{\alpha\alpha}(\mathbf{p}_1)$ about $f_{\text{MB}}(\mathbf{p}_1, T_\alpha)$ are negligibly small for large N* . That is to say, an energy eigenstate which satisfies Berry’s conjecture predicts a thermal distribution for the momentum of a single constituent particle. We will refer to this remarkable phenomenon as *eigenstate thermalization*.

Given a system which exhibits eigenstate thermalization, it is not hard to understand why almost any initial state will thermalize. In fact, the problem now is primarily to *prevent* the system from having a thermal distribution for the momentum of each particle at *all* times. To do so at $t = 0$, we must carefully superpose energy eigenstates in order to construct an initial state with whatever nonthermal features we might want. Once this superposition is prepared, however, the delicate phase relationships we have set up to avoid thermal behavior will gradually be destroyed by hamiltonian time evolution, and the system will equilibrate. We will see how this works in more detail in Sect. V. First, however, we digress briefly to discuss the scars, and check to see that they do not change any of our conclusions so far.

IV. FADED SCARS

The theory of scar formation has been developed by Heller [15,18], Bogomolny [24], and Berry [25,10]. We will be rather schematic here; readers unfamiliar with scar theory should consult the cited references for more details.

We first consider any system governed by a hamiltonian $H(\mathbf{P}, \mathbf{X})$ which is time-reversal invariant and which results in classical chaos. For consistency of notation with the previous sections, we take \mathbf{P} and \mathbf{X} to be vectors with $3N$ components.

We begin by introducing the Wigner density for an eigenstate,

$$\rho_\alpha(\mathbf{P}, \mathbf{X}) = h^{-3N} \int d^{3N}S \exp(i\mathbf{P} \cdot \mathbf{S}/\hbar) \psi_\alpha(X + \frac{1}{2}\mathbf{S}) \psi_\alpha(X - \frac{1}{2}\mathbf{S}), \quad (4.1)$$

where $\psi_\alpha(\mathbf{X})$ is real. The Wigner density has the useful properties that

$$\begin{aligned} \int d^{3N}P \rho_\alpha(\mathbf{P}, \mathbf{X}) &= \psi_\alpha^2(\mathbf{X}), \\ \int d^{3N}X \rho_\alpha(\mathbf{P}, \mathbf{X}) &= |\tilde{\psi}_\alpha(\mathbf{P})|^2, \end{aligned} \quad (4.2)$$

which imply the normalization condition

$$\int d^{3N}P d^{3N}X \rho_\alpha(\mathbf{P}, \mathbf{X}) = 1. \quad (4.3)$$

Scar theory begins with a semiclassical formula for $\rho_\alpha(\mathbf{P}, \mathbf{X})$:

$$\rho_\alpha(\mathbf{P}, \mathbf{X}) = n_\alpha^{-1} h^{-3N} \delta(H(\mathbf{P}, \mathbf{X}) - U_\alpha) \left\{ 1 + \sum_p A_p e^{iS_p/\hbar} \exp[(i/\hbar)\mathbf{Z}_p \cdot \mathbf{W}_p(T_p) \cdot \mathbf{Z}_p] \right\}. \quad (4.4)$$

The sum is over all periodic orbits on the surface with constant energy U_α ; S_p is the action of the orbit; T_p is a coordinate in phase space along the orbit; \mathbf{Z}_p are the $6N-2$ coordinates in the energy surface which are perpendicular to the orbit; and A_p and $\mathbf{W}_p(T_p)$ are purely classical quantities which depend on the monodromy matrix of the orbit. The constant n_α is fixed by the normalization condition, eq. (4.3), and can be interpreted physically as the energy eigenvalue density near U_α . If we ignore the sum over periodic orbits in eq. (4.5), we obtain the ‘‘Weyl rule’’ for n_α :

$$n_\alpha = h^{-3N} \int d^{3N}P d^{3N}X \delta(H(\mathbf{P}, \mathbf{X}) - U_\alpha) . \quad (4.5)$$

In the case of a hard-sphere gas of $3N$ distinguishable particles, this becomes

$$n_\alpha = \frac{1}{\Gamma(3N/2)U_\alpha} \left(\frac{mL^2U_\alpha}{2\pi\hbar^2} \right)^{3N/2} . \quad (4.6)$$

For bosons or fermions, the right-hand side should be divided by $N!$. Even so, n_α is fantastically large in any realistic case [22].

The key point for scar theory is that the periodic-orbit terms in eq. (4.4) have no \hbar -dependent prefactors; the peak height of each term is controlled by the classical quantity A_p . A short periodic orbit can have an A_p which is greater than one; this produces an obvious ‘‘scar’’ in phase space along the path of the orbit.

We are interested, however, in $\Phi_{\alpha\alpha}(\mathbf{p}_1)$, and so we must integrate $\rho_\alpha(\mathbf{P}, \mathbf{X})$ over all $3N$ components of \mathbf{X} , and all but three of the $3N$ components of \mathbf{P} . If we consider isolated periodic orbits, we see from eq. (4.4) that an integral over one of the $6N-2$ components of \mathbf{Z}_p yields a prefactor of $\hbar^{1/2}$. Thus the contribution of each isolated periodic orbit to $\Phi_{\alpha\alpha}(\mathbf{p}_1)$ is suppressed, relative to the leading term, by $\hbar^{(6N-3)/2}$, which means that each individual scar on $\Phi_{\alpha\alpha}(\mathbf{p}_1)$ is totally negligible.

Nonisolated periodic orbits are a little more complicated, since moving off a non-isolated orbit in some directions in phase space merely puts the system onto another nonisolated orbit in the same ‘‘family’’; there are a finite number of these families. For the hard-sphere gas, the nonisolated orbits consist of motions where the spheres bounce off the walls but never collide with each other [26]. A given nonisolated orbit of this type can in general be deformed into another one by moving in any direction in coordinate space. Thus when integrating $\rho_\alpha(\mathbf{P}, \mathbf{X})$ over the $3N$ components of \mathbf{X} , we do not get any factors of $\hbar^{1/2}$. We do, however, get a net factor of $\hbar^{(3N-3)/2}$ from integrating over $3N-3$ components of \mathbf{P} . Thus, while the contribution of a family of nonisolated orbits to $\Phi_{\alpha\alpha}(\mathbf{p}_1)$ is much larger than the contribution of a single isolated orbit, it is still negligible. These conclusions are supported by the much more detailed calculation of Gaspard [26] for the periodic-orbit corrections to n_α for the hard-sphere gas.

Therefore, in computing $\Phi_{\alpha\alpha}(\mathbf{p}_1)$, we can safely ignore the short isolated orbits and all of the nonisolated orbits. The most modern version of Berry’s conjecture [10] then assigns

the origin of the gaussian fluctuations in $\psi_\alpha(\mathbf{X})$ to the long isolated orbits. Thus $\psi_\alpha(\mathbf{X})$ is conjectured to behave like a gaussian random variable with a two-point correlation function embodied by the elegant formula [8,11]

$$\langle \rho_\alpha(\mathbf{P}, \mathbf{X}) \rangle_{\text{EE}} = n_\alpha^{-1} h^{-3N} \delta(H(\mathbf{P}, \mathbf{X}) - U_\alpha) . \quad (4.7)$$

There has been important progress recently [27] in bringing the long isolated orbits under analytic control, but so far Berry's conjecture remains just that. Even if a rigorous proof is eventually found, it is likely to apply only for asymptotically high energies. We turn, therefore, to a discussion of the existing numerical evidence.

Berry's conjecture has been studied numerically in some two-dimensional systems, such as a particle in a stadium-shaped box [14–18]. One popular object to study is the correlation function [8]

$$\begin{aligned} \mathcal{C}_\alpha(\mathbf{s}) &\equiv \int d^2x \psi_\alpha(\mathbf{x} + \frac{1}{2}\mathbf{s}) \psi_\alpha(\mathbf{x} - \frac{1}{2}\mathbf{s}) \\ &= \int d^2p d^2x \exp(-i\mathbf{p}\cdot\mathbf{s}/\hbar) \rho_\alpha(\mathbf{p}, \mathbf{x}) , \end{aligned} \quad (4.8)$$

where in the simplest case the integral over x covers the entire box, whose area we will call L^2 . For a particular eigenstate, the numerically computed $\mathcal{C}_\alpha(\mathbf{s})$ is compared to its expectation value in the eigenstate ensemble:

$$\begin{aligned} \langle \mathcal{C}_\alpha(\mathbf{s}) \rangle_{\text{EE}} &= \int d^2p d^2x \exp(-i\mathbf{p}\cdot\mathbf{s}/\hbar) \langle \rho_\alpha(\mathbf{p}, \mathbf{x}) \rangle_{\text{EE}} \\ &= n_\alpha^{-1} h^{-2} L^2 \int d^2p \delta(\mathbf{p}^2/2m - U_\alpha) \\ &= J_0(k_\alpha s) , \end{aligned} \quad (4.9)$$

where $J_0(z)$ is a Bessel function, $k_\alpha = (2mU_\alpha/\hbar^2)^{1/2}$, and $s = |\mathbf{s}|$. In [16], only moderately good agreement was found with this prediction, with discrepancies of approximately 0.1 for $k_\alpha = 65$ and $L = \sqrt{\pi}$; see fig. 7 of [16]. However, these discrepancies are entirely explained by consideration of the fluctuations in $\mathcal{C}_\alpha(\mathbf{s})$ which are predicted by the eigenstate ensemble:

$$\begin{aligned} [\Delta \mathcal{C}_\alpha(\mathbf{s})]^2 &\equiv \langle \mathcal{C}_\alpha^2(\mathbf{s}) \rangle_{\text{EE}} - \langle \mathcal{C}_\alpha(\mathbf{s}) \rangle_{\text{EE}}^2 \\ &= \int d^2x d^2y \left[\langle \psi_\alpha(\mathbf{x} + \frac{1}{2}\mathbf{s}) \psi_\alpha(\mathbf{y} + \frac{1}{2}\mathbf{s}) \rangle_{\text{EE}} \langle \psi_\alpha(\mathbf{x} - \frac{1}{2}\mathbf{s}) \psi_\alpha(\mathbf{y} - \frac{1}{2}\mathbf{s}) \rangle_{\text{EE}} \right. \\ &\quad \left. + \langle \psi_\alpha(\mathbf{x} + \frac{1}{2}\mathbf{s}) \psi_\alpha(\mathbf{y} - \frac{1}{2}\mathbf{s}) \rangle_{\text{EE}} \langle \psi_\alpha(\mathbf{x} + \frac{1}{2}\mathbf{s}) \psi_\alpha(\mathbf{y} - \frac{1}{2}\mathbf{s}) \rangle_{\text{EE}} \right] \\ &= L^{-4} \int d^2x d^2y \left[J_0^2(k_\alpha |\mathbf{x} - \mathbf{y}|) + J_0(k_\alpha |\mathbf{x} - \mathbf{y} + \mathbf{s}|) J_0(k_\alpha |\mathbf{x} - \mathbf{y} - \mathbf{s}|) \right] . \end{aligned} \quad (4.10)$$

The first term in the last line dominates over the second for all \mathbf{s} , and is $O(1/k_\alpha L)$. That is, we expect discrepancies of roughly $(k_\alpha L)^{-1/2}$ between $\mathcal{C}_\alpha(\mathbf{s})$ as computed numerically for a particular eigenstate and $\langle \mathcal{C}_\alpha(\mathbf{s}) \rangle_{\text{EE}}$ as given by eq.(4.9). This is *exactly what is seen* in fig.7 of [16]. Similar comments apply to figs.14–17 of [20]. The fact that these discrepancies are *predicted* by the eigenstate ensemble does not seem to have been noticed previously.

We note finally that the gaussian nature of the eigenstate ensemble [which is used crucially in eq.(4.10)] has also been directly tested. The prediction is that

$$\langle \psi_\alpha^{2n}(\mathbf{x}) \rangle_{\text{EE}} = (2n - 1)!! \langle \psi_\alpha^2(\mathbf{x}) \rangle_{\text{EE}}^n = (2n - 1)!! L^{-2n} , \quad (4.11)$$

but this just means that the probability distribution for the amplitude ψ at any point is

$$P(\psi) = \frac{L}{\sqrt{2\pi}} \exp\left[-\frac{1}{2}L^2\psi^2\right] , \quad (4.12)$$

which is well supported by the numerical results [16,19,20].

V. TIME EVOLUTION AND EQUILIBRATION

In Sect. III, we saw that an individual energy eigenstate which satisfies Berry's conjecture predicts a thermal distribution for the momentum of each constituent particle. Now we must see what happens when we consider more general states. We will once again express the initial state as a wave function in momentum space, and expand it in energy eigenfunctions, as in eq.(3.1). We assume that the uncertainty Δ in the total energy, eq.(3.3), is much smaller than the average energy \bar{U} , eq.(3.2). This is easy to arrange in practice.

The predicted momentum distribution of a single particle at time t is $f_{\text{QM}}(\mathbf{p}_1, t)$, as given by eq.(3.5). Now take the average of eq.(3.5) in the eigenstate ensemble. From eq.(2.4), it is immediately obvious that $\langle \Phi_{\alpha\beta}(\mathbf{p}_1) \rangle_{\text{EE}} = 0$ if $\alpha \neq \beta$, and so we get

$$\begin{aligned} \langle f_{\text{QM}}(\mathbf{p}_1, t) \rangle_{\text{EE}} &= \sum_{\alpha} |C_\alpha|^2 \langle \Phi_{\alpha\alpha}(\mathbf{p}_1) \rangle_{\text{EE}} \\ &= \sum_{\alpha} |C_\alpha|^2 (2\pi mkT_\alpha)^{-3/2} e^{-\mathbf{p}_1^2/2mkT_\alpha} , \end{aligned} \quad (5.1)$$

where we have used eq.(3.11) in the second line. Now, since $\Delta \ll \bar{U}$, we can with negligible error replace each T_α in this sum with \bar{T} , where $\bar{U} = \frac{3}{2}Nk\bar{T}$, and then $\sum_{\alpha} |C_\alpha|^2 = 1$ gives us

$$\langle f_{\text{QM}}(\mathbf{p}_1, t) \rangle_{\text{EE}} = f_{\text{MB}}(\mathbf{p}_1, \bar{T}) [1 + O(\Delta/\bar{U})] , \quad (5.2)$$

the desired result.

Once again, though, we must study the fluctuations of $f_{\text{QM}}(\mathbf{p}_1, t)$ that are predicted by the eigenstate ensemble. We can write

$$f_{\text{QM}}(\mathbf{p}_1, t) = f_{\text{MB}}(\mathbf{p}_1, \bar{T}) + \sum_{\alpha\beta} C_\alpha^* C_\beta e^{i(U_\alpha - U_\beta)t/\hbar} \tilde{\Phi}_{\alpha\beta}(\mathbf{p}_1), \quad (5.3)$$

where we have defined

$$\tilde{\Phi}_{\alpha\beta}(\mathbf{p}_1) \equiv \Phi_{\alpha\beta}(\mathbf{p}_1) - \langle \Phi_{\alpha\beta}(\mathbf{p}_1) \rangle_{\text{EE}}. \quad (5.4)$$

Our problem is to understand the double-sum term on the right-hand side of eq. (5.3).

For a fixed value of \mathbf{p}_1 , each $|\tilde{\Phi}_{\alpha\beta}(\mathbf{p}_1)|$ is given roughly by its RMS value in the eigenstate ensemble, which is $\Delta\Phi_{\alpha\beta}(\mathbf{p}_1)$ as given by eq. (3.13). We have already seen that $\Delta\Phi_{\alpha\alpha}(\mathbf{p}_1)$ is extremely small, and $\Delta\Phi_{\alpha\beta}(\mathbf{p}_1)$ is not going to be any bigger when $\alpha \neq \beta$. In fact, using the gaussian approximation of eq. (3.14) in eq. (3.13), we find

$$[\Delta\Phi_{\alpha\beta}(\mathbf{p}_1)]^2 \simeq [\Delta\Phi_{\alpha\alpha}(\mathbf{p}_1)]^2 \exp[-m(U_\alpha - U_\beta)^2 L^2 / 8\pi\hbar^2 U_\alpha]. \quad (5.5)$$

We see that we will have $\Delta\Phi_{\alpha\beta}(\mathbf{p}_1) \ll \Delta\Phi_{\alpha\alpha}(\mathbf{p}_1)$ if $|U_\alpha - U_\beta|/U_\alpha$ is much bigger than $(\hbar^2/mU_\alpha L^2)^{1/2} \sim \lambda_\alpha/N^{1/2}L$, a very small number. [Note, though, that the precisely gaussian form of the falloff is an artifact of eq. (3.14).] For simplicity, let us assume that $\Delta/\bar{U} \lesssim \bar{\lambda}/N^{1/2}L$, where $\bar{\lambda} = (2\pi\hbar^2/mk\bar{T})^{1/2}$. Then for the range of α and β of interest, each $\Delta\Phi_{\alpha\beta}(\mathbf{p}_1)$ is given by the right-hand-side of eq. (3.15) with U_α replaced by \bar{U} . We will need only the crudest approximations here, and so we write

$$|\tilde{\Phi}_{\alpha\beta}(\mathbf{p}_1)| \sim \Delta\Phi_{\alpha\beta}(\mathbf{p}_1) \sim (L/\bar{\lambda})^{-3N/2}. \quad (5.6)$$

However, we expect that the phase of $\tilde{\Phi}_{\alpha\beta}(\mathbf{p}_1)$ varies wildly with α and β .

Let N_C be the number of nonnegligible C_α 's which appear in eq. (5.3); N_C can be defined precisely via $N_C^{-1} = \sum_\alpha |C_\alpha|^4$, and crudely estimated as $N_C \sim \bar{n}\Delta$, where \bar{n} is the energy level density near $U = \bar{U}$ [cf. eq. (4.6)]. The order of magnitude of each nonnegligible $|C_\alpha|$ is then $N_C^{-1/2}$ (so that $\sum_\alpha |C_\alpha|^2 = 1$).

Now consider doing the double sum in eq. (5.3). If the phases of the C_α 's are not carefully correlated with those of the $\tilde{\Phi}_{\alpha\beta}(\mathbf{p}_1)$'s, then each of the two sums will yield a random-walk result: the square root of the number of "steps", $N_C^{1/2}$, times the size of each step, $C_\alpha \sim N_C^{-1/2}$. With an overall factor of $(L/\bar{\lambda})^{-3N/2}$ from eq. (5.6), we get

$$\sum_{\alpha\beta} C_\alpha^* C_\beta e^{i(U_\alpha - U_\beta)t/\hbar} \tilde{\Phi}_{\alpha\beta}(\mathbf{p}_1) \sim (L/\bar{\lambda})^{-3N/2}, \quad (5.7)$$

which is again extremely small. If we let Δ/\bar{U} be bigger than $\bar{\lambda}/N^{1/2}L$, then the result is even smaller.

On the other hand, we can certainly set up an initial state which is very far from thermal. For example, we could give each particle the same initial value (to within quantum uncertainties) for its individual momentum, leading to an $f_{\text{QM}}(\mathbf{p}_1, 0)$ which is sharply peaked at that value. In this case, though, the phases of the C_α 's must be correlated with those of the $\tilde{\Phi}_{\alpha\beta}(\mathbf{p}_1)$'s in exactly the right way to produce the desired nonthermal distribution $f_{\text{QM}}(\mathbf{p}_1, 0)$. In this case, we want to see what happens as time evolves.

Let us begin with eq. (5.3) at $t = 0$, with the phases of the C_α 's carefully chosen to give us a nonthermal distribution. Now let the clock run. Each of the off-diagonal ($\alpha \neq \beta$) terms in the double sum begins acquiring an extra phase; there are roughly N_C^2 off-diagonal terms in all. The growing phase of each individual term will cause its contribution to the sum to have a random orientation in the complex plane once $|U_\alpha - U_\beta|t/\hbar \gtrsim 2\pi$. We will say that such a term has *decohered*. The first terms to decohere (those with the largest difference between U_α and U_β) do so at a time $t \sim h/\Delta$. The fraction of terms which have decohered at later times is given roughly by $(\Delta - h/t)^2/\Delta^2$. Thus the fraction of still coherent terms at this time is roughly $1 - (\Delta - h/t)^2/\Delta^2 \sim (h/\Delta)/t$ for $t \gg h/\Delta$.

Now, each of the coherent terms should give its usual contribution to the sum, since its phase is still (almost) properly aligned, but the net contribution of all the coherent terms will be suppressed by a factor of $O(h/\Delta)t^{-1}$ due to their reduced population. On the other hand, the terms which have decohered will contribute with random phases. Since almost all terms have decohered for $t \gg h/\Delta$, their total contribution will be given by eq. (5.6), and is negligibly small. Thus, overall we expect that *any nonthermal features present in the initial distribution $f_{\text{QM}}(\mathbf{p}_1, 0)$ will decay away with time like $O(h/\Delta)t^{-1}$.*

We can test this conclusion with a very simple example. The system we will analyze is classically integrable, and so chaos plays no role in the following discussion.

Consider a single particle with mass $m = 100$ in a two-dimensional circular box with radius $R = 1$; we also set $\hbar = 1$. The initial wave function for the particle is taken to be

$$\psi(\mathbf{x}, 0) = \pi^{-1/2} a^{-1} \exp(i\mathbf{p}_0 \cdot \mathbf{x}) \exp(-\mathbf{x}^2/2a^2). \quad (5.8)$$

This is a gaussian wave packet of width a at the center of the box, moving with momentum \mathbf{p}_0 . If we Fourier transform into momentum space, we get

$$\tilde{\psi}(\mathbf{p}, 0) = \pi^{-1/2} a \exp[-\frac{1}{2}a^2(\mathbf{p} - \mathbf{p}_0)^2]. \quad (5.9)$$

We will take $a = 0.1$ and $p_0 = 100$. Classically, the particle has energy $E = p_0^2/2m = 50$, and just bounces back and forth, changing directions at times $t = 1, 3, 5, \dots$. Quantum mechanically, the uncertainty in the particle's energy is $\Delta = p_0/\sqrt{2}ma \simeq 7$. We can solve this problem exactly by expanding $\tilde{\psi}(\mathbf{p}, 0)$ in the energy eigenstate basis and using eq. (3.4). Then we can compute the probability density for the particle to have its initial momentum at time t ; that is, we compute $|\tilde{\psi}(\mathbf{p}_0, t)|^2$. Let us see what we should expect for this quantity, based on the general arguments outlined above.

First of all, note that the infinite time average of $|\tilde{\psi}(\mathbf{p}_0, t)|^2$ is given by

$$\lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^\tau dt |\tilde{\psi}(\mathbf{p}_0, t)|^2 = \sum_{\alpha} |C_{\alpha}|^2 |\tilde{\psi}_{\alpha}(\mathbf{p}_0)|^2, \quad (5.10)$$

where $\tilde{\psi}_{\alpha}(\mathbf{p}_0)$ is an energy eigenfunction in momentum space. We expect $|\tilde{\psi}(\mathbf{p}_0, t)|^2$ to approach its infinite time average at late times, with late-time fluctuations of the same order of magnitude. If $|\tilde{\psi}(\mathbf{p}_0, t)|^2$ does not start out close to its infinite time average at $t = 0$, then it should decay towards that value like $O(h/\Delta)t^{-1}$.

The exact result for $|\tilde{\psi}(\mathbf{p}_0, t)|^2$, normalized to its value at $t = 0$, is shown in fig. 1. We clearly see the classical bounces, as the probability to have the initial momentum drops to zero at the first turning point, $t = 1$, then returns at $t = 3$, etc. However, the quantum probability does not return to its initial value, but follows the $(h/\Delta)/t$ envelope predicted by the general argument outlined above. It finally drops down to its infinite time average, with fluctuations of the expected size. Thus we see that the simple phase decoherence argument works very well for this example.

If we now compare the right-hand sides of eqs. (5.1) and eq. (5.10), we see the analogy between the infinite time average of $|\tilde{\psi}(\mathbf{p}_0, t)|^2$ and the eigenstate ensemble average of $f_{\text{QM}}(\mathbf{p}_1, t)$. The main difference is that, because we have integrated out almost all the degrees of freedom, the fluctuations of $f_{\text{QM}}(\mathbf{p}_1, t)$ about its average value are very small.

There is more we can learn from our simple example, however. First, we have seen that the classical motion is reflected in the quantum probabilities, a fact which is expected to be true for classically chaotic systems as well [28]. This means that quantum initial states which can be understood as representing classical initial conditions may thermalize even faster, due to the effects of classical chaos. If we can follow classical trajectories (with initial quantum uncertainties) for some time, and classical chaos spreads these out over a constant energy surface in phase space, then the system has thermalized classically. This argument may be needed in cases where the initial distribution is so far from thermal that the quantum $O(h/\Delta)t^{-1}$ decay of its nonthermal features seems to take too long. It also shows that the $O(h/\Delta)t^{-1}$ rule need not be related to more traditional diffusion times, which are more likely to reflect classical physics.

Second, consider fig. 2, which shows the $|C_{\alpha}|$'s for this problem plotted against the corresponding energy eigenvalues, E_{α} . While they form a nice envelope, with mean energy $\bar{E} = 50$ and uncertainty $\Delta = 7$, there is a great deal of fine structure. This is needed to get the very special initial state, localized at the origin and moving in the x direction at a particular speed. We cannot, therefore, think of replacing C_{α} by a smooth function of E_{α} . This is unfortunate, since if we average eq. (4.4) over a smooth distribution of energy eigenvalues, the contributions of the long periodic orbits are suppressed [24,25,10], and the problem becomes much more tractable. However, as we see in fig. 2, such smoothing is physically far too restrictive, since it would prevent us from considering a wide variety of initial states which we could actually prepare in a real experiment.

Let us summarize the results of this section. If we construct a particular initial state for the hard-sphere gas at low density by superposing energy eigenstates, each of which individually satisfies Berry's conjecture, then we find that, at sufficiently late times, the quantum mechanical prediction for the probability that any one particle has momentum \mathbf{p} is simply given by the Maxwell–Boltzmann distribution of eq. (1.1). The probability that this will *not* be the case is negligible, if we wait long enough. Any nonthermal features of the initial distribution for a single particle's momentum will decay away at least as fast as $O(\hbar/\Delta)t^{-1}$, where Δ is the quantum uncertainty in the total energy. Faster decays are possible, and likely if the initial state has a classical interpretation. Absolutely no averaging over initial states or times of measurement is needed, in contrast with the classical case.

This concludes our analysis of the high energy, low density, hard-sphere gas in the case that we assume no symmetries of the wave function on exchange of individual particles. We will return to discuss lower energies and higher densities in Sect. VII. Now, though, we turn our attention to wave functions which are either completely symmetric or completely antisymmetric functions of the positions of the N particles.

VI. BOSONS AND FERMIONS

The detailed analysis in Sects. II and III required the assumptions of high energy ($\lambda_\alpha \lesssim a$) and low density ($Na^3 \ll L^3$), which combine to give $N\lambda_\alpha^3 \ll L^3$. In Sect. II we noted that this is precisely the condition needed for the Bose–Einstein and Fermi–Dirac distributions to be well approximated by the Maxwell–Boltzmann distribution. Nevertheless, even though the corrections due to quantum statistics may be numerically small, a valid formalism should be able to reproduce them. In this section we will see that the present formalism meets this test.

Define a symmetrization operator \mathcal{P}_\pm via

$$\mathcal{P}_\pm f(\mathbf{p}_1 \dots \mathbf{p}_N) = \frac{1}{N!} \sum_{\text{perms}} (\pm 1)^P f(\mathbf{p}_{i_1}, \dots, \mathbf{p}_{i_N}), \quad (6.1)$$

where the sum is over the permutations of the indices, and P is even (odd) if the permutation is even (odd). Now we can construct completely symmetric and antisymmetric energy eigenfunctions analogous to those of eq. (2.2):

$$\psi_\alpha^\pm(\mathbf{X}) = \mathcal{N}_\alpha^\pm \int d^{3N}P A_\alpha(\mathbf{P}) \delta(\mathbf{P}^2 - 2mU_\alpha) \mathcal{P}_\pm \exp(i\mathbf{P} \cdot \mathbf{X}/\hbar). \quad (6.2)$$

We will need the generalization of eq. (2.9). Using the same assumptions as in Sect. III, namely $\lambda_\alpha \lesssim a$ and $Na^3 \ll L^3$, we get

$$\langle \tilde{\psi}_\alpha^{\pm*}(\mathbf{P}) \tilde{\psi}_\beta^\pm(\mathbf{P}') \rangle_{\text{EE}} = \delta_{\alpha\beta} (\mathcal{N}_\alpha^\pm)^2 h^{3N} \delta(\mathbf{P}^2 - 2mU_\alpha) \mathcal{P}_\pm \delta_D^{3N}(\mathbf{P} - \mathbf{P}'). \quad (6.3)$$

We now want to compute

$$\langle \Phi_{\alpha\alpha}^{\pm}(\mathbf{p}_1) \rangle_{\text{EE}} = \int d^3p_2 \dots d^3p_N \langle \tilde{\psi}_{\alpha}^{\pm*}(\mathbf{P}) \tilde{\psi}_{\alpha}^{\pm}(\mathbf{P}) \rangle_{\text{EE}}. \quad (6.4)$$

For nonsymmetric wave functions, we found in Sect. III that $\langle \Phi_{\alpha\alpha}^{\pm}(\mathbf{p}_1) \rangle_{\text{EE}}$ was equal to a Maxwell–Boltzmann distribution at a temperature T_{α} related to the energy eigenvalue U_{α} by the ideal gas formula $U_{\alpha} = \frac{3}{2}NkT_{\alpha}$. We therefore expect to find that $\langle \Phi_{\alpha\alpha}^{\pm}(\mathbf{p}_1) \rangle_{\text{EE}}$ is given by a Bose–Einstein distribution $f_{\text{BE}}(\mathbf{p}_1, T_{\alpha}) \equiv f^{+}(\mathbf{p}_1, T_{\alpha})$ or a Fermi–Dirac distribution $f_{\text{FD}}(\mathbf{p}_1, T_{\alpha}) \equiv f^{-}(\mathbf{p}_1, T_{\alpha})$. In statistical mechanics, these are usually computed using the grand canonical ensemble, but in our case the number of particles is firmly fixed at N . Thus we expect to find that $\langle \Phi_{\alpha\alpha}^{\pm}(\mathbf{p}_1) \rangle_{\text{EE}}$ is equal to $f^{\pm}(\mathbf{p}_1, T_{\alpha})$ as given by the canonical, rather than the grand canonical, ensemble. Relevant formulae from the less familiar canonical ensemble are gathered in the Appendix.

Let us warm up by computing $\mathcal{N}_{\alpha}^{\pm}$. The normalization condition we need is

$$\int d^3p_1 \dots d^3p_N \langle \tilde{\psi}_{\alpha}^{\pm*}(\mathbf{P}) \tilde{\psi}_{\alpha}^{\pm}(\mathbf{P}) \rangle_{\text{EE}} = 1. \quad (6.5)$$

We must first evaluate

$$\mathcal{P}_{\pm} \delta_D^{3N}(\mathbf{P} - \mathbf{P}')|_{\mathbf{P}'=\mathbf{P}} = \frac{1}{N!} \sum_{\text{perms}} (\pm 1)^P \delta_D^3(\mathbf{p}_1 - \mathbf{p}_{i_1}) \dots \delta_D^3(\mathbf{p}_N - \mathbf{p}_{i_N}), \quad (6.6)$$

where $\delta_D^3(\mathbf{p})$ is assumed to satisfy the substitution rules of eq. (2.8) with $N \rightarrow 1$. Now examine a particular term in this sum. If a particular momentum is paired with itself, we will say that it comprises a “1-cluster.” If a particular momentum is not paired with itself, it will be part of an “ m -cluster” of momenta which are all set equal to each other by the (approximate) delta functions. For each term, let m_l be the number of momenta in the l th cluster, with $m_1 \leq \dots \leq m_C$. Also let C_m be the number of m -clusters, and C be the total number of clusters. Obviously, we have the relations

$$\begin{aligned} m_1 + \dots + m_C &= N, \\ C_1 + \dots + C_N &= C, \end{aligned} \quad (6.7)$$

$$C_1 + 2C_2 + \dots + NC_N = N.$$

Each term in the sum in eq. (6.6) can now be labeled by a set of nondecreasing integers $\{m\} \equiv \{m_1, \dots, m_C\}$. The number of terms with the same label is

$$A_{\{m\}} = \prod_{l=1}^C (m_l - 1)!, \quad (6.8)$$

where $(m_l - 1)!$ counts the number of ways momenta in the l th cluster can be rearranged without breaking it into smaller clusters, and

$$A_{\{m\}} = \frac{N!}{(m_1! \dots m_C!)(C_1! \dots C_N!)} \quad (6.9)$$

counts the number of inequivalent ways of assigning momenta to clusters. Each cluster has one redundant delta function, which results in a factor of $(L/h)^{3C}$. Furthermore the l th cluster contributes a factor of $(\pm 1)^{m_l - 1}$ to $(\pm 1)^P$. Now from eqs. (6.3) and (6.5) we see that to determine \mathcal{N}_α^\pm we must multiply each term in eq. (6.6) by $\delta(\mathbf{P}^2 - 2mU_\alpha)$ and then integrate over all the momenta. Under the integral, when multiplied by a term labeled by $\{m\}$, we can make the replacement

$$\delta(\mathbf{P}^2 - 2mU_\alpha) \rightarrow \delta(m_1 \mathbf{p}_1^2 + \dots + m_C \mathbf{p}_C^2 - 2mU_\alpha), \quad (6.10)$$

All together, then, we have

$$\begin{aligned} (\mathcal{N}_\alpha^\pm)^{-2} &= h^{3N} \sum_{\{m\}} A_{\{m\}} (L/h)^{3C} \int d^3 p_1 \dots d^3 p_C \\ &\times \delta(m_1 \mathbf{p}_1^2 + \dots + m_C \mathbf{p}_C^2 - 2mU_\alpha) \prod_{l=1}^C (\pm 1)^{m_l - 1} (m_l - 1)!. \end{aligned} \quad (6.11)$$

The sum is over all $\{m\}$ with fixed N . We now make the change of variable $\mathbf{p}_i \rightarrow m_i^{-1/2} \mathbf{k}_i$, which yields

$$(\mathcal{N}_\alpha^\pm)^{-2} = h^{3N} \sum_{\{m\}} A_{\{m\}} (L/h)^{3C} I_{3C}(2mU_\alpha) \prod_{l=1}^C (\pm 1)^{m_l - 1} (m_l - 1)! m_l^{-3/2}, \quad (6.12)$$

where $I_D(x)$ is defined in eq. (3.9). It turns out that terms with $C \gg 1$ dominate, and so we can use the large- C formula

$$h^{3N} (L/h)^{3C} I_{3C}(2mU_\alpha) \simeq \lambda_\alpha^{3N} (L/\lambda_\alpha)^{3C} I_{3N}(2mU_\alpha), \quad (6.13)$$

where $\lambda_\alpha = (2\pi\hbar^2/mkT_\alpha)^{1/2}$, to rewrite eq. (6.12) as

$$(\mathcal{N}_\alpha^\pm)^{-2} = \lambda_\alpha^{3N} I_{3N}(2mU_\alpha) \sum_{\{m\}} A_{\{m\}} \prod_{l=1}^C (L/\lambda_\alpha)^3 (\pm 1)^{m_l - 1} (m_l - 1)! m_l^{-3/2}. \quad (6.14)$$

Now we can apply the Mayer cluster-expansion theorem [29], which can be written as

$$\sum_{\{m\}} A_{\{m\}} \prod_{l=1}^C W_{m_l} = \frac{\partial^N}{\partial z^N} \left\{ \exp \left[\sum_{m=1}^{\infty} \frac{z^m}{m!} W_m \right] \right\} \Big|_{z=0}, \quad (6.15)$$

where, in our case,

$$W_m = (L/\lambda_\alpha)^3 (\pm 1)^{m-1} (m-1)! m^{-3/2}. \quad (6.16)$$

From eq. (A.3) of the Appendix, we have

$$\sum_{m=1}^{\infty} \frac{z^m}{m!} W_m = (L/\lambda_\alpha)^3 g_{5/2}^\pm(z). \quad (6.17)$$

So putting all of this together, we find

$$\begin{aligned} (\mathcal{N}_\alpha^\pm)^{-2} &= \lambda_\alpha^{3N} I_{3N}(2mU_\alpha) \frac{\partial^N}{\partial z^N} \left\{ \exp \left[(L/\lambda_\alpha)^3 g_{5/2}^\pm(z) \right] \right\} \Big|_{z=0} \\ &= \lambda_\alpha^{3N} I_{3N}(2mU_\alpha) N! Z_C^\pm, \end{aligned} \quad (6.18)$$

where Z_C^\pm is the canonical partition function for a gas of noninteracting bosons (+) or fermions (-) at a temperature T_α in a box of volume L^3 [cf. eq. (A.8)].

Clearly we are on the right track! Now we have to do it all over again, this time leaving one of the N momenta unintegrated.

Following the same logic which led us to eq. (6.12), we get

$$\begin{aligned} \langle \Phi_{\alpha\alpha}^\pm(\mathbf{p}_1) \rangle_{\text{EE}} &= (\mathcal{N}_\alpha^\pm)^2 h^{3N} \sum_{\{m\}} A_{\{m\}} (L/h)^{3C} \sum_{i=1}^C (m_i/N) I_{3C-3}(2mU_\alpha - m_i \mathbf{p}_1^2) \\ &\quad \times (\pm 1)^{m_i-1} (m_i - 1)! \prod_{l \neq i} (\pm 1)^{m_l-1} (m_l - 1)! m_l^{-3/2}. \end{aligned} \quad (6.19)$$

The differences from eq. (6.12) arise as follows. First, we must choose which cluster contains the unintegrated momentum \mathbf{p}_1 ; this gives the sum over $i = 1$ to C . Then we must choose which of the m_i momenta in the i th cluster is unintegrated; this gives the factor of m_i . Now we have overcounted by N , which results in the factor of $1/N$. The change to the subscript and argument of I results from not integrating \mathbf{p}_1 , and the factor of $m_i^{-3/2}$ is missing because we did not have to rescale \mathbf{p}_1 .

Again, terms with $C \gg 1$ dominate, and so we have

$$I_{3C-3}(2mU_\alpha - m_i \mathbf{p}_1^2) \simeq (2\pi m k T_\alpha)^{-3/2} \exp(-m_i \mathbf{p}_1^2 / 2m k T_\alpha) I_{3C}(2mU_\alpha). \quad (6.20)$$

Then using eq. (6.13), we get

$$\langle \Phi_{\alpha\alpha}^\pm(\mathbf{p}_1) \rangle_{\text{EE}} = (\mathcal{N}_\alpha^\pm)^2 \lambda_\alpha^{3N} I_{3N}(2mU_\alpha) \sum_{\{m\}} A_{\{m\}} \sum_{i=1}^C V_{m_i} \prod_{l \neq i} W_{m_l}, \quad (6.21)$$

where W_m is given by eq. (6.16), and

$$V_k = (L^3/Nh^3) (\pm 1)^{k-1} k! [\exp(-\mathbf{p}_1^2/2mT_\alpha)]^k. \quad (6.22)$$

Starting with eq. (6.15), it is not hard to prove a generalization of it which reads

$$\sum_{\{m\}} A_{\{m\}} \sum_{i=1}^C V_{m_i} \prod_{l \neq i} W_{m_l} = \frac{\partial^N}{\partial z^N} \left\{ \left[\sum_{k=1}^{\infty} \frac{z^k}{k!} V_m \right] \exp \left[\sum_{m=1}^{\infty} \frac{z^m}{m!} W_m \right] \right\} \Big|_{z=0}. \quad (6.23)$$

In the present case, we have

$$\sum_{k=1}^{\infty} \frac{z^k}{k!} V_m = \frac{L^3}{Nh^3} \frac{z}{\exp(\mathbf{p}_1^2/2mT_\alpha) \mp z}. \quad (6.24)$$

Combining eqs. (6.17), (6.18), (6.21), (6.23), and (6.24), we finally get

$$\begin{aligned} \langle \Phi_{\alpha\alpha}^{\pm}(\mathbf{p}_1) \rangle_{\text{EE}} &= \frac{1}{Z_C^{\pm}} \frac{1}{N!} \frac{\partial^N}{\partial z^N} \left\{ \exp \left[(L/\lambda)^3 g_{5/2}^{\pm}(z) \right] \frac{L^3}{Nh^3} \frac{z}{\exp(\mathbf{p}_1^2/2mT_\alpha) \mp z} \right\} \Big|_{z=0} \\ &= f^{\pm}(\mathbf{p}_1, T_\alpha), \end{aligned} \quad (6.25)$$

where $f^{\pm}(\mathbf{p}_1, T_\alpha)$ is the Bose–Einstein (+) or Fermi–Dirac (–) distribution as predicted by the canonical ensemble [cf. eq. (A.12)]. As expected, then, symmetrization or anti-symmetrization of the wave function changes the statistics from Maxwell–Boltzmann to Bose–Einstein or Fermi–Dirac.

For the last time, we must study the fluctuations of $\Phi_{\alpha\alpha}(\mathbf{p}_1)$ that are predicted by the eigenstate ensemble. The relevant object is $\Delta\Phi_{\alpha\beta}^{\pm}(\mathbf{p}_1)$, defined by the obvious replacements in eq. (3.12). $\Delta\Phi_{\alpha\beta}^{\pm}(\mathbf{p}_1)$ is then given by eq. (3.13) with \mathcal{P}_{\pm} acting on $\delta_D^{3N}(\mathbf{P}-\mathbf{P}')$. Explicit evaluation of $\Delta\Phi_{\alpha\beta}^{\pm}(\mathbf{p}_1)$ is a fearsome combinatoric problem, but luckily a simple variation of the general argument presented after eq. (3.13) still applies, and can be used to show that $\Delta\Phi_{\alpha\beta}^{\pm}(\mathbf{p}_1)$ is very small compared to $\langle \Phi_{\alpha\alpha}^{\pm}(\mathbf{p}_1) \rangle_{\text{EE}} \langle \Phi_{\beta\beta}^{\pm}(\mathbf{p}_1) \rangle_{\text{EE}}$. Therefore eigenstate thermalization still holds, and the previous analysis (in Sect. V) of time evolution still applies.

VII. DISCUSSION AND SPECULATION

Let us begin with a brief recap of the central results. Berry’s conjecture, as applied to a gas of N hard spheres in a box, states that each energy eigenfunction appears to be a superposition of plane waves with wavelength fixed by the energy eigenvalue, but with random phases and gaussian random amplitudes. It is expected to apply only to systems which are classically chaotic, and has been found to be valid (with corrections that do

not affect our conclusions) in simple chaotic systems. Given Berry’s conjecture for the hard-sphere gas, we have discovered the phenomenon of *eigenstate thermalization*: each energy eigenstate predicts a thermal distribution for the momentum of each constituent particle. This distribution is Maxwell–Boltzmann, Bose–Einstein, or Fermi–Dirac, depending on whether the energy eigenfunctions are nonsymmetric, completely symmetric, or completely antisymmetric functions of the N particle positions. Then, a superposition of energy eigenstates with a small fractional uncertainty in the total energy will also appear to be thermal, *unless* the amplitudes and phases of the superposition coefficients are carefully selected to avoid thermal behavior. If this is done initially, then the usual phase changes produced by hamiltonian time evolution destroy the needed coherence, and any nonthermal features disappear as $O(\hbar/\Delta)t^{-1}$, where Δ is the uncertainty in the total energy. However, classical effects which are reflected in the quantum theory can result in faster thermalization.

All of the analysis in Sects. II, III, and VI was done in the limits of low density: $Na^3 \ll L^3$, where a is the radius of a hard sphere and L^3 is the volume of the box, and high energy: $\lambda_\alpha \lesssim a$, where $\lambda_\alpha = (2\pi\hbar^2/mkT_\alpha)^{1/2}$ is the typical wavelength of one particle when the energy eigenvalue is $U_\alpha = \frac{3}{2}NkT_\alpha$; numerically this means $T_\alpha \gtrsim (300/ma^2)$ Kelvin, where a is in angstroms and m is in amu. But what happens if we relax these constraints?

There are no fundamental difficulties with carrying out the analysis for moderately higher densities. All we need to do is use the exact formula for the smeared delta function in momentum space, eq. (2.7). In practice, though, this greatly complicates the calculations. It would be very interesting to try to develop some sort of perturbative (in $a/N^{1/3}L$) analysis, and compare the results with more standard treatments of the hard-sphere Bose or Fermi gas [30].

Lower energies present an entirely different problem, since if we go low enough in energy, Berry’s conjecture will break down. The question is, how low can we go? The generic expectation is that Berry’s conjecture will be valid if the relevant wavelengths are small enough to “see” the features which produce classical chaos [16]. For the hard-sphere gas, the relevant feature is the nonzero radius a of each particle, which leads to $\lambda_\alpha \lesssim a$. However, this may not be good enough at high density [31]. Classically, if the density is large enough to result in very slow diffusion of the particles, then their positions will be correlated over long times; the Lyapunov exponents are all very small. We would then naturally expect that these correlations are reflected in the quantum energy eigenfunctions, which would mean that Berry’s conjecture is not valid. In this case, a possible alternative criterion for the validity of Berry’s conjecture is $\lambda_\alpha \lesssim \ell$, where ℓ is the classical mean free path of a particle, which can be much less than a .

Whatever the correct criterion turns out to be, at a low enough energy Berry’s conjecture will break down, and we must ask what happens at lower energies. One possibility is that eigenstate thermalization will still be valid for a wide range of energy eigenvalues, even though Berry’s conjecture is not. The reason for this speculation appears in the re-

sults of eqs. (3.15) and Sect. IV. In eq. (3.15), we see that the fluctuations about the mean, thermal value of $\Phi_{\alpha\alpha}(\mathbf{p}_1)$ in the eigenstate ensemble are extremely small; experimentally, we can tolerate much larger fluctuations. Thus, we may also be able to tolerate significant violations of Berry’s conjecture without destroying eigenstate thermalization. In Sect. IV, this speculation receives some more support. Scars represent violations of Berry’s conjecture which are quite obvious when one looks at the Wigner density of an energy eigenstate in phase space, since there the scars appear with a “signal-to-noise” ratio of 1:1. Once we integrate out all of the coordinates and most of the momenta, however, the scars fade away almost completely. The same should be true of more generic violations of Berry’s conjecture. Thus, eigenstate thermalization may still be valid at energies well below the threshold for the validity of Berry’s conjecture.

If we go even lower in energy, though, presumably eigenstate thermalization will eventually cease to be valid. If the system is this low in energy, it will not be able to thermalize itself. To find thermal behavior in a system below its threshold for eigenstate thermalization, we must couple it to an external heat bath, such as the refrigeration apparatus in a low-temperature experiment. Of course, once we have contact with a large, pre-existing heat bath, all the usual results of statistical mechanics can be applied without further worry.

The basic question we have been trying to address in this paper is how such a heat bath might form in the first place. We have seen that this will happen for a hard-sphere gas, provided that Berry’s conjecture is satisfied by the energy eigenstates which are superposed to form the initial state. Whether or not other mechanisms exist for self-thermalization of isolated quantum systems is an open question, one to which we hope to return. Meanwhile we believe that the present results constitute a new foundation for quantum statistical mechanics. In particular, we have at least one answer to the question of which quantum systems will approach thermal equilibrium. It is satisfying that this answer (those systems which obey Berry’s conjecture) is closely related to the answer from classical physics (those systems which exhibit chaos). In fact the situation in the quantum theory is even better than it is in the classical theory, because we no longer need to consider an ensemble of initial states. Each and every superposition of energy eigenstates obeying Berry’s conjecture will eventually yield a thermal distribution for the momentum of a constituent particle, provided that we wait long enough. Absolutely no averaging of any kind is needed: not over initial states, not over times of measurement, and not over hamiltonians.

Finally we would like to comment on the much-discussed question of an appropriate definition for quantum chaos. Some time ago, van Kampen suggested that quantum chaos be defined as “that property that causes a quantum system to behave statistically” [32]. If we replace “behave statistically” with “obey the laws of statistical mechanics,” then we have seen that the key feature is Berry’s conjectured properties of the energy eigenstates. In particular, properties of the energy eigenvalues (such as GOE rather than Poisson statistics for the unfolded level spacings [33]) have played no role at all in the present

work. Steiner has suggested [21] that Berry’s conjecture be elevated to the status of the best definition of quantum chaos, a proposal which we see to be equivalent to (our version of) van Kampen’s. More generally, in quantum mechanics, where time evolution is always linear and therefore essentially trivial, the only place to encode the complexities of the classical limit is in the energy eigenfunctions: that is where quantum chaos, like thermal behavior, must be sought.

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APPENDIX. THE CANONICAL ENSEMBLE FOR BOSONS AND FERMIONS

We will use a notation close to that of [5]. We ignore spin degrees of freedom.

The canonical partition function for N noninteracting bosons or fermions in a box is given by

$$Z_C^\pm = \prod_{l=0}^{\infty} \sum_{n_l=0}^{N_\pm} e^{-\beta n_l E_l} \delta_{N, n_1+n_2+\dots}, \quad (\text{A.1})$$

where $\beta = 1/kT$, E_l is the l th energy eigenvalue for a single particle in the box, and $N_+ = \infty$ for bosons and $N_- = 1$ for fermions.

Introducing the fugacity z , the grand canonical partition function for N noninteracting bosons or fermions in a box is given by

$$\begin{aligned} Z_{\text{GC}}^\pm &= \prod_{l=0}^{\infty} \sum_{n_l=0}^{N_\pm} z^{n_l} e^{-\beta n_l E_l} \\ &= \exp \left[\mp \sum_{l=0}^{\infty} \log \left(1 \mp z e^{-\beta E_l} \right) \right] \\ &= \exp \left[\mp L^3 h^{-3} \int d^3 p \log \left(1 \mp z e^{-\beta \mathbf{p}^2/2m} \right) \right] \\ &= \exp \left[(L/\lambda)^3 g_{5/2}^\pm(z) \right]. \end{aligned} \quad (\text{A.2})$$

In the third line, we have replaced the sum over levels by an integral over momenta (without separating out the zero mode, which would be necessary for a discussion of

Bose condensation). In the fourth line, we have introduced the thermal wavelength $\lambda \equiv (2\pi\hbar^2/mkT)^{1/2}$, and the Lerch transcendent

$$g_\nu^\pm(z) \equiv \sum_{m=1}^{\infty} \frac{(\pm)^{m-1} z^m}{m^\nu}. \quad (\text{A.3})$$

Z_{GC}^\pm must be supplemented with the condition

$$\begin{aligned} N &= z \frac{\partial}{\partial z} \log Z_{\text{GC}}^\pm \\ &= (L/\lambda)^3 g_{3/2}^\pm(z), \end{aligned} \quad (\text{A.4})$$

which can be thought of as fixing the value of z . We will call the positive real solution of this equation z_0 .

The relation between Z_{C}^\pm and Z_{GC}^\pm can be found by writing the Kronecker delta in eq. (A.1) as

$$\delta_{N, n_1+n_2+\dots} = \frac{1}{2\pi i} \oint dz z^{-N-1} z^{n_1+n_2+\dots}, \quad (\text{A.5})$$

where the contour encloses the origin. Substituting this into eq. (A.1) and using the first and fourth lines of eq. (A.2) yields

$$\begin{aligned} Z_{\text{C}}^\pm &= \frac{1}{2\pi i} \oint dz z^{-N-1} Z_{\text{GC}}^\pm \\ &= \frac{1}{2\pi i} \oint dz z^{-N-1} \exp\left[(L/\lambda)^3 g_{5/2}^\pm(z)\right]. \end{aligned} \quad (\text{A.6})$$

Evaluating this integral approximately by stationary phase, treating both N and $(L/\lambda)^3$ as large, results in

$$Z_{\text{C}}^\pm = \left[2\pi (L/\lambda)^3 g_{1/2}^\pm(z_0)\right]^{-1/2} Z_{\text{GC}}^\pm, \quad (\text{A.7})$$

where Z_{GC}^\pm is to be evaluated at $z = z_0$. The fractional error in this approximate equality is of order $1/N$. Note also that, using Cauchy's theorem, we can rewrite eq. (A.6) as

$$Z_{\text{C}}^\pm = \frac{1}{N!} \frac{\partial^N}{\partial z^N} \left\{ \exp\left[(L/\lambda)^3 g_{5/2}^\pm(z)\right] \right\} \Big|_{z=0}. \quad (\text{A.8})$$

We would now like to compute the expected fraction $\langle f^\pm(\mathbf{p}) \rangle d^3p$ of particles with momentum in a range d^3p around \mathbf{p} . The expected fraction of particles with energy E_l is given in either formalism by

$$\begin{aligned} \langle f_l^\pm \rangle &= \langle n_l^\pm \rangle / N \\ &= - \frac{1}{N\beta} \frac{1}{Z^\pm} \frac{\partial Z^\pm}{\partial E_l}, \end{aligned} \quad (\text{A.9})$$

where Z^\pm is either Z_C^\pm or Z_{GC}^\pm . Then converting to the normalization required for continuous momenta gives $\langle f^\pm(\mathbf{p}) \rangle = (L/h)^3 \langle f_l^\pm \rangle$ with $E_l = \mathbf{p}^2/2m$. In the grand canonical case this gives the well-known result

$$\langle f^\pm(\mathbf{p}) \rangle_{GC} = \frac{L^3}{Nh^3} \frac{z_0}{e^{\beta \mathbf{p}^2/2m} \mp z_0}. \quad (\text{A.10})$$

In the canonical case, this procedure gives

$$\langle f^\pm(\mathbf{p}) \rangle_C = \frac{1}{Z_C^\pm} \frac{1}{2\pi i} \oint dz z^{-N-1} \exp\left[(L/\lambda)^3 g_{5/2}^\pm(z)\right] \frac{L^3}{Nh^3} \frac{z}{e^{\beta \mathbf{p}^2/2m} \mp z}. \quad (\text{A.11})$$

Approximate evaluation of this integral by stationary phase gives $\langle f^\pm(\mathbf{p}) \rangle_C = \langle f^\pm(\mathbf{p}) \rangle_{GC}$, again with a fractional error of order $1/N$. Also, we can again use Cauchy's theorem to write

$$\langle f^\pm(\mathbf{p}) \rangle_C = \frac{1}{Z_C^\pm} \frac{1}{N!} \frac{\partial^N}{\partial z^N} \left\{ \exp\left[(L/\lambda)^3 g_{5/2}^\pm(z)\right] \frac{L^3}{Nh^3} \frac{z}{e^{\beta \mathbf{p}^2/2m} \mp z} \right\} \Big|_{z=0}. \quad (\text{A.12})$$

In the main text, we simplify the notation a bit via $\langle f^\pm(\mathbf{p}) \rangle_C \rightarrow f^\pm(\mathbf{p}, T)$.

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FIGURE CAPTIONS

Fig. 1. Solid line: $|\tilde{\psi}(\mathbf{p}_0, t)|^2/|\tilde{\psi}(\mathbf{p}_0, 0)|^2$ vs t for a single particle in a two-dimensional circular box; the initial wave function is a narrow gaussian at the center with momentum \mathbf{p}_0 . Classically, the particle bounces off the wall at $t = 1, 3, 5, \dots$. Dashed line: $(2\pi\hbar/\Delta)/t$, where Δ is the uncertainty in the energy. Dotted line: the infinite time average of the solid line.

Fig. 2. Expanding the wave function of fig. 1 in energy eigenstates yields expansion coefficients C_α ; here $|C_\alpha|$ is plotted vs the energy eigenvalues E_α . There are 1736 energy eigenvalues in the plotted range, $20 \leq E \leq 90$.



