Employing Trapped Cold Ions to Verify the Quantum Jarzynski Equality

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We propose a scheme to investigate the nonequilibrium work distribution of a quantum particle under well controlled transformations of the external potential, exploiting the versatility of a single ion in a segmented linear Paul trap. We describe in detail how the motional quantum state of a single ion can be prepared, manipulated, and finally readout to fully determine the free energy difference in both harmonic and anharmonic potentials. Uniquely to our system, we show how an ion may be immersed in an engineered laser-field reservoir. Trapped ions therefore represent an ideal tool for investigating the Jarzynski equality in open and closed quantum systems.

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Nonequilibrium phenomena at the nanoscale are dominated by fluctuations and by quantum effects. The interplay of nonequilibrium thermodynamics and quantum theory is hence of fundamental interest. Only a decade ago Jarzynski published a major discovery in *classical* nonequilibrium physics [1], relating the free energy difference ΔF after a given transformation to the probability distribution of the total work W done on the system:

$$\Delta F = -kT \ln\langle e^{-W/kT}\rangle, \tag{1}$$

where $\langle e^{-W/kT}\rangle = \int dW e^{-W/kT} P(W)$ is the average exponentiated work and k denotes the Boltzmann constant. This remarkable equality highlights the role of work fluctuations and provides a generic way of computing the free energy difference for any transformations, quasistatic or not, once the work distribution $P(W)$ is known. Most importantly, the Jarzynski relation allows us to determine ΔF even in the case of arbitrarily fast transformations, when irreversible thermodynamics is not applicable. Prior to the discovery of Eq. (1), the determination of the free energy difference in such far from equilibrium conditions was not believed to be possible [2]. Recently, the classical Jarzynski equality and its generalization by Crooks [3] have been successfully tested in single-molecule stretching experiments [4,5]. Later, the work distribution was recovered from repeated measurements of the mechanical work done on a colloidal particle [6].

The situation is much different at the *quantum* level. So far only studied theoretically, the Jarzynski equation holds in its classical form for closed quantum systems [7], while quantum corrections appear in the case of open systems due to the coupling to an external reservoir [8]. Further difficulties arise when considering the quantum-mechanical nature of work [9] and the question of how to measure it experimentally. It is evident that the classical definition of work as force times displacement cannot simply be taken over unmodified. It has recently been established that work is actually not an observable in the usual sense, as it is not given by an expectation value of some Hermitian work operator, but rather by a time-ordered correlation function [10]. On the other hand, the problem of how to determine quantum work still remains unsolved, explaining the absence of an experimental verification of the Jarzynski equality in the quantum domain.

We show in this Letter how to experimentally measure nonequilibrium work using a single ion in a segmented linear Paul trap. A unique property of ion traps is the possibility to study the quantum Jarzynski equality, as well as the quantum Crooks relation [11], for systems that are either isolated or coupled to tailored quantum environments using reservoir engineering [12,13]. Single ions trapped in radio frequency Paul traps are quantum nanosystems with remarkable properties. They can be laser cooled to very low temperatures, reaching to the motional ground state in the potential. Arbitrary quantum states can be prepared, manipulated, and measured with high fidelity [14,15]. Using the so-called electron shelving method, the quantum state is revealed with close to unity detection efficiency. The use of a segmented trap further allows for engineering a vast variety of time-dependent trapping potentials and hence the implementation of different model Hamiltonians. In the following, we generalize the detection methods for the motional state [16,17] in order to realize an efficient filter for vibrational number states. We show that trapped ions are not only good candidates for quantum computing, but may also allow us to experimentally approach the emergent field of quantum thermodynamics.

Quantum Jarzynski equality.—We begin by considering an isolated quantum system whose time-dependent Hamiltonian is varied from an initial value $H(0)$ to a final value $H(\tau)$. We denote by ϕ_n^t and E_n^t the respective eigenfunctions and eigenvalues of the Hamiltonian $H(t)$ at any given time t. We further assume that the system is initially thermalized at temperature T. The free energy difference ΔF between final and initial state is then given by the

Jarzynski equality, Eq. (1). The probability distribution of the random work W is given by [10]

$$P(W) = \sum_{m,n} \delta[W - (E_m^\tau - E_n^0)] P_{m,n}^\tau P_n^0, \quad (2)$$

where $P_n^0 = (1/Z_0)\exp(-E_n^0/kT)$ is the initial (thermal) occupation probability and $P_{m,n}^\tau$ are the transition probabilities between initial and final states n and m,

$$P_{m,n}^\tau = \left| \int dx_0 \int dx \phi_m^{\tau *}(x) U(x, x_0; \tau) \phi_n^0(x_0) \right|^2. \quad (3)$$

Here $U(x, x_0; \tau)$ is the propagator of the quantum system. The physical meaning of Eq. (2) is clear: the total work done during a given transformation of the Hamiltonian is obtained from the energy difference between final and initial eigenstates, $E_m^\tau - E_n^0$, averaged over all possible initial and final states. Equation (2) shows in addition that the randomness of the work stems from the initial thermal distribution P_n^0, and from the quantum nature of transitions between states, as described by $P_{m,n}^\tau$. The origin of work fluctuations is therefore of both thermodynamical and quantum-mechanical nature. The free energy difference can be evaluated for an arbitrary transformation of the Hamiltonian with the help of the Jarzynski relation, once the work probability density $P(W)$ has been determined. We next describe a method to realize a quantum nonequilibrium situation for a single ion in a linear Paul trap and how to measure its corresponding work distribution.

Harmonic ion trap.—Linear Paul traps are characterized by a strong dynamical confinement in the radial direction (yz plane) and electrostatically bound in the axial direction (x axis). With a radial confinement much stronger than the axial, we will restrict ourselves to the axial external degree of freedom. Near the center of the axial potential, the confinement is harmonic and the axial frequency ω can be varied in time by changing the control voltages [18]. The quantum state of motion along the axial direction can be described by the Hamiltonian

$$H(t) = \frac{p^2}{2M} + \frac{M}{2}\omega^2(t)x^2, \quad (4)$$

where M is the mass of the ion. For this simple potential, the nonequilibrium work distribution (2) can be studied analytically [19]. Besides the external, motional degree of freedom, the ion provides an internal, electronic level scheme. In our case, we consider a Λ system comprising the ground state $S_{1/2}$ and two excited states $P_{1/2}$ and $D_{5/2}$. The $P_{1/2}$ state rapidly decays into the $S_{1/2}$, thus providing a high spontaneous photon scatter rate used for fluorescence detection. Laser-induced transitions from the ground to the metastable $D_{5/2}$ state are induced on the narrow quadrupole transition [linewidth $\Gamma_D \ll \omega(t)$], if the spectral bandwidth of the $S_{1/2} - D_{5/2}$ exciting light field is small compared to the sideband structure. Coherent laser pulses on this narrow band optical transition allow us to exploit and to store the motional quantum state information in the internal quantum states.

The experimental *measurement protocol* of the work distribution consists of four consecutive steps.

(I) The ion is first prepared in a thermal state with mean phonon number, $\bar{n} = [\exp(\hbar\omega_0/kT) - 1]^{-1}$, in the electronic ground state S level by laser cooling and optical pumping. We prepare this state deterministically by resolved-sideband laser cooling [20] into the vibrational ground state $|n = 0\rangle$ and subsequently allowing the ion to heat up for a certain time without laser cooling. As the heating rate of the ion within the trap can be precisely measured, this procedure is favorable for very low values of $\bar{n}$. An alternative method, suited for higher values of $\bar{n}$, is Doppler cooling on the $S_{1/2}$ to $P_{1/2}$ transition. Varying the detuning of the cooling laser from the atomic resonance results in different thermal states with mean phonon numbers down to the Doppler limit.

(II) In the second step, we measure the initial phonon number n using the filtering scheme described in detail below. In this way, we determine the initial energy eigenstate E_n^0 (from spectroscopy measurements).

(III) In the third step, we transform the trap potential from an initial value $\omega(0)$ to a final value $\omega(\tau)$. This changing potential will in general modify the ion's motional state into a nonequilibrium state, while its internal state remains unaffected. For simplicity, we consider a linear variation of the axial potential $\omega^2(t)$ from $\omega^2(0)$ to $\omega^2(\tau)$. Figures 1 and 2 show a numerical evaluation, based on the results of Ref. [19], of the transition probabilities (3) and the work distribution (2) for realistic experimental parameters and different transformation times τ.

(IV) In the last step, we measure the new phonon number m using the filtering scheme and determine the final energy eigenstate E_m^τ. The distribution of the nonequilibrium work, $W = E_m^\tau - E_n^0$, Eq. (2), is then reconstructed by

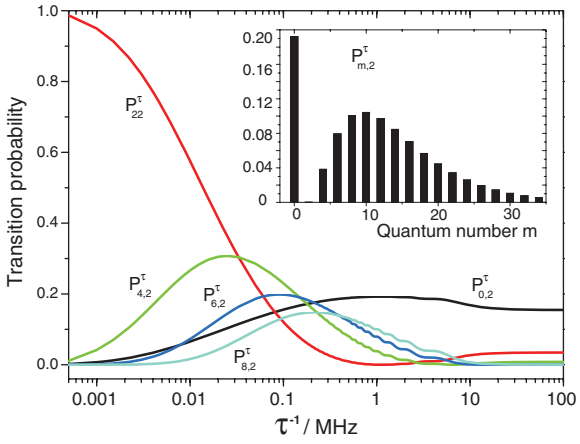

FIG. 1 (color). Transition probabilities $P_{m,n}^\tau$ for quantum numbers $n = 2$, $m = 0$–8 as a function of the inverse switching time τ^{-1} for a linear transformation of $\omega^2(t)$ with $\omega(0) = 0.1$ MHz and $\omega(\tau) = 3.0$ MHz. The inset shows the transition probabilities $P_{m,2}^\tau$ for a transformation time of $\tau = 1$ μs.

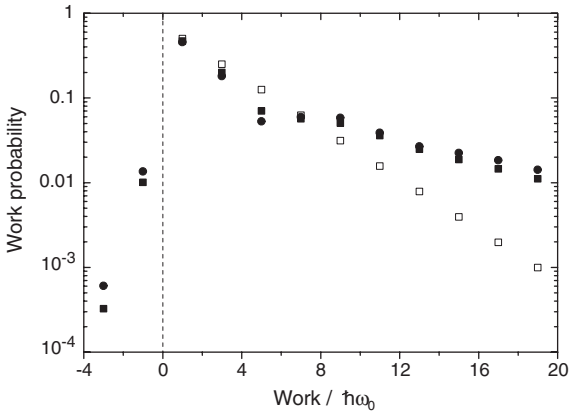

FIG. 2. Work probability distribution, Eq. (2), for a linear change of the harmonic potential $\omega^2(t)$ with $\omega(0) = 1$ MHz and $\omega(\tau) = 3$ MHz, for $\bar{n} = 1$. Shown are the adiabatic case $\tau \to \infty$ (□) and two fast transformations with $\tau = 0.1$ μs (■) and $\tau = 0.05$ μs (●). For the latter, deviations from the adiabatic case are clearly visible. Even negative work processes arise: the probability contribution at $W = -\hbar\omega_0$ mainly stems from the transition $n = 2 \to m = 0$, which occurs with probability $P^{\tau}_{2,0} = 10\%$ (for $\tau = 0.05$ μs). This contribution can be readily tested by the number state filter.

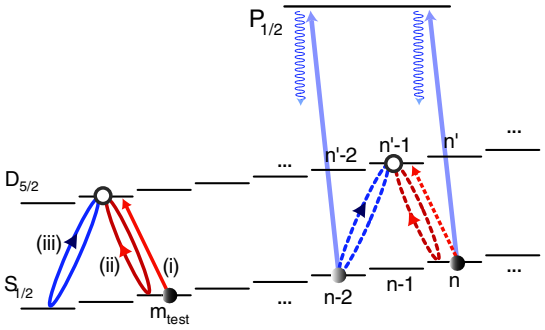

FIG. 3 (color online). Levels and transitions involved in the filtering scheme. Shown are transitions driven by the initial π pulse (i) and the successive 2π red sideband (ii) and 2π blue sideband pulses (iii), respectively. For $|m_{\text{test}}\rangle$, these pulses induce perfect π and 2π transitions between the metastable $D_{5/2}$ and the ground state level $S_{1/2}$ (left side). No fluorescence is observed when the ion is exposed to resonant light on the S to P transition. For any other $|n\rangle$, the transfer will be imperfect (dashed lines, right side) and there will be population in the S. Thus, the excitation to the P level is successful and we observe the emission of fluorescence photons.

repeating the measurement sequence. By evaluating Eq. (1) for adiabatic and nonadiabatic processes, we can verify the Jarzynski equality.

Filtering scheme.—A sequence of laser pulses on the narrow S to D transition is applied to the ion, coherently processing its internal and external degrees of freedom [21]. We tailor this pulse sequence such that the ion will end in the metastable $D_{5/2}$ state with certainty if the vibrational quantum state was $|m_{\text{test}}\rangle$. Subsequently, the ion is illuminated with light resonant to the $S_{1/2}$ to $P_{1/2}$ transition. If we observe no fluorescence, the ion is measured in the D state. However, for vibrational states different from $|m_{\text{test}}\rangle$, the laser pulse sequence leads to a superposition state, $\alpha|S\rangle + \beta|D\rangle$, such that there remains a nonvanishing probability $|\beta|^2$ of projecting the superposition into $|D\rangle$, and thus observing no fluorescence. We therefore repeat the procedure a few times such that a high quality of the filtering procedure is ensured. Considering the evolution of the quantum state itself, the influence of the above sequence reminds one of the operating principle of a filter: its projective "transmission" is unity for a certain input state $|m_{\text{test}}\rangle$ and zero otherwise. We adapt the laser pulse sequence timing to reach all relevant eigenstates $|n\rangle$ and $|m\rangle$ with the filter.

The crucial requirement for a well-suited filter procedure is to ensure the nonzero fluorescence outcome for all states but $|m_{\text{test}}\rangle$. It is sufficient to design the number state filter to have high suppression factors in a vicinity of $|m_{\text{test}}\rangle$, since $P^{\tau}_{m,n}$ is rapidly vanishing for high values of $|m - n|$. Varying the duration of the pulses, we use the following procedure; see Fig. 3. Starting from state $|S, m_{\text{test}}\rangle$, we apply a π pulse on the first red sideband leaving the ion in $|D, m_{\text{test}} - 1\rangle$. As the Rabi frequency $\Omega_{n,n'}$ between vibrational states n and n' depends on both initial n and final n', the laser pulse does not completely transfer other vibrational states to the D state. When we expose the ion to resonant light on the S to P transition, zero fluorescence is observed if the ion was in $|m_{\text{test}}\rangle$, but for other vibrational states there is a certain probability to observe fluorescence. To sharpen the discrimination, we apply 2π pulses on the red and blue sideband, respectively, interleaved by a fluorescence detection trial after each pulse. Again, the 2π pulses and detections leave the ion in the dark state $|D, m_{\text{test}} - 1\rangle$, but yield a nonzero fluorescence signal for all other states. This resembles so-called trapping states which have been investigated in cavity QED experiments [22]. This probability for zero fluorescence detection decreases exponentially with the number N of pulse or detection runs, as shown in Fig. 4, for a wide range of states $m_{\text{test}} \geq 3$. After $N = 10$ runs, all probabilities but for $|m_{\text{test}}\rangle$ drop below 5%. As no coherence is remaining after each detection interval, the scheme has modest requirements on the phase stability. The driving laser needs preserving phase only for one single 2π pulse, but not during the entire filter sequence. The two lowest vibrational states are treated even simpler: For $m_{\text{test}} = 0$, a π pulse on the carrier transition brings the ion into $|D, 0\rangle$. Successive red sideband π pulses do not affect this state, but fluorescence is observed with nonzero probability for all other states. This scheme has been proposed for stochastic cooling [16,17]. For $m_{\text{test}} = 1$, the carrier pulse is simply replaced by a red sideband π pulse $|S, 1\rangle \to |D, 0\rangle$. Then the procedure continues as for $m_{\text{test}} = 0$. The length of the pulses is specific for each choice of m_{test}; varying the pulse allows us to access measurements over a wide range of vibrational levels.

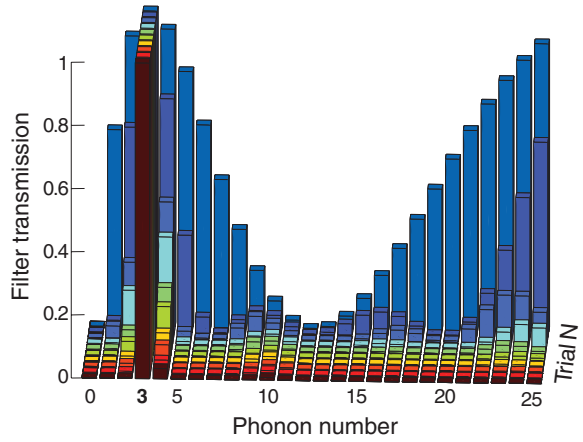

FIG. 4 (color). Probability for detection of zero fluorescence, called filter transmission, after $N = 1, 2, \ldots, 10$ pulse or detection trial cycles. With increasing number of trials (from back to front) the Fock state to be tested for, here $m_{\text{test}} = 3$, always remains dark under excitation with resonant light on the $S_{1/2}$ to $P_{1/2}$ transition. All other states show an exponential decrease of zero fluorescence detection probability.

To estimate the time taken by one experimental cycle from preparation to detection, we assume a few 10 μs for sideband pulses and a few hundred μs fluorescence detection time; one cycle with multiple filtering iterations will then take less than 10 ms, short compared to the lifetime of the D state (1.2 s for $^{40}Ca^{+}$). To also assure that unwanted dissipative effects do not introduce errors, the trap's heating rate needs to be smaller than 1 phonon within the cycle time. Traps with much lower rates have been reported. The statistical error of the values $P^{\tau}_{m,n}$ is further reduced by repeating the measurement sequence.

Designing the bath properties and the potential shape.— As discussed before, single trapped ions are highly isolated from external reservoirs. However, it has been shown theoretically [12], and also in first experiments [13], that it is possible to introduce a coupling between the ion and an artificially laser-induced bath. The variation of laser frequencies and intensities allows one to engineer the coupling and select the master equation describing the motion of the ion. Here, the interaction is mediated by sideband transitions between the $S_{1/2}$ and $D_{5/2}$ level; see Fig. 3. For example, a zero-temperature reservoir can be implemented by a light field tuned to the (cooling) red sideband transition. A large variety of other tailored reservoirs, such as squeezed baths, can be generated as well. Within the framework of this proposal, it is therefore possible to investigate nonequilibrium transformations of open systems with tailored couplings between system and reservoir. In particular, the distribution of the heat exchanged with a reservoir can be determined using the same measurement protocol by keeping the trap frequency constant, that is, performing no work.

Exploiting the flexibility provided by a segmented trap design, it is moreover feasible to investigate anharmonic trapping potentials. Especially in the situation of a nonadiabatic transport along the segments of the trap [18], the ion is shifted out of the harmonic center of the electric potential and experiences nonharmonic potential contributions [20]. For future work, one might include forces by laser light on the ion, which depend on its internal electronic state, investigating the influence of quantum thermodynamics on qubit gate operations [23].

In conclusion, we have shown how the quantum Jarzynski equality can be experimentally investigated using a single ion in the time-varying electrical potential of a Paul trap, for both open and closed quantum systems. Our proposal is based on the state of the art in many laboratories working with single trapped ions and uses realistic parameters. Experiments with such a device would allow us to shine more light on the amazing interplay of quantum mechanics and thermodynamics.

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