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Jarzynski equality for the Jepsen gas

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Abstract. – We illustrate the Jarzynski equality on the exactly solvable model of an ideal gas in uniform expansion or compression. The analytical results for the probability density $P(W)$ of the work W performed by the gas are compared with the results of molecular dynamics simulations for a two-dimensional dilute gas of hard spheres, a prototype for a real, slightly non-ideal gas.

Exactly solvable models play an important role in statistical mechanics. They complement and verify results that are derived from general and usually abstract arguments, while at the same time they offer insight and intuition. They are particularly useful in far-from-equilibrium situations, for which few generic exact results are available. In this letter, we focus on a remarkable result in nonequilibrium statistical mechanics, namely the *Jarzynski equality* [1,2], which has given rise to a certain amount of confusion about its validity and interpretation [3]. The Jarzynski equality relates the statistics of the amount of work W performed by a system in a nonequilibrium transition between two equilibrium states, to the difference in the free energies of these states, as

$$\langle \exp[\beta W] \rangle = \exp[-\beta \Delta F], \tag{1}$$

where W is the work delivered *by the system*([1]) upon varying an external control parameter following a specified schedule between an initial and a final value, starting from an initial state of the system sampled from a canonical distribution at temperature T ($\beta^{-1} = k_B T$). W is a random variable due to the sampling of the initial state. The first surprise is that the above specified average $\langle \ldots \rangle$ with respect to W is independent of the schedule according to which the control parameter is changed between the specified initial and final values. In particular it is independent of whether this schedule keeps the system close to equilibrium (quasi-static transformation) or whether it entails large deviations from equilibrium. As a consequence, the average is expressed in terms of the difference ΔF in free energy of the canonical equilibrium states at temperature T at the final and initial values of the control parameter, respectively. The second surprise is then that the equilibrium quantity ΔF can be obtained by an ensemble average over nonequilibrium measurements. Finally and foremost, the appearance of an equality in far-from-equilibrium dynamics is very surprising. In fact, the

([1])In Jarzynski's original paper and most of the references in [1], W is the work done *on the system*. Thus the sign of W in the present letter is opposite to that used in these papers.

equality (1) leads, upon application of the Jensen inequality, to the familiar inequality $\langle W\rangle \leqslant W_{rev} = -\Delta F$, corresponding to the formulation of the second principle of thermodynamics for a system in contact with a heat bath.

Our purpose here is to verify and complement the discussion of the Jarzynski equation by deriving the analytic expression of the probability density $P(W)$ for the work W in a system with Newtonian dynamics. We will consider the so-called *Jepsen gas*, for which a number of other exact equilibrium and nonequilibrium results have been derived [4]. The Jepsen gas consists of N identical point particles of mass m moving on a line and undergoing perfectly elastic collisions. Actually, since the speeds are merely exchanged upon collision, and the identity of the particles is irrelevant, the same model can represent an ideal gas in which particles do not interact with each other. We consider a system initially at thermal equilibrium at temperature T, *i.e.*, the particles are uniformly distributed in the interval $[-L, 0]$, and their velocities are randomly and independently chosen from the Maxwellian distribution $\phi(u) = \sqrt{m\beta/2\pi}\,\exp[-\beta m u^2/2]$. The right-hand side of the interval is formed by a piston of infinite mass, which is moved according to a specified schedule. Although more complicated situations can be considered, we will concentrate on the case of a piston moving at a constant velocity V (positive or negative, *i.e.*, corresponding to gas expansion or compression, respectively), from the initial position $X = 0$ to the final position $X = Vt$.

A similar "ideal gas" model has been discussed by Lua and Grosberg [5]. In their more academic setup, the system size is finite, and correlated recollisions of the particles with the piston are allowed and contribute to the work distribution function. In contrast, we are studying here the so-called *thermodynamic limit* of an infinite system, with $L \to \infty$, $N \to \infty$ and fixed density $n = N/L$, which is a more relevant physical limit. In this limit, recollisions of particles with the piston are no longer possible for the considered schedule, and the gas acquires properties of an irreversible system. Lua and Grosberg also investigated a system of large volume, but their results are limited to short-time behavior, where only a single particle collides with the piston. Our present results are more general, and agree with their findings in the short-time limit. Furthermore, the results of the present model are compared with molecular dynamics simulations for dilute hard-disk gases, as prototypes of real, slightly non-ideal systems. The formalism we are proposing can be put in parallel with the mean-field approximation of the general theory developed by Ritort and later on by Imparato *et al.* [1].

To evaluate W, we first note that a particle of velocity $u_i > V$ colliding with the piston will recoil with the velocity $u_i' = 2V - u_i$. Hence there is an energy transfer in the interval $[0, t]$ from this particle to the piston given by $\Delta W_i = 2mV(u_i - V)\theta(x_i + u_i t - Vt)$, where the Heaviside θ function expresses that the collision between the particle (with initial position $x_i < 0$ and velocity u_i) and the piston has to take place before time t. We conclude that the probability to have a total energy transfer W from the gas to the piston during the time interval $[0, t]$ is given by

$$\begin{aligned} P(W) &= \left\langle \delta\Big(W - \sum_{j=1}^{N} \Delta W_j\Big)\right\rangle_0 = \left\langle \int_{-\infty}^{\infty} \frac{\mathrm{d}k}{2\pi} \exp\left[ik\left[W - \sum_{j=1}^{N} \Delta W_j\right]\right]\right\rangle_0 \\ &= \int_{-\infty}^{\infty} \frac{\mathrm{d}k}{2\pi}\, \exp[ikW]\, \langle \exp[-ik\Delta W_j]\rangle_0^N \\ &= \int_{-\infty}^{\infty} \frac{\mathrm{d}k}{2\pi}\, \exp\left[ikW - nt \int_V^{\infty} \mathrm{d}u\, (u - V)\phi(u)\big[1 - \exp\left[-2ikmV(u - V)\right]\big]\right]. \quad (2) \end{aligned}$$

The average $\langle \ldots \rangle_0$ is taken over the distribution of the initial positions and velocities of the particles. Note that we have not taken into account recollisions of the particles with the

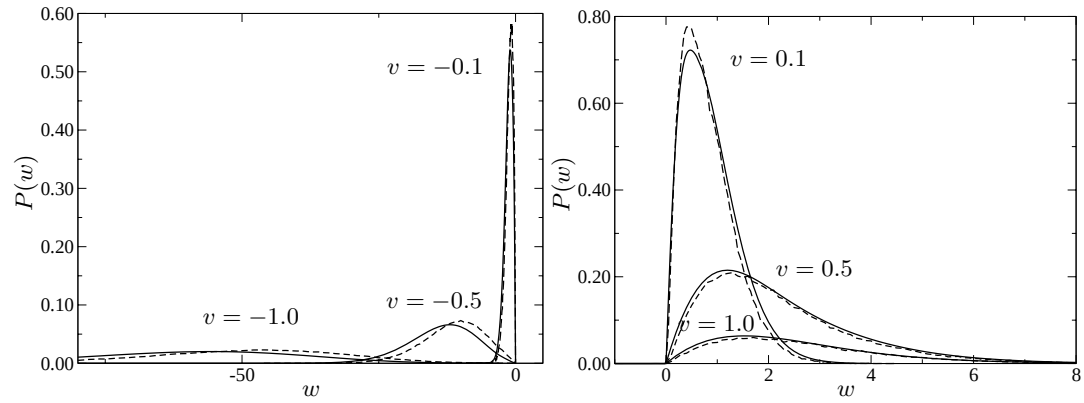

Fig. 1 – Profiles of the nonsingular part of $P(w)$ for various velocities v of the piston at a fixed time $\tau = 5$ (left: gas compression; right: gas expansion). The area below the curves represents the probability to have a nonzero value of w and is equal to $[1 - \exp[-\tau C_0]]$. The graphs illustrate the agreement between analytical calculations (solid lines) and molecular dynamics simulations results (dashed lines), see the main text.

piston, hence only the final line, in which the thermodynamic limit has been taken, gives the exact result for $P(W)$.

The schedule under consideration can be conveniently characterized by the following two dimensionless variables: $v = V(\beta m/2)^{1/2}$ and $\tau = nt/(2m\beta)^{1/2}$, which are, essentially, the velocity of the piston measured in terms of the thermal speed of the gas particles, and the average number of collisions during the considered time interval $[0, t]$ for a stationary piston. In terms of the scaled work $w = \beta W$, the expression (2) for the probability density becomes

$$P(w) = \int_{-\infty}^{\infty} \frac{\mathrm{d}q}{2\pi} \exp\left[iqw - \tau C(q)\right], \tag{3}$$

where the function $C(q)$ can be written as the sum of two parts, $C(q) = C_0 + \tilde{C}(q)$. The "collisionless" part, $C_0 = 1/\sqrt{\pi}\,\exp[-v^2] - v\,\mathrm{erfc}(v)$ (where $\mathrm{erfc}(\ldots)$ is the complementary error function) corresponds to the absence of collisions between the gas particles and the piston, *i.e.*, when no work is performed. This leads to a singular contribution $\exp[-\tau C_0]\,\delta(w)$ in the expression (3) of $P(w)$. This contribution is exponentially decaying with respect to the scaled time τ, while the damping exponent C_0 is a rapidly decaying function of v. The second part,

$$\tilde{C}(q) = v(1+2iq)\,\mathrm{erfc}\left[v(1+2iq)\right] \exp\left[v^2(1+2iq)^2 - v^2\right] - 1/\sqrt{\pi}\,\exp\left[-v^2\right] \tag{4}$$

is determined by the collisions between the gas particles and the piston, and leads to a monomodal nonsingular contribution to $P(w)$, as illustrated in figs. 1, 2, and 4.

Based on this exact result, we first turn to the explicit verification of the Jarzynski equality. One has

$$\begin{aligned} \langle \exp[\beta W] \rangle &= \langle \exp[w] \rangle = \int_{-\infty}^{\infty} \frac{\mathrm{d}q}{2\pi} \exp[-\tau C(q)] \int_{-\infty}^{\infty} \mathrm{d}w \, \exp[iqw + w] \\ &= \exp[-\tau C(i)] = \exp[2\tau v] = \exp[ntV]. \end{aligned} \tag{5}$$

On the other hand, the change in the equilibrium free energy of the ideal gas due to the

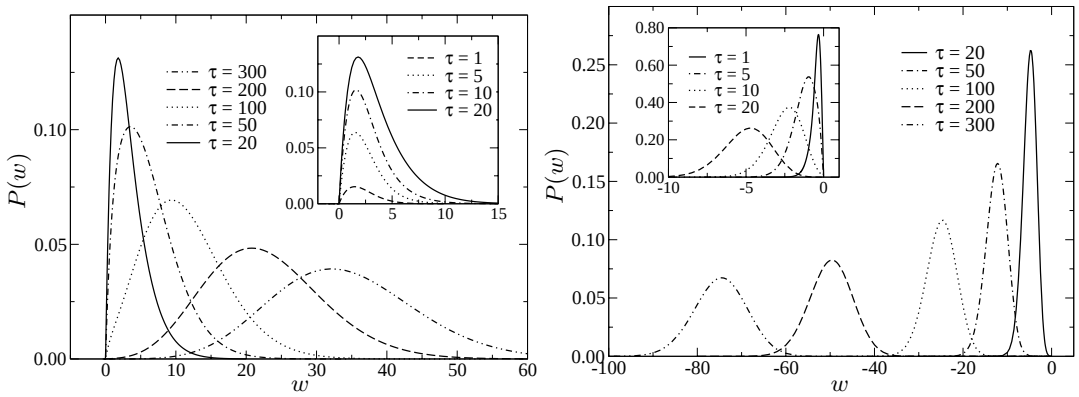

Fig. 2 – Profiles of the nonsingular part of $P(w)$ at different times τ for fixed velocities of the piston, $v = 1$ (left) and $v = -0.1$ (right). Note the evolution from a highly asymmetric profile at short times, eq. (12), to an asymptotic Gaussian shape with mean and standard deviation given by eqs. (8) and (9), respectively.

variation of its volume is a purely entropic factor given by

$$\exp[-\beta\Delta F] = \left(\frac{L+Vt}{L}\right)^N \xrightarrow{\text{thermodynamic limit}} \exp[ntV], \tag{6}$$

so that the Jarzynksi equality (1) is indeed reproduced.

We next examine the characteristic properties of $P(w)$. While an explicit evaluation of the Fourier transform (3) appears to be difficult, one can easily obtain exact results for the moments using the characteristic function of the probability density, namely

$$G(q) = \langle \exp[-iqw] \rangle = \sum_{n=0}^{\infty} \frac{(-iq)^n}{n!} \langle w^n \rangle = \exp[-\tau\, C(q)]. \tag{7}$$

In particular, one obtains the mean value of the transferred energy

$$\langle w \rangle = 2v\tau \, \left[(1+2v^2)\,\mathrm{erfc}(v) - 2/\sqrt{\pi}\, v \, \exp\left[-v^2\right] \right] , \tag{8}$$

that increases linearly with time and has a maximum as a function of v (see fig. 3). The

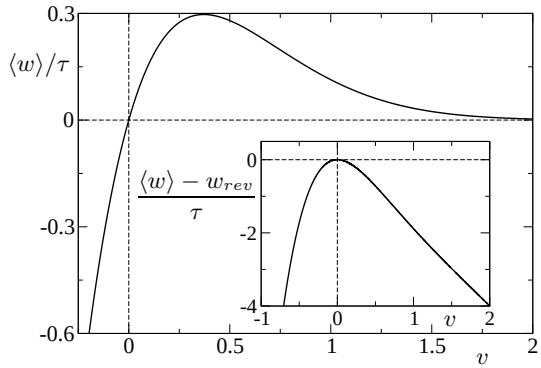

Fig. 3 – The mean value of the energy transfer per unit time $\langle w \rangle/\tau$, and, in inset, $(\langle w \rangle - w_{rev})/\tau$, both as a function of v. Note that $\langle w \rangle \leqslant w_{rev}$, in agreement with the second law of thermodynamics.

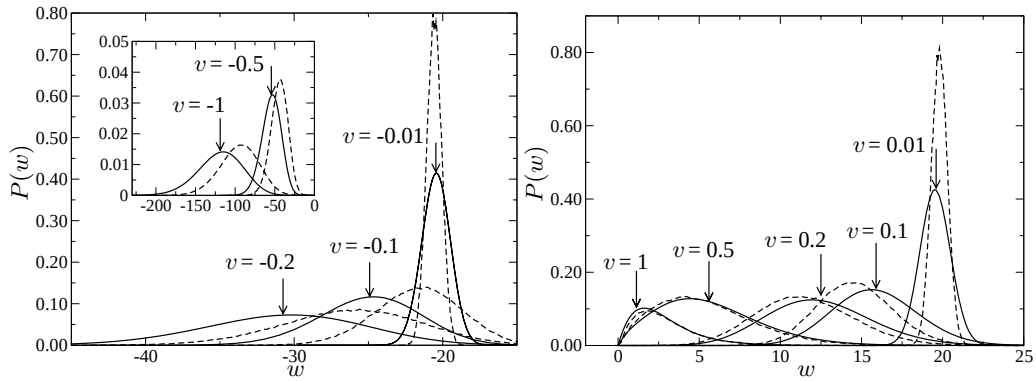

Fig. 4 – Profiles of the nonsingular part of $P(w)$ for a fixed value of $|w_{rev}| = 2|v|\tau = 20$ and different velocities v of the piston (left: compression, right: expansion). The inset shows the same plots for faster compression. The arrows indicate the theoretical means, eq. (8). The theoretical results (solid lines) agree qualitatively with the computer simulation (dashed lines). Quantitative disagreement for fast compression and slow expansion are presumably due to recollisions and finite-size effects.

centered moments of second through fourth order are

$$\sigma^2 = \langle w^2\rangle - \langle w\rangle^2 = 8v^2\tau\left[2/\sqrt{\pi}\,(1+v^2)\,\exp\left[-v^2\right] - v(3+2v^2)\,\mathrm{erfc}(v)\right], \tag{9}$$

$$\langle (w-\langle w\rangle)^3\rangle = 16v^3\tau\left[(3+12v^2+4v^4)\,\mathrm{erfc}(v) - 2/\sqrt{\pi}\,v\,(5+2v^2)\,\exp\left[-v^2\right]\right], \tag{10}$$

$$\langle (w-\langle w\rangle)^4\rangle = 3\sigma^4 + 64v^4\tau\left[2/\sqrt{\pi}\,(4+9v^2+2v^4)\exp\left[-v^2\right] - v\,(15+20v^2+4v^4)\,\mathrm{erfc}(v)\right]. \tag{11}$$

The explicit analytical expression of $P(w)$ can be derived in specific limits.

i) In the *limit of large number of collisions* $\tau \gg 1$, the work is the sum of a large number of independent contributions. One finds, in agreement with the central limit theorem, that the distribution function $P(w)$ converges to a Gaussian. The mean and standard deviation are given by eqs. (8) and (9). The skewness $\gamma_3 = \langle (w-\langle w\rangle)^3\rangle/\sigma^3 = \mathcal{O}(\tau^{-1/2})$ and the kurtosis $\gamma_4 = \langle (w-\langle w\rangle)^4\rangle/\sigma^4 - 3 = \mathcal{O}(\tau^{-1})$ decay to zero.

ii) For the *limit of small number of collisions* $\tau \ll 1$, the moment-generating function reads $G(q) \approx 1 - \tau C(q)$, hence

$$P(w) \approx (1-\tau C_0)\delta(w) + \frac{\tau}{8\sqrt{\pi}v^2}\,|w|\,\exp\left[-\left(\frac{w}{4v}+v\right)^2\right]\,\theta(wv)\,, \tag{12}$$

corresponding to an asymmetric probability density profile (compare, for $v > 0$, with eq. (18) from ref. [5] for the case of a single particle, $n = 1/L$).

iii) The *quasi-static limit*. The reversible work W_{rev} delivered by the ideal gas during an expansion over a distance Δx is $P\Delta x$, with the pressure P given by nk_BT. This result has to be compared with the irreversible expansion at a finite speed V over the same distance, *i.e.*, $\Delta x = Vt$. In terms of the previously introduced dimensionless variables, this implies $w_{rev} = 2v\tau$. This result is indeed recovered in the limit $|v| \ll 1$, since $C(q) \approx 2viq$, and $P(w) \approx \delta(w - w_{rev})$. By including a first-order correction, $C(q) \approx 8v^2q^2/\sqrt{\pi} + 2viq(1-4v/\sqrt{\pi})$, the probability density $P(w)$ assumes a Gaussian profile, with mean and variance:

$$\langle w\rangle \approx w_{rev} - 8\tau v^2/\sqrt{\pi}, \qquad \sigma^2 \approx 16\tau v^2/\sqrt{\pi}. \tag{13}$$

TABLE I – *Comparison of the mean values and higher moments obtained from the molecular dynamics simulations with analytical results (values in parentheses), for different values of the velocity v of the piston and a fixed value of $|w_{rev}| = 2|v|\tau = 20$. The agreement is satisfactory, except for a few cases, cf. the discussion in the main text.*

v	Mean	Variance	Skewness	Kurtosis	v	Mean	Variance	Skewness	Kurtosis
0.01	19.8	0.25	0.015	0.0016	−0.01	−20.60	0.26	−0.014	0.0041
	(19.6)	(0.88)	(0.057)	(0.0036)		(−20.46)	(0.93)	(−0.055)	(0.0035)
0.1	14.5	5.42	0.18	0.013	−0.1	−21.75	8.42	−0.14	0.030
	(15.9)	(6.88)	(0.20)	(0.044)		(−24.92)	(11.71)	(−0.16)	(0.029)
1.0	1.07	3.37	2.09	5.06	−1.0	−97.47	585.8	−0.25	0.044
	(1.13)	(3.50)	(2.03)	(4.81)		(−118.9)	(803.5)	(−0.27)	(0.077)

Note that the Jarzynski equality, eq. (1), implies that for a Gaussian distribution the fluctuation-dissipation ratio

$$\mathcal{R} = \frac{\sigma^2}{2(w_{rev} - \langle w \rangle)} \tag{14}$$

is equal to 1. This is indeed the case in the quasi-static limit, cf. eq. (13), but *not* in the long-time limit, cf. eqs. (8) and (9). The origin of this problem can be traced back to the contribution of large deviations to the Jarzynski average: this average corresponds to the characteristic function evaluated at the complex unit, $G(q = i)$, cf. eqs. (5) and (7). Even when higher-order cumulants converge to zero for the rescaled variable $(w - \langle w \rangle)/\sigma$ (central limit theorem), there is no guarantee that the contribution of the non-Gaussian tails can be neglected in the Jarzynski average. Hence the application of the Jarzynski equality using a Gaussian ansatz is not reliable and can lead, in a numerical or real experiment where a Gaussian distribution is observed, to an erroneous value of the corresponding free energy difference.

We finally turn to the practical and experimental relevance of the Jarzynski equality. In particular one may wonder to which extent the above ideal-gas results are representative of experimentally accessible measurements in a dilute gas. As a first step in answering this question, we have performed extensive molecular dynamics simulations of a dilute two-dimensional gas of hard disks. Note that such simulations allow to investigate parameter regions of high piston speed and short times which may be difficult to reach in experiment. The obtained simulation results represent an average over a half million runs, for a dilute hard disk gas with $N = 2000$ disks (diameter $d = 1$, mass $m = 1$). The initial positions and velocities of the disks are sampled from a microcanonical ensemble in a cylinder of length $L = 10^4$ and cross-section $S = 10^2$ (*i.e.*, initial gas density $\rho = 0.002$), and initial "temperature" $T = 1$. Extra caution was taken to reduce correlations between samples. To compare the results with the one-dimensional model, the effective projected density $n = \rho S$ has to be used.

A systematic comparison between analytical and simulation results was performed for a wide range of values of the speed v and of time τ, cf. figs. 1 and 4 for an illustration. Overall, the analytical and the simulation results agree qualitatively. In particular, the progressive change in the general shape of the probability distribution from adiabatic to non-adiabatic regime is well reproduced by the numerics. The comparison of moments given in table I confirms this agreement. There are, however, some notable discrepancies, namely for the mean and variance for the compression case ($v < 0$) and the variance for the slow piston ($|v| = 0.01$ in table I and fig. 4). These deviations can be explained by the fact that the molecular dynamics simulation deviates in two basic assumptions from the analytical model, namely the ideality of the gas and the thermodynamic limit. Although a rather low density is used, recollisions of the gas particles with the piston are not negligible. In particular, they

are clearly visible in the simulations when the piston compresses the gas. This presumably causes the shift in the mean value and the variance for $v < 0$. For very slow piston motion, recollisions are not a major problem, but the absence of the thermodynamic limit causes discrepancies between theory and simulations. Since $\tau = 1000$ for $|v| = 0.01$, several hundreds to a thousand particles collide with the piston out of the limited number of $N = 2000$. Clearly, the absence of fast particles in the tail of the Maxwellian distribution will cause a narrowing of the observed $P(w)$ distribution.

In conclusion, the verification or exploitation of the Jarzynski equality to measure free energy differences appears to be quite intricate. Due to the role of extreme events, the gain in computational time, when using a fast route between initial and final values of the control parameter, is outdone by the exponential increase in the required statistics [6]. The above explicit calculation and molecular dynamics simulations provide a dramatic example of this problem: even in the limit when a Gaussian distribution correctly describes the whole probability mass (in the sense of the central limit theorem), extreme events may still be needed to correctly perform the Jarzynski average. In particular, the fluctuation-dissipation ratio (14) need not approach the value 1 in a limit where $P(w)$ converges to a Gaussian distribution.

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