Work fluctuations for Bose particles in grand canonical initial states

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We consider bosons in a harmonic trap and investigate the fluctuations of the work performed by an adiabatic change of the trap curvature. Depending on the reservoir conditions such as temperature and chemical potential that provide the initial equilibrium state, the exponentiated work average (EWA) defined in the context of the Crooks relation and the Jarzynski equality may diverge if the trap becomes wider. We investigate how the probability distribution function (PDF) of the work signals this divergence. It is shown that at low temperatures the PDF is highly asymmetric with a steep fall-off at one side and an exponential tail at the other side. For high temperatures it is closer to a symmetric distribution approaching a Gaussian form. These properties of the work PDF are discussed in relation to the convergence of the EWA and to the existence of the hypothetical equilibrium state to which those thermodynamic potential changes refer that enter both the Crooks relation and the Jarzynski equality.

I. INTRODUCTION

In recent years fluctuation theorems that allow us to infer equilibrium properties of a system from nonequilibrium processes have attracted considerable attention. The Jarzynski equality (JE) [1] reading

$$\langle e^{-\beta w} \rangle = e^{-\beta \Delta F} \tag{1}$$

provides a prominent example of these relations. It relates the free energy change, ΔF, to the statistics of work, w, that is performed by a time-dependent force acting on a system that initially is prepared in a canonical equilibrium state at the temperature $T = 1/k_B \beta$. The weight with which the average of the exponentiated work is performed is determined by the probability density function (PDF) of work, $p(w)$. It represents the frequency of outcomes from independent runs of the same force protocol starting in equilibrium at the same temperature. The free energy change ΔF gives the difference between free energies of the initial state and of a hypothetical thermal equilibrium state of the considered system at the initial temperature T with clamped forces at the values at the end of the force protocol. First, the JE was found for classical systems and later on confirmed for quantum mechanical systems [2–8].

A similar form of the JE holds for grand canonical initial states (GCIs), which allow both energy and particle number fluctuations. It then takes the form [9–11]

$$\langle e^{-\beta w} e^{\beta \mu n} \rangle_{gc} = e^{-\beta \Delta \Phi}, \tag{2}$$

where w and β are defined as above. Further, μ denotes the chemical potential of the reservoir, and n the difference of the particle numbers at the end and at the beginning of the force protocol. Similarly as the work w, also the particle number change n is a random quantity. These random outcomes are described by a joint PDF $p(w,n)$. Here, $\Delta \Phi = \Phi_f - \Phi_i$ is given by the difference of the grand canonical potentials Φ_i and

Φ_f, which, respectively, correspond to the initial equilibrium state and to a hypothetical equilibrium state at the inverse temperature β and chemical potential μ with clamped force values at the end of the force protocol.

While temperature is universally confined to positive values, the upper admissible bound of the chemical potential is system dependent. To illustrate this fact we consider a system of noninteracting identical particles, for which the average particle number in a grand canonical potential at inverse temperature β and chemical potential μ is determined by [12]

$$N_{av} = \sum_\epsilon \frac{1}{e^{\beta(\epsilon - \mu)} \mp 1}, \tag{3}$$

where the sum is performed over the single particle energy spectrum, and the $+$ and $-$ signs refer to Fermi-Dirac and Bose-Einstein statistics, respectively. Considering the case of a single particle spectrum, which is bounded from below by the ground state, for fermions, the $+$ sign guarantees the convergence of the sum for any real value of the chemical potential. However, for a system made of bosons, this sum only converges if the chemical potential is smaller than the ground state energy. With the divergence of the average particle number, the grand canonical partition function diverges and accordingly the grand canonical potential becomes negatively divergent. In the context of the fluctuation theorem given by Eq. (2), this implies that the averaged exponentiated linear combination of work and number change, that is, the left-hand side of Eq. (2), diverges for bosonic systems under the action of protocols which lead to a lowering of the single particle ground state energy below the level of the chemical potential of the initial grand canonical equilibrium state.

The purpose of this work is to address this issue of the fluctuation theorem for GCIs, Eq. (2). For a concrete discussion, we consider noninteracting bosons residing in

a three-dimensional harmonic potential. Such systems have been treated as theoretical models of trapped atomic gases undergoing Bose-Einstein condensation [13–15]. Section II is devoted to a brief introduction to the considered model system and the required procedure for obtaining the work statistics. In Sec. III, we present a symmetry relation of the Crooks-Tasaki type for GCIs and point out the condition of its existence. Section IV specifies the work protocol to be considered in this work. The analytic properties of the corresponding characteristic function are discussed in Sec. V. The PDFs for extreme temperature regimes are analytically obtained in Sec. VI. It is shown that the PDF at very low temperatures has a long tail being responsible for the divergence of the exponentiated work average (EWA). In Sec. VII, the convergence of this average for general temperatures is examined by a numerical evaluation of the PDFs, and discussed in relation to the existence of the hypothetical equilibrium state.

II. SYSTEM

We consider N identical Bose particles of mass m moving in a three-dimensional symmetric harmonic trap with a curvature changing in time t. The governing Hamiltonian at an instantaneous time t reads

$$\mathcal{H}(t) = \sum_{i=1}^{N} \left[\frac{\mathbf{p}_i^2}{2m} + \frac{1}{2} m\omega^2(t) \mathbf{x}_i^2 \right]. \tag{4}$$

This Hamiltonian is widely studied as a simple model of the Bose-Einstein condensation [16–18]. However, the feature of nonequilibrium work statistics to be drawn here is not specifically related to the condensation transition. The single particle energy spectrum at time t is given by

$$\epsilon_\ell(t) = (\ell_x + \ell_y + \ell_z + 3/2)\hbar\omega(t) \tag{5}$$

with a set of nonnegative integers $\ell \equiv (\ell_x, \ell_y, \ell_z)$.

A. Equilibrium properties

This many particle system is supposed to initially stay in equilibrium with a reservoir having prescribed values of the chemical potential μ and the inverse temperature β. For this initial equilibrium state the initial grand canonical partition function and the initial average number of particles are determined by

$$\mathcal{Q}_i = \prod_\ell [1 - z e^{\beta\epsilon_\ell(0)}]^{-1},$$

$$N_{av} = \sum_\ell \frac{1}{z^{-1}e^{\beta\epsilon_\ell(0)} - 1}, \tag{6}$$

where $z = e^{\beta\mu}$ denotes the fugacity. The condensation fraction is given by N_0/N_{av} with N_0 denoting the particle occupancy in the ground state, $N_0 = 1/(z^{-1}e^{\beta\epsilon_0(0)} - 1)$. For sufficiently large N_{av}, the condensation curve falls onto the critical line, $N_0/N_{av} = 1 - (T/T_c^{(0)})^3$ if $T \leqslant T_c^{(0)}$ and $N_0/N_{av} = 0$, otherwise, with the critical temperature $T_c^{(0)} = [N_{av}/\zeta(3)]^{1/3}(\hbar\omega/k_B)$, where $\zeta(3) \approx 1.202$. When the number of particles is finite, the transition becomes smeared out and the critical temperature is modified as [18]

$$T_c/T_c^{(0)} = \left(1 - 0.7275 N_{av}^{-1/3}\right). \tag{7}$$

In the sequel we shall use T_c as temperature unit.
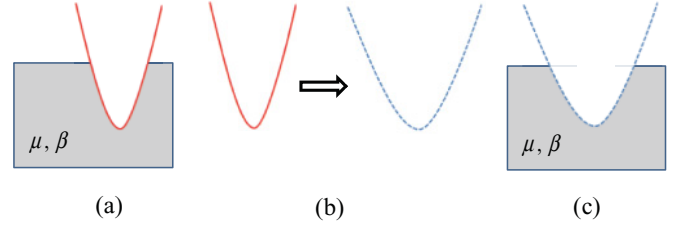

FIG. 1. (Color online) (a) Grand canonical initial states of Bose particles in a harmonic potential that are in equilibrium with a reservoir of chemical potential μ and inverse temperature β. (b) The system is decoupled from the reservoir and then work is performed by changing the curvature of the potential (expansion of the potential in the figure). At the end of the protocol indicated by the dashed parabola, the particles will stay out of equilibrium. (c) Provided that the hypothetical equilibrium of the system with the finally reached potential curvature exists for the initial temperature and chemical potential, this state can in principle be reached by weakly coupling a grand canonical heat bath at the initial inverse temperature β and chemical potential μ to the system. We emphasize that this last step is not a part of the protocol but only serves as an illustration of the resulting expression for the exponential work average.

B. Doing work

We here sketch a gedanken experiment that elucidates the relevant steps implied by Eq. (2). Figure 1(a) depicts the initial equilibrium state of the considered many particle system in weak contact with a reservoir that may exchange particles and energy with the system controlled by the chemical potential μ and the inverse temperature β. The grand potential $\Phi_i = -k_B T \ln \mathcal{Q}_i$ for this initial state is determined by the reservoir parameters as well as by the microscopic details, such as the initial curvature of the potential defining the oscillation frequency ω. Once the system has approached the grand canonical equilibrium state, it is decoupled from the reservoir, its energy and particle number are determined, and afterward the curvature of the trap is changed according to a designed protocol. Finally energy and particle number are again measured. The change of energy determines the work w performed on the system in this particular realization. The work w and the particle number change n are finally registered. This procedure must be repeated many times, always starting from the same equilibrium state and following the same protocol such that the joint probability $p(w,n)$, or directly the exponential average $\langle e^{-\beta(w-\mu n)} \rangle$, can be estimated.

Note that in general the state of the system reached at the end of the protocol is out of equilibrium, even if the forcing is adiabatically slow as in the present study. Since the system is isolated from the heat bath during the protocol, transitions between the instantaneous eigenstates of the Hamiltonian do not occur for slow driving. Hence, the occupation probabilities of these states remain constant while the corresponding eigenvalues undergo changes. States with energy eigenvalues $\epsilon_\ell(t)$ are then populated with weights that are determined by Boltzmann factors at the initial energies, $\exp[-\beta\epsilon_\ell(0)]$, rather than at the actual energies, $\exp[-\beta\epsilon_\ell(t)]$. Nevertheless, according to Eq. (2) the exponential average of work coincides with the ratio of two partition functions. The denominator is given by the partition function of the initial system and hence determined by the initial trap curvature as well as by β and μ.

The numerator refers to a *hypothetical* grand canonical equilibrium state of the system with the *final* trap curvature and the *initial* temperature and chemical potential; see Fig. 1(c).

There is no restriction for the finally reached trap curvature. In particular, the trap may be widened to such an extent that the ground state energy falls below the chemical potential of the initial state. Then the hypothetical equilibrium state is not properly defined and formally leads to a divergent grand canonical partition function and a negative, divergent grand canonical potential. At the same time the exponential average of $-\beta(w - \mu n)$ also diverges.

III. CHARACTERISTIC FUNCTION

Along with the JE, the Tasaki-Crooks relation [2,19] reading

$$e^{-\beta w} p(w) = e^{-\beta \Delta F} p_b(-w) \qquad (8)$$

provides a connection between the PDFs $p(w)$ of the original process and the PDF $p_b(w)$ of the backward process for systems initially prepared in a canonical equilibrium state. Here the backward process starts at the hypothetical equilibrium state retracing the force protocol from its final to the initial value of the forward process. From the correspondence between Eq. (1) and Eq. (2), one may expect the existence of a Crooks-Tasaki relation for the GCI of the form

$$e^{-\beta(w-\mu n)} p(w,n) = e^{-\beta \Delta \Phi} p_b(-w, -n). \qquad (9)$$

Integrating over w and summing over all possible values of n, we indeed obtain the generalized form of JE for the GCI, as given in Eq. (2).

The proof of this relation may be obtained in an analogous way as for the canonical case [2,5,8] based on the characteristic function $G(u,v)$. It is given as the Fourier transform of the joint PDF $p(w,n)$ with respect to both w and n and can be expressed as a two-time correlation function:

$$G(u,v) = \sum_{n=-\infty}^{\infty} \int dw\, e^{iuw+ivn} p(w,n)$$
$$= \langle e^{iu\mathcal{H}_H(\tau)+iv\mathcal{N}_H(\tau)} e^{-iu\mathcal{H}(0)-iv\mathcal{N}(0)} \rangle_{\rho_i}, \qquad (10)$$

where the average $\langle X \rangle_{\rho_i} = \mathrm{Tr} X e^{-\beta\mathcal{H}(0)} e^{\beta\mu\mathcal{N}(0)}/\mathcal{Q}_i$ is performed over the initial grand canonical state with $\mathcal{Q}_i$ being the grand canonical partition function of the initial state. Here the index H indicates operators in the Heisenberg picture given by $O_H(\tau) = U^\dagger(\tau,0)O(\tau)U(\tau,0)$. Based on the microreversibility of the time evolution, $U(\tau,t) = \Theta^\dagger U_b(t - \tau,0)\Theta$, relating the time evolution U of the original process to the time evolution U_b for the reversed protocol by means of the antiunitary time-reversal operator Θ [8], one obtains the following relation between characteristic functions of the forward and the backward process:

$$\mathcal{Q}_i G(u,v) = G_b(-u + i\beta, -v - i\beta\mu)\mathcal{Q}_f. \qquad (11)$$

Taking the inverse Fourier transform of this relation leads to Eq. (9), where $\beta\Delta\Phi = -(\ln \mathcal{Q}_f - \ln \mathcal{Q}_i)$.

IV. PROTOCOL

The protocol according to which the trap curvature is changed specifies the time-dependent change of the frequency $\omega(t)$ within a time interval $[0,\tau]$. In the present investigation we assume that it consists in an adiabatically slow change connecting the boundary values

$$\omega(0) = \omega, \quad \omega(\tau) = (1 + \gamma)\omega. \qquad (12)$$

A positive (negative) value of γ indicates that the system is compressed (expanded) during the protocol. With the adiabatic variation of the frequency the occupation numbers n_ℓ of the ℓ's single particle eigenstates remain unchanged such that the time evolution operator takes the form

$$U(t,0) = \sum_{\{n_\ell\}} |\{n_\ell\},t\rangle\langle\{n_\ell\},0|, \qquad (13)$$

where $|\{n_\ell\},t\rangle = |n_0,n_1,\dots;t\rangle$ with $\sum_\ell n_\ell = N$ is an eigenfunction of the N-particle Hamiltonian (4), and hence a solution of

$$\mathcal{H}(t)|\{n_\ell\},t\rangle = E(t)|\{n_\ell\},t\rangle,$$
$$E(t) = \sum_\ell \epsilon_\ell(t)n_\ell. \qquad (14)$$

The corresponding N-particle eigenvalue $E(t)$ is expressed in terms of the single-particle energy eigenvalues $\epsilon_\ell(t)$ given by Eq. (5) and the occupation numbers n_ℓ of these states. We consider this adiabatic protocol for the sake of simplicity. Although the shape of the work PDF will depend on the details of the specific protocol, their relevant qualitative features leading to a diverging EWA are expected to be independent of those details.

V. ANALYTIC PROPERTIES OF THE CHARACTERISTIC FUNCTION

Using Eqs. (13) and (14), we obtain the Hamiltonian and the number operator in the Heisenberg picture at the final time τ of the protocol

$$\mathcal{H}_H(\tau) = \sum_{\{n_\ell\}}{}' E(\tau)|\{n_\ell\},0\rangle\langle\{n_\ell\},0|,$$
$$\mathcal{N}_H(\tau) = \sum_{\{n_\ell\}}{}' n_\ell|\{n_\ell\},0\rangle\langle\{n_\ell\},0| = \mathcal{N}(0), \qquad (15)$$

where $\sum_{\{n_\ell\}}'$ denotes the summation under the constraint $\sum_\ell n_\ell = N$. As a consequence of the number conservation for the considered protocol, the characteristic function becomes independent of the variable v which is conjugate to the number change n. Hence, we get $G(u,v) = G(u)$, implying $p(w,n) = p(w)\delta_{n,0}$ for the joint probability.

Since all operators entering the characteristic function (10) under the trace are diagonal with respect to the eigenbasis of the initial Hamiltonian, all of them commute with each other and it therefore is straightforward to write

$$G(u) = \mathcal{Q}_i^{-1} \sum_{N=0}^{\infty} \sum_{\{n_\ell\}}{}' \prod_\ell e^{iu\epsilon_\ell(\tau)n_\ell} e^{-i(u-i\beta)\epsilon_\ell(0)n_\ell} z^{n_\ell}$$
$$= \mathcal{Q}_i^{-1} \prod_{l=0}^{\infty}[1 - z e^{(iu\gamma-\beta)\hbar\omega(l+3/2)}]^{-g(l)}. \qquad (16)$$

Here the product on the right-hand side of the first line extends over the triple index $\ell = (\ell_x,\ell_y,\ell_z)$. The restriction in the

second sum on the right-hand side of the first line is lifted by the first sum over N. Therefore all sums over the n_ℓs can be performed in closed form leading to the expression in the second line. Because of the degeneracy of the single particle energies $\epsilon_\ell(t)$ having the same value for a given $l = \ell_x + \ell_y + \ell_z$, see Eq. (5), the product in the second line can be taken for $l = 0,1,2,\ldots$. The degree of the degeneracy of the single particle energies (5) is given by $g(l) = (l+1)(l+2)/2$.

Since u and γ only enter in the combination $u\gamma$, the work PDF, which is given by the inverse Fourier transform of the characteristic function through Eq. (10), depends on w and γ in terms of the ratio w/γ:

$$p(w) = \frac{1}{|\gamma|} f(w/\gamma), \qquad (17)$$

where $f(x) = (2\pi)^{-1} \int_{-\infty}^{\infty} d\xi \, e^{-ix\xi} G(\xi)$ with $\xi = u\gamma$. This leads to a symmetry relation between the work PDFs for compression ($\gamma > 0$) and expansion ($\gamma < 0$):

$$p(w)|_\gamma = p(-w)|_{-\gamma}. \qquad (18)$$

In presenting numerical results of the PDFs, we only consider the expansion case for a specific value of γ. However, thanks to the relations Eqs. (17) and (18), PDFs for other cases not shown here can be visualized.

It is worthwhile here to mention that the convergence of $\langle e^{-\beta w} \rangle_{gc}$ is determined by the structure of the singularities of the characteristic function. The poles of $G(u)$ are located in the complex u plane, where $G(u)^{-1} = 0$, yielding

$$u_{l,n} = \frac{-i\beta[\epsilon_l(0) - \mu] + 2\pi n}{\epsilon_l(0)\gamma}, \quad l = 1,2,\ldots,$$
$$\text{and} \quad n = 0, \pm 1, \pm 2, \ldots. \qquad (19)$$

If $\gamma > 0$, then all poles are located in the lower half plane [$\text{Im}(u_{l,n}) < 0$] for $\beta > 0$, because $\epsilon_l(0) > \mu$. Therefore a divergence of $G(u_{l,n}) = \langle e^{iu_{l,n}w} \rangle_{gc}$ could only occur in the unphysical regime of negative temperatures. On the other hand, for $\gamma < 0$ all pole positions are at positive imaginary values, $\text{Im}(u_{l,n}) > 0$. If the inverse temperature lies below the pole position $\text{Im}(u_{0,0}) = \beta[\epsilon_l(0) - \mu]/[\epsilon_l(0)|\gamma|]$ the EWA $\langle e^{-\beta w} \rangle_{gc}$ is finite. The opposite case, $\text{Im}(u_{0,0}) > \beta$, leads to a divergent EWA. Hence the condition for a finite EWA becomes

$$(1 + \gamma)\epsilon_0(0) > \mu. \qquad (20)$$

Since $(1 + \gamma)\epsilon_0(0) = \epsilon_0(\tau)$ is the single particle ground state in the trap at the end of the protocol, this condition is identical with the condition of the existence of the hypothetical equilibrium state as explained at the end of Sec. II.

So far, we have considered the chemical potential and the temperature as independent thermodynamic variables, characterizing the initial state. In many practical applications it is more convenient to consider the average particle number as prescribed, instead of the chemical potential. As a consequence, the chemical potential then becomes a function of the average particle number and temperature, and also the existence of a finite EWA then depends on temperature.

VI. ASYMPTOTIC RESULTS

In the extreme temperature limits, closed analytic forms of the characteristic function of work can be obtained. Simple analytic expressions for the work PDF follow if additionally the change of the trap curvature is sufficiently small.

A. High temperatures

At high temperatures, the ground state energy is much smaller than the thermal energy, $\epsilon_0 \ll k_B T$, and hence $\beta\epsilon_0$ serves as an expansion parameter. The mean number of the particles and the initial grand partition function then are approximately given by

$$N_{av} \approx z \sum_{l=0}^{\infty} g(l) e^{-\beta\epsilon_l(0)} \approx \frac{e^{\beta\mu}}{(\beta\epsilon_0)^3},$$
$$\ln \mathcal{Q}_i = -\sum_{l=1}^{\infty} g(l) \ln[1 - z e^{-\beta\epsilon_l(0)}] \approx N_{av}. \qquad (21)$$

The second line gives the equation of states of an ideal gas. In the high temperature regime, positively or negatively large values of the work have highest probability for widening or narrowing, respectively, the trap. It is therefore sufficient to consider the contributions of the small values of u to the characteristic function yielding

$$\ln G_{ht}(u) = \frac{e^{\beta\mu}}{(\beta\hbar\omega)^3} \left[-1 + \frac{1}{(1 - i\gamma u/\beta)^3} \right]. \qquad (22)$$

This asymptotic high temperature result agrees with the characteristic function of work for a classical system of noninteracting particles in a harmonic trap that initially stays in equilibrium with a reservoir and then experiences an adiabatic change of the trap curvature; see the Appendix. The PDF corresponding to the high temperature limit characteristic function is not known analytically. However, in the case of small curvature changes, i.e., $|\gamma| \ll 1$, one can perform an expansion in powers of γ, leading to

$$\ln G_{ht}(u) \approx \frac{e^{\beta\mu}}{(\beta\hbar\omega)^3}(3i\gamma u/\beta - 6\gamma^2 u^2/\beta^2). \qquad (23)$$

Within this approximation the work average and its standard deviation become

$$\langle w \rangle = 3N_{av}\gamma/\beta, \qquad (24)$$
$$\sigma_w^2 = 4\gamma\langle w \rangle/\beta.$$

The corresponding Gaussian distribution function of the work is then given by

$$p(w) = \frac{1}{\sqrt{2\pi\sigma_w^2}} \exp\left[-\frac{(w - \langle w \rangle)^2}{2\sigma_w^2} \right]. \qquad (25)$$

As shown in Fig. 2(a), this PDF obtained for high temperatures and small curvature deformations is in good agreement with the numerical evaluation of the PDF to be detailed in the next section. In the high temperature approximation, Eq. (25), the EWA becomes

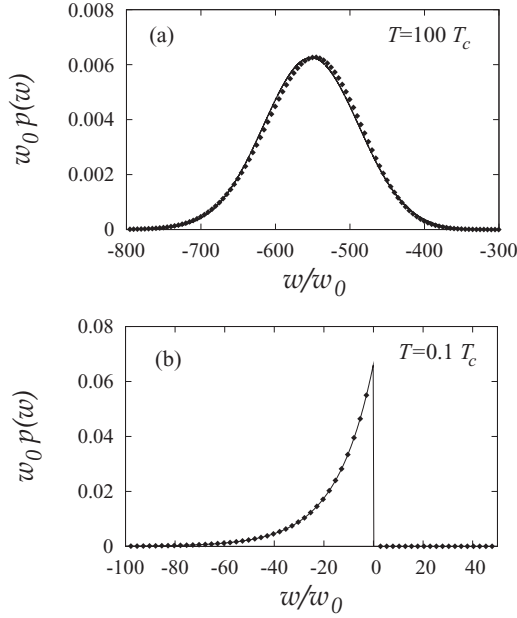$$\ln\langle e^{-\beta w} \rangle_{gc} \approx -3N_{av}\gamma(1 - 2\gamma). \qquad (26)$$

FIG. 2. Probability density functions of the work (in units of $w_0 \equiv \hbar\omega$) for $\gamma = -0.1$ and $N_{av} = 100$. (a) High temperature behavior at $T = 100 T_c$, where the line is given by the analytic form, Eq. (25). The panel (b) displays the low temperature behavior at $T = 0.1 T_c$. The analytic result of Eq. (30) is depicted by the solid line. For comparison, we present the numerical results (points) obtained by using Eqs. (10) and (16), which are well consistent with the analytic forms in the respective temperature limits.

On the other hand, the grand canonical partition function of the hypothetical equilibrium state reads, up to the second order in γ,

$$\ln \mathcal{Q}_f = -\sum_l g(l) \ln[1 - z e^{-\beta(1+\gamma)(l+\epsilon_0)}]$$
$$\approx N_{av}(1 - 3\gamma + 6\gamma^2).$$

This, together with $\mathcal{Q}_i$ in Eq. (21), leads to $\ln[\mathcal{Q}_f/\mathcal{Q}_i] = \langle e^{-\beta w}\rangle_{gc}$, validating the Jarzynski equality, Eq. (2), within the Gaussian approximation. In passing we note that this need not be expected since the Gaussian approximation often fails to describe the wings of the work distribution with sufficient accuracy to conform with the Jarzynski equality [20].

B. Low temperatures

At sufficiently low temperatures, the behavior of the system is determined by the ground state energy level ($l = 0$). The characteristic function, Eq. (16), can be written as

$$G(u) \approx \frac{1 - z e^{-\beta\epsilon_0(0)}}{1 - z e^{-\beta\epsilon_0(0)} e^{iu\gamma\epsilon_0(0)}}, \qquad (27)$$

which yields a distribution of work values $w_n = \gamma\epsilon_0(0)n$ with probabilities p_n given by

$$p_n = (1 - z e^{-\beta\epsilon_0(0)}) z^n e^{-\beta\epsilon_0(0)n}. \qquad (28)$$

For the EWA one obtains from this work distribution

$$\langle e^{-\beta w}\rangle = (1 - e^{-\beta[\epsilon_0(0)-\mu]})/(1 - e^{-\beta[\epsilon_0(\tau)-\mu]}). \qquad (29)$$

The right-hand side of this equation coincides with the ratio of the grand canonical partition functions (6) at the end and the

beginning of the protocol, each of which being evaluated at sufficiently low temperatures such that other than the ground state contributions can be neglected. Hence, the Jarzynski equality also holds for the approximate low temperature work PDF (28). Note that any protocol ending with a ground state $\epsilon_0(\tau)$ which lies below the chemical potential μ formally leads to the nonsensical result of a negative EWA, indicating the actual divergence of the sum representing this average. Finally we note that for small values of the deformation parameter γ, the spacing between the allowed values of the work becomes smaller, suggesting to approximate the discrete work distribution by a continuous PDF which can be written as a generalized exponential PDF

$$p(w) = \frac{1}{|\langle w\rangle|} e^{-w/\langle w\rangle} \Theta(\gamma w), \qquad (30)$$

where $\Theta(x)$ denotes the Heaviside step function. The average work $\langle w\rangle$ follows from Eq. (28) as

$$\langle w\rangle = \gamma\epsilon_0(0) \frac{z e^{-\beta\epsilon_0(0)}}{1 - z e^{-\beta\epsilon_0(0)}}. \qquad (31)$$

The sign of the average work is determined by that of γ: Compressing the trap leads to positive, widening to negative average work. In accordance with Eq. (20), there is no restriction for the existence of the EWA in the compression case. For widening though, the characteristic scale on which the exponential distribution decays must be small enough that the increase of the exponentiated work $e^{-\beta w}$ for negative w is overcompensated and a finite EWA exists. The quantitative condition $\beta|\langle w\rangle| < 1$ following from Eq. (31) is identical with the condition implied by the existence of the hypothetical equilibrium state, $\epsilon_0(0) > \mu$.

VII. NUMERICAL RESULTS

In order to investigate the behavior of the work PDFs in the intermediate temperature regime, we numerically evaluated the characteristic function in Eq. (16) and obtained the work PDF by means of an inverse transformation of Eq. (10). For that purpose, we used the fast Fourier transform algorithm proposed by Danielson and Lanczos [21]. Figure 3(a) displays the PDFs for $\gamma = -0.1$ and $N_{av} = 100$ at various temperatures. At $T = 1.7 T_c$ (see the curve labeled by E), the work PDF exhibits a decay that, on the logarithm scale, is faster than linear. At lower temperatures, the PDF becomes negatively skewed, developing a more pronounced tail in the region of large negative work. At the extremely low temperature, $T = 0.1 T_c$ (labeled by A in Fig. 3), the PDF approaches the generalized exponential distribution, Eq. (30). The overall feature of this temperature dependence is confirmed also for smaller average particle numbers $N_{av} = 10$, the PDFs of which are shown in the panel (b).

As mentioned, the divergence of the EWA sets in when the ground state energy at the end of the work protocol is identical to the chemical potential of the reservoir. Figure 4(a) displays the critical line determined by $\gamma_c\epsilon_0 = \mu - \epsilon_0$ for a given average number of particles. The hypothetical equilibrium state exists only in the region II ($\gamma > \gamma_c$) of Fig. 4(a). This is the case when the work is done by compressing the potential ($\gamma > 0$) but also in the limit of high temperatures. On the other
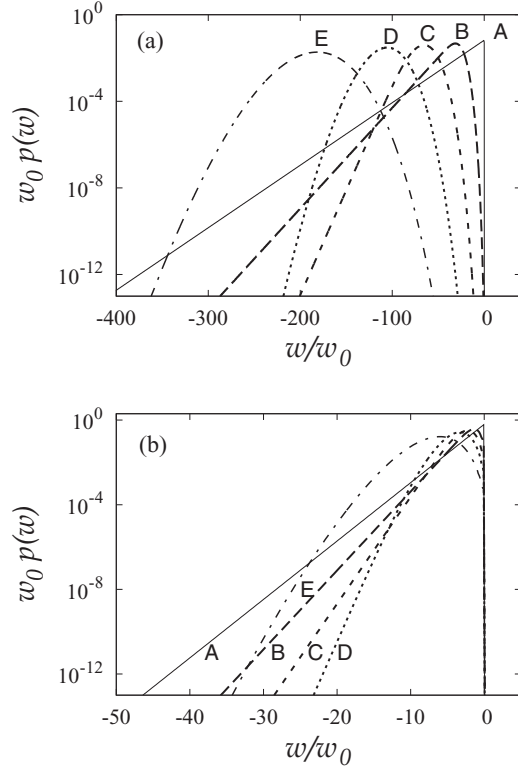
FIG. 3. Probability distribution functions of the work (in units of $w_0 \equiv \hbar\omega$) for the potential expansion $\gamma = -0.1$. The panels (a) and (b) are for $N_{av} = 100$ and $N_{av} = 10$, respectively. The curves in each panel are obtained for various temperatures $T/T_c = 0.1$ (A), 0.7 (B), 0.9 (C), 1.1 (D), and 1.7 (E), which correspond to the crosses in Fig. 4(a) below. At the highest temperature, the PDF for $N_{av} = 100$ is approximately Gaussian. With decreasing temperature, the asymmetry of the PDF becomes more pronounced in the form of a heavier tail in the negative work region, and finally converges into an exponential PDF (see the curve A). For a system of smaller number of particles, the PDF is more asymmetric already at higher temperatures and becomes even more skewed at low temperatures.

hand, upon expanding the potential, the EWA diverges at low temperatures. The key signature of this divergence is reflected in the tail of the PDF at negative work values. This property of the PDF can be conveniently quantified by the parameter

$$\alpha = -\beta + \left(\frac{\partial \ln p(w)}{\partial w} \right)_{w=w_c}, \qquad (32)$$

which determines the convergence rate of the integral $\int_{w_c}^{\infty} dw\, e^{-\beta w} p(w)$. In our numerical investigation we chose w_c as the negative work for which the probability reaches the smallest possible value $p(w_c) = 10^{-13}$ within the numerical precision of our calculations. Figure 4(b) displays the temperature dependence of the convergence factor α. In presenting the results, we show only the α values for PDFs whose negative work tails approach an exponential behavior such that a reliable value of α results. In the high temperature region the α values are negative. Positive α values, which occur in the low temperature regime, indicate the divergence of $\langle e^{-\beta w} \rangle_{gc}$. The regions of positive α indeed coincide with the instability regions given in Fig. 4(a).
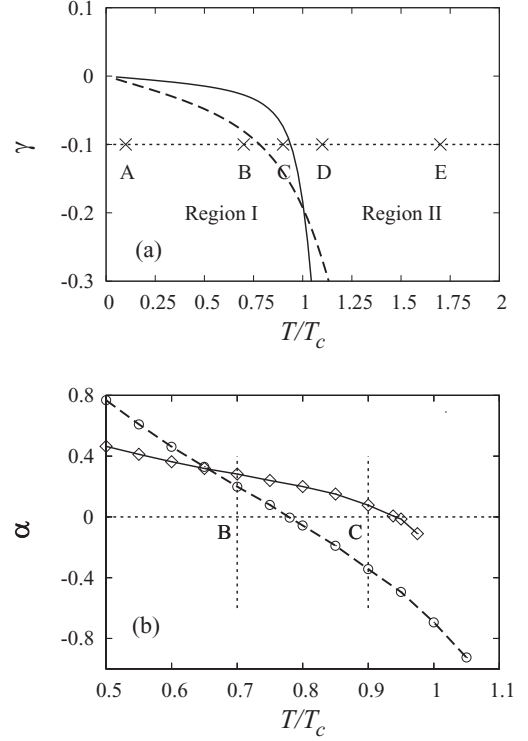

FIG. 4. (a) Phase diagram depicting the region of existence of the hypothetical grand canonical state in the γ-T/T_c plane. The borders separating the two regions of existence (II) and nonexistence (I) are depicted by a solid line for $N_{av} = 100$ and by a dotted line for $N_{av} = 10$. Compression ($\gamma > 0$) belongs to the region II irrespective of the temperature. If the potential is expanded the hypothetical equilibrium ceases to exist and region I is entered provided the temperature is low enough. At the expansion factor $\gamma = -0.1$ (dotted horizontal line), the region I is entered at $T \approx 0.95 T_c$ for $N_{av} = 100$ and at $T \approx 0.77 T_c$ for $N_{av} = 10$. The points A, B, C, D, and E (crosses) correspond to the accordingly marked work PDFs that are displayed in Fig. 3. The convergence measure α introduced in Eq. (32) is displayed in panel (b) as a function of T/T_c for $\gamma = -0.1$ and for $N_{av} = 100$ ($\diamond$) and $N_{av} = 10$ ($\circ$). The temperature values at which α changes sign indicate the transition between finite and divergent EWA in agreement with the corresponding temperature values read off from panel (a). The vertical lines refer to the temperatures of the points B and C. For $N_{av} = 10$, the crossing points with the lines corresponding to B and C give positive and negative α values, respectively, in accordance with panel (a). For $N_{av} = 100$ both points yield positive α values in agreement with panel (a).

VIII. SUMMARY

We studied a subtlety of fluctuation theorems specific for Bose particles which initially are prepared in a grand canonical equilibrium state. When the considered protocol finally leads to a Hamiltonian whose ground state energy per particle is less than the chemical potential of the initial state, the hypothetical equilibrium state is ill defined and its corresponding grand canonical partition function and grand potential do not exist. For the statistics of work fluctuations this means that the exponential work average diverges, in spite of the fact that the moments of the work of all orders are finite. In this situation, the Jarzynski equality looses its meaning, and also the Tasaki-Crooks relation becomes pointless because the

initial equilibrium state for the backward process does not exist, and therefore cannot be prepared.

In order to illustrate this issue, we considered Bose particles in a three-dimensional harmonic trap, and investigated the statistics of the work done by changing the trap curvature adiabatically. The probability distribution of the work at low temperatures follows a generalized exponential distribution, which has a more pronounced tail than the Gaussian high-temperature work distribution. We presented analytic forms of the PDFs in the extreme temperature regimes, which are in good agreement with numerical results. In the intermediate regime, the numerical results illustrate the transition between the extreme temperature cases. As a quantitative measure for the decay of the PDFs we examined the decay rate α, the sign of which governs the convergence of $\langle e^{-\beta w} \rangle$. When the work is done by compressing the trap, α is always negative to guarantee the convergence. On the other hand, when the trap is expanded, α undergoes a sign change upon varying the temperature at constant average particle numbers. Hence, in the low temperature regime the average $\langle e^{-\beta w} \rangle_{gc}$ diverges.

APPENDIX: CLASSICAL LIMIT

If the Hamiltonian $\mathcal{H}(t)$ commutes with $\mathcal{N}$ for all times during the protocol then the particle number is conserved, and the characteristic function, Eq. (10), can be decomposed into N-particle components:

$$G(u) = \mathcal{Q}_i^{-1} \sum_N e^{\beta \mu N} \mathrm{Tr}_N e^{iu\mathcal{H}_H(\tau)} e^{-iu\mathcal{H}} e^{-\beta H}$$
$$= \mathcal{Q}_i^{-1} \sum_N e^{\beta \mu N} Z_N g_N(u), \qquad (A1)$$

where Z_N is the canonical partition function of the N-particle system, and $g_N(u)$ is the characteristic function of work for the N-particle system with initial canonical equilibrium state. In the particular case of noninteracting Boltzmann particles, the canonical N-particle partition function can be expressed by the single-particle partition function Z_s as $Z_N = (Z_s)^N/N!$ similarly the canonical N-particle generating function in terms of the one-particle generating function $g_s(u)$ as $g_N(u) = [g_s(u)]^N$. Using $\mathcal{Q}_i = \sum_N e^{\beta \mu N} Z_N = \exp[e^{\beta \mu} Z_s]$ and summing up the series, one obtains the characteristic function for the classical particles,

$$G_c(u) = \exp\{e^{\beta \mu} Z_s [g_s(u) - 1]\}. \qquad (A2)$$

For the example of particles subject to a three-dimensional isotropic harmonic potential undergoing a change of its curvature, the single-particle characteristic function becomes

$$g_s(u) = \left\{ \int \frac{dp\,dq}{Z_s h} e^{iu[H(p(\tau),q(\tau),\tau) - H(p,q,0)]} e^{-\beta H(p,q,0)} \right\}^3,$$

where h is Planck's constant. In the particular case of an adiabatically slow change of the potential curvature the time-dependent Hamiltonian can be expressed in terms of the action I to yield

$$H(p(t),q(t),t) = \frac{1}{2m} p(t)^2 + \frac{m}{2} \omega^2(t) q(t)^2 = \omega(t) I. \quad (A3)$$

With the invariance of the action under adiabatic changes we get

$$H(p(\tau),q(\tau),\tau) - H(p,q,0) = [\omega(\tau) - \omega(0)]I = \gamma \omega I.$$

Combined with $\int dp\,dq = 2\pi \int_0^\infty dI$, this gives

$$Z_s g_s(u) = \hbar^{-3} \left[\int_0^\infty dI e^{-(\beta - i\gamma u)\omega I} \right]^3$$
$$= \frac{1}{(\beta - i\gamma u)^3 (\hbar \omega)^3} \qquad (A4)$$

and $Z_s = 1/(\beta \hbar \omega)^3$. Hence we find for the grand canonical characteristic function

$$G_c(u) = \exp\left\{ \frac{e^{\beta \mu}}{(\beta \hbar \omega)^3} \left[\frac{1}{(1 - i\gamma u/\beta)^3} - 1 \right] \right\}, \qquad (A5)$$

which coincides with the quantum expression of characteristic function at high temperatures, Eq. (22).

[1] C. Jarzynski, Phys. Rev. Lett. **78**, 2690 (1997).

[2] H. Tasaki, e-print arXiv:cond-mat/0009244.

[3] S. Mukamel, Phys. Rev. Lett. **90**, 170604 (2003); M. Esposito and S. Mukamel, Phys. Rev. E **73**, 046129 (2006).

[4] P. Talkner, E. Lutz, and P. Hänggi, Phys. Rev. E **75**, 050102 (2007).

[5] P. Talkner and P. Hänggi, J. Phys. A **40**, F569 (2007).

[6] P. Talkner, P. Hänggi, and M. Morillo, Phys. Rev. E **77**, 051131 (2008).

[7] M. Esposito, U. Harbola, and S. Mukamel, Rev. Mod. Phys. **81**, 1665 (2009).

[8] M. Campisi, P. Hänggi, and P. Talkner, Rev. Mod. Phys. **83**, 771 (2011).

[9] T. Schmiedl and U. Seifert, J. Chem. Phys. **126**, 044101 (2007).

[10] D. Andrieux, P. Gaspard, T. Monnai, and S. Tasaki, New J. Phys. **11**, 043014 (2009).

[11] J. Yi, P. Talkner, and M. Campisi, Phys. Rev. E **84**, 011138 (2011).

[12] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Butterworth-Heinemann, Oxford, 1980).

[13] M. H. Anderson, J. R. Ensher, M. R. Matthews, C. E. Wieman, and E. A. Cornell, Science **269**, 198 (1995).

[14] C. C. Bradley, C. A. Sackett, J. J. Tollett, and R. G. Hulet, Phys. Rev. Lett. **75**, 1687 (1995).

[15] K. B. Davis, M.-O. Mewes, M. R. Andrews, N. J. van Druten, D. S. Durfee, D. M. Kurn, and W. Ketterle, Phys. Rev. Lett. **75**, 3969 (1995).

[16] S. Grossmann and M. Holthaus, Phys. Lett. A **208**, 188 (1995).

[17] K. Kirsten and D. J. Toms, Phys. Lett. A **222**, 148 (1996).

[18] W. Ketterle and N. J. van Druten, Phys. Rev. A **54**, 656 (1996).

[19] G. E. Crooks, Phys. Rev. E **60**, 2721 (1999).

[20] J. Yi and P. Talkner, Phys. Rev. E **83**, 041119 (2011).

[21] W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes in C++: The Art of Scientific Computing*, 2nd ed. (Cambridge University Press, 2002).