Charged particle in a magnetic field: Jarzynski equality

A. M. Jayannavar* and Mamata Sahoo
Institute of Physics, Bhubaneswar 751005, India

(Received 20 November 2006; revised manuscript received 19 January 2007; published 26 March 2007)

We describe some solvable models which illustrate the Jarzynski theorem and related fluctuation theorems. We consider a charged particle in the presence of a magnetic field in a two-dimensional harmonic well. In the first case the center of the harmonic potential is translated with a uniform velocity, while in the other case the particle is subjected to an ac force. We show that the Jarzynski identity complements the Bohr–van Leeuwen theorem on the absence of diamagnetism in an equilibrium classical system.

DOI: 10.1103/PhysRevE.75.032102 PACS number(s): 05.70.Ln, 05.40.Jc

Most processes that occur in nature are far from equilibrium and hence cannot be treated within the framework of classical thermodynamics. The traditional nonequilibrium statistical mechanics deals with systems near equilibrium in the linear response regime. Its success has led to the the formulation of fluctuation-dissipation relation, Onsagar's reciprocity relations, and the Kubo-Green formulas, etc. However, very recent developments in nonequilibrium statistical mechanics have resulted in the discovery of some exact theoretical results for systems driven far away from equilibrium and are collectively called fluctuation theorems [1]. These results include entropy production theorems [2], the Jarzynski equality [3], Crooks relations [4], the Hatano-Sasa identity [5], etc. Some of the above relations have been verified experimentally on single nanosize systems in physical envirnoments where fluctuations play a dominant role [6,7].

The concept of free energy is of central importance in statistical mechanics and thermodynamics. With the help of free energy one can calculate all the phases of a system and their physical properties. However, the free energy of the system relative to an arbitrary reference state is often difficult to determine. The Jarzynski equality (JE) relates nonequilibrium quantities with equilibrium free energies [3]. In this prescription, initially the system is assumed to be in an equilibrium state determined by a thermodynamic parameter A defined by a control parameter λ_A and is kept in contact with a heat bath at temperature T. The nonequilibrium process is obtained by changing the thermodynamic control parameter λ in a finite time τ according to a prescribed protocol $\lambda(t)$, from $\lambda_A=\lambda(t=0)$ to some final value $\lambda_B=\lambda(t=\tau)$. The final state of the system at time τ (at the end of the protocol) will in general not be at equilibrium. It will equilibrate to a final state $B(\equiv\lambda_B)$ if it is further allowed to evolve by keeping the parameter λ_B fixed. The JE states that

$$\left\langle \exp\left(\frac{-W}{k_BT}\right)\right\rangle = \exp\left(\frac{-\Delta F}{k_BT}\right) \tag{1}$$

where ΔF is the free energy difference between equilibrium states A and B. The angular brackets $\langle\cdots\rangle$ denote the average taken over different realizations for a fixed protocol $\lambda(t)$. W is the work expended during each repitition of the protocol and is a realization-dependent random variable. Jarzynski's theorem has been derived using various methods with different system dynamics [3–5,8]. This remarkable identity provides a practical tool to determine equilibrium thermodynamic potentials from processes carried out arbitrarily far away from equilibrium. This identity has been used to extract equilibrium free energy differences in experiments. Work distributions have been calculated analytically for several model systems and tested against various fluctuation theorems [9–11]. The JE has been generalized to arbitrary transitions between nonequilibrium steady states by Hatano and Sasa [5], which has also been verified experimentally [7].

In our present work, we determine the work distributions analytically for two different models. In both these cases the charged particle dynamics in a two-dimensional harmonic trap in the presence of a magnetic field is considered. In the first case (i), the center of the harmonic trap is dragged with a uniform velocity whereas in case (ii) the particle is subjected to an ac force. We show that the JE is consistent with Bohr–van Leeuwen theorem. We also discuss steady state fluctuation theorems (SSFTS) and energy loss in driven systems.

We consider a charged particle motion in two dimensions (x-y plane) in the presence of a time-dependent potential U [$\equiv U(x,y,t)$]. An external magnetic field B along the z direction will produce a Lorentz force on the charged particle. The interaction of the particle with the environment can be treated via the frictional force along with concomitant fluctuations. The appropriate equations of motion are given by the Langevin equations [12,13]

$$m\ddot{x} = -\gamma\dot{x} - \frac{|e|}{c}B\dot{y} - \frac{\partial U}{\partial x} + \xi_x(t), \tag{2}$$

$$m\ddot{y} = -\gamma\dot{y} + \frac{|e|}{c}B\dot{x} - \frac{\partial U}{\partial y} + \xi_y(t), \tag{3}$$

where the random force field $\xi_\alpha(t)$ is a Gaussian white noise, i.e.,

$$\langle \xi_\alpha(t)\xi_\beta(t')\rangle = D\delta_{\alpha\beta}\delta(t-t'), \tag{4}$$

with $\alpha,\beta=x,y$ and e and the charge of the particle. $D=2\gamma k_BT$ is a consistency condition for the system to approach equilibrium in the absence of a time-independent potential. The friction coefficient is denoted by γ.

*Electronic address: jayan@iopb.res.in

This problem (for time-independent potentials) was earlier considered [13] to elucidate the crucial role played by the boundary conditions in the celebrated theorem of Bohr and van Leeuwen on the absence of diamagnetism in classical systems [13,14]. This theorem states that in equilibrium for classical systems the free energy is independent of the magnetic field. Hence, diamagnetism does not exist in classical statistical mechanics.

We restrict our analysis to the overdamped regime where the corresponding dynamical equations become

$$\gamma\dot{x} = -\frac{|e|B}{c}\dot{y} - \frac{\partial U}{\partial x} + \xi_x(t), \tag{5}$$

$$\gamma\dot{y} = \frac{|e|B}{c}\dot{x} - \frac{\partial U}{\partial y} + \xi_y(t). \tag{6}$$

The associated Fokker-Planck equation [15] leads to an equilibrium distribution $P_e \propto e^{-[U(x,y)/k_BT]}$ in a stationary regime for a time-independent potential $U(x,y)$. This distribution P_e is independent of the magnetic field consistent with the Bohr–van Leeuwen theorem.

We consider in this work two cases of time-dependent potentials. For case (i) $U(x,y,t)=\frac{1}{2}k|\vec{r}-\vec{r}^{\,*}(t)|^2$, where $\hat{r}$ is a two-dimensional vector $\vec{r}=\hat{i}x+\hat{j}y$ and $\vec{r}^{\,*}(t)=vt(\hat{i}+\hat{j})$, with $\hat{i}$ and $\hat{j}$ unit vectors along the x and y directions, respectively. Here the particle is in a harmonic potential whose center is dragged along with a uniform speed $\sqrt{2}v$ in a diagonal direction. This problem can also be solved for the motion of the center in an arbitrary direction with a different protocol. For case (ii), $U(x,y,t)=\frac{1}{2}k(x^2+y^2)-Ax\sin(\omega t)$. Here the particle in a two-dimensional harmonic well is subjected to an ac force in the x direction. This problem can also be solved for ac drivings in both x and y direction with different amplitudes and with a phase difference.

We rewrite Eqs. (5) and (6) using the variable [12] $z=x+iy$ ($i=\sqrt{-1}$). For the case (i) we get

$$\dot{z} = \frac{-kpz}{\gamma} + \frac{kpg^*(t)}{\gamma} + \frac{p\xi(t)}{\gamma}, \tag{7}$$

where $p=(1+iC)/(1+C^2)$, $\xi(t)=\xi_x(t)+i\xi_y(t)$, $g^*(t)=vt(1+i)$, and $C=e|B|/\gamma c$.

For the case (ii), we get

$$\dot{z} = \frac{-kpz}{\gamma} + \frac{p}{\gamma}[A\sin(\omega t) + \xi(t)]. \tag{8}$$

The thermodynamic work W done on the system by an external agent during a time interval t is given by [9,10], for case (i),

$$W = -kv\int_0^t [(x-vt') + (y-vt')]dt', \tag{9}$$

and for case (ii)

$$W = -A\omega\int_0^t \cos(\omega t')x(t')dt, \tag{10}$$

The formal solutions of Eqs. (7) and (8), respectively, are

$$z(t) = z_0\exp\left(-\frac{k}{\gamma}pt\right) + \frac{p}{\gamma}\int_0^t dt'\,\exp\left(-\frac{k}{\gamma}p(t-t')\right)[kg^*(t') + \xi(t')] \tag{11}$$

and

$$z(t) = z_0\exp\left(-\frac{k}{\gamma}pt\right) + \frac{p}{\gamma}\int_0^t dt'\,\exp\left(-\frac{k}{\gamma}p(t-t')\right)[\xi(t') + A\sin(\omega t')]. \tag{12}$$

where $z_0=x_0+iy_0$, and x_0 and y_0 are the initial coordinates of the particle. The initial distribution for x_0 and y_0 is assumed to be the equilibrium canonical distribution $P_e(x_0,y_0,t)=(\beta k/2\pi)\exp[-\beta k(x_0^2+y_0^2)/2]$. It may be readily noted from Eqs. (10)–(13) that the work done as well as the particle coordinates at later times are linear functionals of Gaussian variables $\xi_x(t)$ and $\xi_y(t)$ and hence their distributions are Gaussian. We calculate the full probability distribution for W for both cases following closely the procedures adopted in Refs. [9,10]. Without going into further details of the algebra we give our final results which will be further analyzed.

For the case (i), the average work done $\langle W\rangle$ is

$$\langle W\rangle = 2\gamma v^2\left(t - \frac{\gamma}{k}[1-\exp(-k^*t)\cos(\Omega t)] - \frac{C\gamma}{k}\sin(\Omega t)\exp(-k^*t)\right) - \gamma v^2 2C\left(\frac{\gamma}{k}\sin(\Omega t)\exp(-k^*t) - \frac{C\gamma}{k}[1-\exp(-k^*t)\cos(\Omega t)]\right), \tag{13}$$

where $\Omega=kC/\gamma(1+C^2)$ and $k^*=k/\gamma(1+C^2)$. The above equation (13) agrees with the result obtained in Refs. [9,10] for $B=0$. The variance of the work is given by

$$\langle W^2\rangle - \langle W\rangle^2 = \frac{2\langle W\rangle}{\beta}, \tag{14}$$

where $\beta=1/k_BT$. The full probability distribution $P(W)$ is

$$P(W) = \frac{1}{\sqrt{4\pi\langle W\rangle/\beta}}e^{-(W-\langle W\rangle)^2/(4\langle W\rangle/\beta)}. \tag{15}$$

The JE given in Eq. (1) follows immediately from the above expression, with

$$\langle e^{-\beta W}\rangle = e^{-\beta\Delta F} = 1. \tag{16}$$

Equation (16) implies $\Delta F=0$, indicating that the equilibrium free energy of a particle in a harmonic potential is independent of magnetic field, consistent with the Bohr–van Leeuwen theorem. Needless to say that in the present case the free energy of the oscillator is also independent of the position of the center of the harmonic potential as expected on general grounds. However, it is interesting to note that the thermodynamic work W in the transient state depends explicitly on the magnetic field B. In the presence of a magnetic field relaxation rate of the system $\tau_r[=\gamma(1+C^2)/k]$ depends on the magnetic field. It increases with the strength of the magnetic field. Hence the magnetic field gives an additional control over the relaxation time in an experimental situation to verify the above and subsequent results.

Only in the asymptotic time limit $t \to \infty (t \gg \tau_r)$, where the system does not retain the memory of the initial state, does one obtain for the averaged work done $\langle W_s \rangle$ in a system in time interval t,

$$\langle W_s \rangle \approx 2\gamma v^2 t. \tag{17}$$

Hence the power (p) delivered to the system in the steady state is constant $(p = 2\gamma v^2)$. In this state the thermodynamic work is essentially mechanical work delivered to the system by a moving trap with a speed $\sqrt{2}v$ along the diagonal direction in the x-y plane. The particle in this state settles to a Gaussian distribution with the same dispersion as in the case of the canonical equilibrium distribution. However, the center of the position of the particle distribution lags behind the instantaneous minimum of the confining potential by a distance $l = \sqrt{2}v\gamma/k$ along the diagonal line. The harmonic potential pulls the particle with a force kl, at speed $\sqrt{2}v$. Thus the power delivered is $kl\sqrt{2}v = 2\gamma v^2$. This power is dissipated as heat into the surrounding medium. In this regime, the fluctuations in the work $\langle W_s \rangle$ is

$$\langle W_s^2 \rangle = \langle W_s \rangle^2 + \frac{2}{\beta} \langle W_s \rangle. \tag{18}$$

In the steady state the distribution of work W_s obeys the SSFT [9], namely,

$$\frac{P(W_s)}{P(-W_s)} = e^{\beta W_s}. \tag{19}$$

It is important to note that both the work and its distribution in the steady state do not depend on the magnetic field. Hence the experimentally obtained results [7] to verify the Hatano-Sasa identity [5] for transition between nonequilibrium steady states remain unaltered irrespective of the magnetic field being present or not. Here transition between nonequilibrium states are induced by varying the speed of the trap [7].

We now turn to case (ii). As mentioned earlier for this case the work distribution is Gaussian and is characterized completely by the first moment and the variance. The expression for $\langle W \rangle$ is very lengthy and is given in the Appendix. The variance is given by

$$\langle W^2 \rangle - \langle W \rangle^2 = \frac{2}{\beta} (\langle W \rangle - \Delta F) \tag{20}$$

where $\Delta F = (-A^2/2k)\sin^2(\omega\tau)$. Using the distribution of work one can readily verify the JE, namely, $\langle e^{-\beta W} \rangle = e^{-\beta \Delta F}$. ΔF is the free energy difference between two thermodynamic states. The initial $(t=0)$ and final $(t=\tau)$ states are characterized by two-dimensional harmonic potentials with a additional tilts of magnitude zero and $-Ax\sin(\omega\tau)$, respectively. Note that ΔF is independent of magnetic field, again confirming the Bohr–van Leeuwen theorem. However, the work distribution is an explicit function of the magnetic field.

We now concentrate on the statistics of the work done, W_s, in the asymptotic regime. In this regime probability distributions are time periodic with a period $2\pi/\omega$. We calculate the average work done over one period $2\pi/\omega$, which is

$$\langle W_s \rangle = \lim_{t \to \infty} \left[\left\langle W\left(t + \frac{2\pi}{\omega}\right) \right\rangle - \langle W(t) \rangle \right], \tag{21}$$

$$\langle W_s \rangle = \frac{\pi A^2 \omega \gamma [k^2 + \omega^2 \gamma^2 (1 + C^2)]}{[k^2 + (1 + C^2)\gamma^2 \omega^2]^2 - 4k^2 C^2 \omega^2 \gamma^2}. \tag{22}$$

Similarly the variance $\langle V_s \rangle$ of the work averaged over a period of oscillation is given by

$$\langle V_s \rangle = \langle W_s^2 \rangle - \langle W_s \rangle^2, \tag{23}$$

$$\langle V_s \rangle = \frac{2}{\beta} \langle W_s \rangle. \tag{24}$$

In the time periodic state the average input energy is dissipated into the system as heat [9]. Thus one can identify $\langle W_s \rangle$ as a hysteresis loss in the medium. Since the problem is linear we find that the time averaged hysteresis loss is independent of temperature. However, it depends explicitly on the magnetic field and is a symmetric function of magnetic field. Thus the magnetic field becomes a relevant variable in the time periodic asymptotic state. However, it must be noted that variance in the input energy cannot be identified with the heat fluctuations [9]. In this time periodic state the work done, W_s, over a period satisfies the SSFT, namely, Eq. (19).

It may be noted that the validity of the SSFT for work done over a single period [Eq. (24)] is restricted only to overdamped linear models as in the present case. In general this will not hold good in nonlinear situations [17]. However, one can show that, if one instead considers work done over a large number of periods, indeed the SSFT holds even for nonlinear models. The convergence of the SSFT on accessible time scales has been studied in the previous literature [18]. We have calculated separately the work distribution for W_s in the inertial regime, which satisfies the SSFT. Moreover we have also shown that one can obtain the orbital magnetic moment in this nonequilibrium state without violating the Bohr–van Leeuwen theorem. These results will be presented elsewhere [16].

In conclusion we have solved analytically the work distribution of a charged particle in the presence of a magnetic field in two different cases. The first is the case where the minimum of the harmonic potential is dragged with a uniform velocity and in the second case the particle is subjected to an ac force. For both cases the JE is verified and this equality complements the Bohr–van Leeuwen theorem on the absence of diamagnetism in a classical system. In case (i) we have shown that such a distribution in the steady state does not depend on magnetic field and satisfies the SSFT. As opposed to this case in a time periodic assymptotic state for case (ii) the magnetic field becomes a relevant variable. The hysteresis loss over a cycle depends explicitly on the magnetic field. The relaxation time in our system can be controlled by the magnetic field. All our results are amenable to experimental verification with charged beads in a magnetic field.

One of us (A.M.J.) thanks Abhishek Dhar for helpful discussions.

APPENDIX

The expression for $\langle W\rangle$ is

$$\langle W\rangle = \frac{1}{\gamma\{[k^2+\omega^2(1-C^2)]^2+4C^2\omega^4\}}\Bigg[[k^2+\omega^2(1-C^2)]\left(\frac{-A^2k\sin^2(\omega t)}{2}+\frac{A^2\omega^2 t}{2}+\frac{A^2\omega\sin(2\omega t)}{4}\right)+2C\omega^2\left(\frac{A^2C\omega^2 t}{2}+\frac{A^2C\omega\sin(2\omega t)}{4}\right)\Bigg]+\frac{A^2\omega^2\exp(-k^*t)}{2\gamma\{[k^2+\omega^2(1-C^2)]^2+4C^2\omega^4\}}\Bigg[\frac{1}{k^{*2}+(\Omega+\omega)^2}(\{[k^2+\omega^2(1-C^2)][k^*+C(\Omega+\omega)]+2C\omega^2[Ck^*-(\Omega+\omega)]\}\cos(\Omega+\omega)t+\{2C\omega^2[k^*-C(\Omega+\omega)]-[k^2+\omega^2(1-C^2)](\Omega+\omega+Ck^*)\}\sin(\Omega+\omega)t)+\frac{1}{k^{*2}+(\Omega-\omega)^2}(\{[k^2+\omega^2(1-C^2)][k^*+C(\Omega-\omega)]+2C\omega^2[Ck^*-(\Omega-\omega)]\}\cos(\Omega-\omega)t+\{2C\omega^2[k^*-C(\Omega-\omega)]-[k^2+\omega^2(1-C^2)](\Omega-\omega+Ck^*)\}\sin(\Omega-\omega)t)\Bigg]+c', \tag{A1}$$

where

$$c' = \frac{a_1a_2}{c_1c_2}, \tag{A2}$$

$$a_1 = -2A^2\omega^2(k^{*2}+\Omega^2+\omega^2),$$

$$a_2 = k^*[k^2+\omega^2(1+C^2)]+\Omega C(k^2+3\omega^2-\omega^2C^2),$$

$$c_1 = [k^{*2}+\omega^2(1-C^2)]^2+4C^2\omega^4,$$

$$c_2 = 2[k^{*2}+(\Omega-\omega)^2][k^{*2}+(\Omega+\omega)^2].$$

Here $\Omega=kC/(1+C^2)$, $k^*=k/(1+C^2)$, and $C=|e|B/\gamma c$ with k here written for k/γ.

In the absence of magnetic field, $\langle W\rangle$ reduces to

$$\langle W\rangle = -\frac{A^2k}{2\gamma(k^2+\omega^2)}\sin^2(\omega t)+\frac{A^2\omega}{4\gamma(\omega^2+k^2)}\sin(2\omega t)+\frac{A^2\omega^2 t}{2\gamma(k^2+\omega^2)}-\frac{A^2\omega^2 k}{\gamma(k^2+\omega^2)^2}+\frac{A^2\omega^2}{\gamma(k^2+\omega^2)^2}\times\exp(-kt)[k\cos(\omega t)-\omega\sin(\omega t)]. \tag{A3}$$

[1] C. Bustamante, J. Liphardt, and F. Ritort, Phys. Today **58** (7), 45 (2005).
[2] D. J. Evans and D. J. Searles, Adv. Phys. **51**, 1529 (2002).
[3] C. Jarzynski, Phys. Rev. Lett. **78**, 2690 (1997); Phys. Rev. E **56**, 5018 (1997).
[4] G. E. Crooks, Phys. Rev. E **60**, 2721 (1999); **61**, 2361 (2000).
[5] T. Hatano and S. I. Sasa, Phys. Rev. Lett. **86**, 3463 (2001).
[6] J. Liphardt *et al.*, Science **296**, 1833 (2002); F. Douarche *et al.*, Europhys. Lett. **70**, 593 (2005); G. M. Wang E. M. Sevick, E. Mittig, D. J. Searles, and D. J. Evans, Phys. Rev. Lett. **89**, 050601 (2002); O. Narayan and A. Dhar, J. Phys. A **37**, 63 (2004).
[7] E. M. Trepangnier *et al.*, Proc. Natl. Acad. Sci. U.S.A. **101**, 15038 (2004).
[8] W. Lechner *et al.*, J. Chem. Phys. **124**, 044113 (2006); G. Hummer and A. Szabo, Proc. Natl. Acad. Sci. U.S.A. **98**, 3658 (2001).
[9] R. van Zon and E. G. D. Cohen, Phys. Rev. E **67**, 046102 (2002); **69**, 056121 (2004).
[10] O. Mazonka and C. Jarzynski, e-print cond-mat/9912121.
[11] F. Ritort, J. Stat. Mech.: Theory Exp. 2004, P10016; R. C. Lua and A. Y. Grosberg, J. Phys. Chem. B **109**, 6805 (2005); L. Bena, C. Van den Broeck and R. Kawai, Europhys. Lett. **71**, 879 (2005); A. Dhar, Phys. Rev. E **71**, 036126 (2005); R. Marathe and A. Dhar, *ibid.* **72**, 066112 (2005); A. Imparato and L. Peliti, Europhys. Lett. **69**, 643 (2005).
[12] S. Chandrasekhar, Rev. Mod. Phys. **15**, 1 (1943).
[13] A. M. Jayannavar and N. Kumar, J. Phys. A **14**, 1399 (1981).
[14] N. Bohr, Dissertation, Copenhagen, 1911 (unpublished); J. H. van Leeuwen, J. Phys. **2**, 3619 (1921); R. E. Peierls, *Surprises in Theoretical Physics* (Princeton University Press, Princeton, NJ, 1979).
[15] H. Risken, *The Fokker Planck Equation* (Springer-Verlag, Berlin, 1984).
[16] A. M. Jayannavar and M. Sahoo (unpublished).
[17] S. Saikia, R. Roy, and A. M. Jayannavar, e-print cond-mat/0701303.
[18] J. C. Reid *et al.*, Phys. Rev. E **70**, 016111 (2004); J. C. Reid, E. M. Sevick, and D. J. Evans, Europhys. Lett. **5**, 726 (2005); G. M. Wang *et al.*, J. Phys.: Condens. Matter **17**, s3239 (2005); F. Douarche S. Joubaud, N. B. Garnier, A. Petrosyan, and S. Ciliberto, Phys. Rev. Lett. **97**, 140603 (2006).