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Work distribution for the adiabatic compression of a dilute and interacting classical gas

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We consider a simple, physically motivated model of a dilute classical gas of interacting particles, initially equilibrated with a heat bath, undergoing adiabatic and quasistatic compression or expansion. This provides an example of a thermodynamic process for which non-Gaussian work fluctuations can be computed exactly from microscopic principles. We find that the work performed during this process is described statistically by a gamma distribution, and we use this result to show that the model satisfies the nonequilibrium work and fluctuation theorems, but not a prediction based on linear response theory.

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When a system is driven away from an initial state of thermal equilibrium by a mechanical perturbation, the statistical distribution of work for that process exhibits universal properties. In particular, the exponential average of the nonequilibrium work is related to an equilibrium free energy difference [1,2],

$$\beta\Delta F = -\ln\langle e^{-\beta W}\rangle = -\ln\int dW\rho(W)e^{-\beta W}. \tag{1}$$

Furthermore, the work distribution for such a process and the corresponding reversed process are related by the following work fluctuation theorem [3,4]:

$$\frac{\rho_{\mathrm{F}}(+W)}{\rho_{\mathrm{R}}(-W)} = e^{\beta(W-\Delta F)}. \tag{2}$$

Here, W is the work performed during a given realization of the process [5]; β is the inverse temperature of a thermal environment with which the system is initially equilibrated; ΔF is the free energy difference between two equilibrium states, both at temperature β^{-1}, corresponding to the initial and final values of the external work parameter [Eq. (13)]; ρ is the work probability distribution; and the subscripts F and R distinguish conjugate forward and reverse processes, where necessary. (See Refs. [1–6] for more details.) For cyclic processes, $\Delta F=0$ and Eq. (1) reduces to a result derived by Bochkov and Kuzovlev [7–9].

The discovery of these relations makes it interesting to find model systems for which the work distributions can be computed analytically. Previous models include harmonic potentials [10], two-level systems [11,12], ideal gas compression [13–16] and effusion [17], Gaussian polymer chains [14,18–20], Joule experiments [21], adiabatically stretched rotors [22,23], and charged particles in magnetic fields [24].

Here we consider a textbook example of a thermodynamic process: the slow, adiabatic compression or expansion of a dilute, *interacting* classical gas. This model was suggested to one of us (C.J.) by Seth Putterman [25] and has also appeared in this setting in a preprint by Sung [26]. Using elementary statistical mechanics, we solve for the work distribution and use this to verify Eqs. (1) and (2). This simple, physically motivated example has a number of attractive features. Unlike an ideal (noninteracting) gas, our model represents a genuine many-body system whose work distribution is both easy to calculate and describe and which is distinctly non-Gaussian [Eq. (12)]. The cumulants of this distribution are known exactly [Eq. (15)]; we exploit this to illustrate problems with applying the central limit theorem to apparently Gaussian distributions. The canonical temperature of the gas remains well-defined throughout the process [Eq. (18)]; we use this to clarify the physical meaning of the quantity ΔF. Finally, our model has considerable pedagogical value as the microscopic counterpart of a familiar macroscopic example of an adiabatic thermodynamic process.

Let us define the model more precisely. Consider the system shown in Fig. 1, a dilute classical gas confined in a piston. We assume that quantum effects are negligible, that the particles have no important internal structure, and that they rarely collide with one another. Specifically, the mean free path between such collisions is finite, but much greater than the characteristic distance between nearby particles. Initially, the piston is held fixed and the gas is brought to thermal equilibrium with an external, infinite heat bath. The bath is then removed, and the piston is very slowly forced inward, performing work as it compresses the gas to a new volume. In the corresponding reverse process the gas begins in equilibrium with the heat bath at the final volume of the forward process and we then adiabatically expand the gas back to the initial volume.

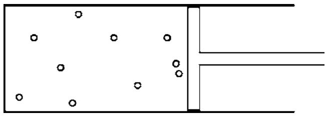

FIG. 1. A gas confined to a cylinder with a controllable piston.

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During the process of adiabatic compression just described, the gas remains in equilibrium locally, but not globally: since no heat is exchanged across the walls of the container, the kinetic temperature of the gas rises as the piston moves inward, resulting in a temperature difference between the gas and the heat bath. By contrast, if the gas were to remain in thermal contact with the heat bath as it was slowly compressed, then the process would be *isothermal* (rather than adiabatic) and global equilibrium would be preserved.

As a first pass at this model, let us use simple arguments to verify Eq. (1). In three spatial dimensions, the average equilibrium energy of a dilute N-particle gas is $\bar{E}=3N/2\beta$ and the entropy is given by the Sackur-Tetrode equation $S/N=\ln(V/N\Lambda^3)+5/2$. Here V is the volume of the box and $\Lambda=\sqrt{\beta h^2/2\pi m}$ is the thermal de Broglie wavelength (h is Planck's constant and m is the particle mass). The free energy $F=\bar{E}-\beta^{-1}S$ is then

$$F(\beta,V)=-\frac{N}{\beta}\left[\ln\left(\frac{V}{N}\right)+\frac{3}{2}\ln\left(\frac{2\pi m}{\beta h^2}\right)+1\right], \tag{3}$$

which satisfies the scaling law (for any $\sigma>0$)

$$\sigma F(\sigma\beta,V)=F(\beta,\sigma^{-3/2}V). \tag{4}$$

When such a gas is prepared in equilibrium, as described above, its energy E can be viewed as a random variable sampled from the canonical distribution,

$$P(E;\beta,V)=\frac{1}{Z(\beta,V)}g(E;V)e^{-\beta E}, \tag{5}$$

where $g(E)$ is the density of states and $Z=e^{-\beta F}$ is the partition function. Since the pressure of a dilute gas is $p=2E/3V$ and its energy during an adiabatic process changes by increments $dE=-pdV$, the product $VE^{3/2}$ is conserved as we slowly change the volume from V_0 to V_1 [26]. The final energy is thus

$$E_1=(V_0/V_1)^{2/d}E_0\equiv qE_0, \tag{6}$$

where $d=3$, and the work performed is

$$W=E_1-E_0=\alpha E_0, \quad \alpha=q-1. \tag{7}$$

Note that α is positive for compression and negative for expansion, and $-1<\alpha<\infty$. For expansion $|W|$ cannot be greater than the initial kinetic energy.

Using Eqs. (5) and (7) we get

$$\begin{aligned}-\ln\langle e^{-\beta W}\rangle&=-\ln\int dE_0P(E_0;\beta,V_0)e^{-\beta W(E_0)}\\&=-\ln\left[\frac{1}{Z(\beta,V_0)}\int dE_0g(E_0;V_0)e^{-q\beta E_0}\right]\\&=-\ln\frac{Z(q\beta,V_0)}{Z(\beta,V_0)}=q\beta F(q\beta,V_0)-\beta F(\beta,V_0).\end{aligned}$$

But $qF(q\beta,V_0)=F(\beta,V_1)$ [Eq. (4)]; hence, the right side is simply $\beta F(\beta,V_1)-\beta F(\beta,V_0)=\beta\Delta F$, as predicted by Eq. (1).

The preceding simple analysis is based on a large-N approximation [Eq. (3)], not an exact result. Moreover, we have invoked macroscopic, thermodynamic arguments in deriving Eq. (7). Such arguments are valid when the aim is to describe the typical behavior of a system, but become suspect in the present context, since the average $\langle\exp(-\beta W)\rangle$ is often dominated by highly atypical realizations. Finally, to verify Eq. (2) we must solve for $\rho(W)$, which requires obtaining the density of states, $g(E)$. We therefore now proceed with a more careful analysis. For the sake of generality, we allow the dimensionality of space to be an arbitrary integer $d>1$, rather than assuming $d=3$.

The density of states is the derivative of $\Phi(E)$, the number of energy states with energy less than E. For a dilute gas in the classical limit,

$$\Phi(E;V)=\frac{1}{h^{2k}}\frac{V^N}{N!}\frac{(2\pi mE)^k}{k\Gamma(k)}, \tag{8}$$

where $k=dN/2$ and $\Gamma(k)$ is the gamma function. On the right side of Eq. (8), the first factor accounts for the quantum graininess of phase space, the factor $V^N/N!$ counts the number of arrangements of N identical particles in a volume V, and the last factor is the volume of a dN-dimensional hypersphere of radius $\sqrt{2mE}$ in momentum space [27]. Hence

$$g(E;V)=\frac{\partial\Phi}{\partial E}=\frac{1}{h^{2k}}\frac{V^N}{N!}\frac{(2\pi m)^k}{\Gamma(k)}E^{k-1}. \tag{9}$$

The partition function $Z=\int dEg(E)e^{-\beta E}$ and free energy F follow by direct integration:

$$F(\beta,V)=-\frac{1}{\beta}\ln Z(\beta,V)=-\frac{1}{\beta}\ln\left[\frac{V^N}{N!}\left(\frac{2\pi m}{\beta h^2}\right)^k\right]. \tag{10}$$

[We recover Eq. (3) using Stirling's approximation $\ln N!\approx N\ln N-N$.] Equations (5), (9), and (10) together give us

$$P(E;\beta)=\frac{\beta}{\Gamma(k)}(\beta E)^{k-1}e^{-\beta E}. \tag{11}$$

The notation $P(E;\beta)$ [compare with Eq. (5)] reflects the result that the canonical energy distribution is independent of container volume V.

Let us now rederive Eq. (7) (for arbitrary $d>1$) using microscopic principles rather than thermodynamic arguments. We will assume the dynamics are ergodic when the container is held fixed. (For a hard-sphere gas, this assumption is reasonable for as few as $N=2$ spheres [28].) An ergodic Hamiltonian trajectory explores all regions of a constant-energy surface in $2dN$-dimensional phase space. It then follows that $\Phi(E;V)$ is an adiabatic invariant [29,30]: when V is varied infinitely slowly, the energy of the gas evolves so as to keep the value of Φ constant. The final energy E_1 is thus determined uniquely by the initial energy E_0 [2,15,31,32]. Specifically, since $\Phi\propto(VE^{d/2})^N$ [Eq. (8)], we again obtain $E_1=(V_0/V_1)^{2/d}E_0$; hence, $W=\alpha E_0$ [Eq. (7)].

Because E_0 determines W, the distribution of initial energies maps onto a distribution of work values:

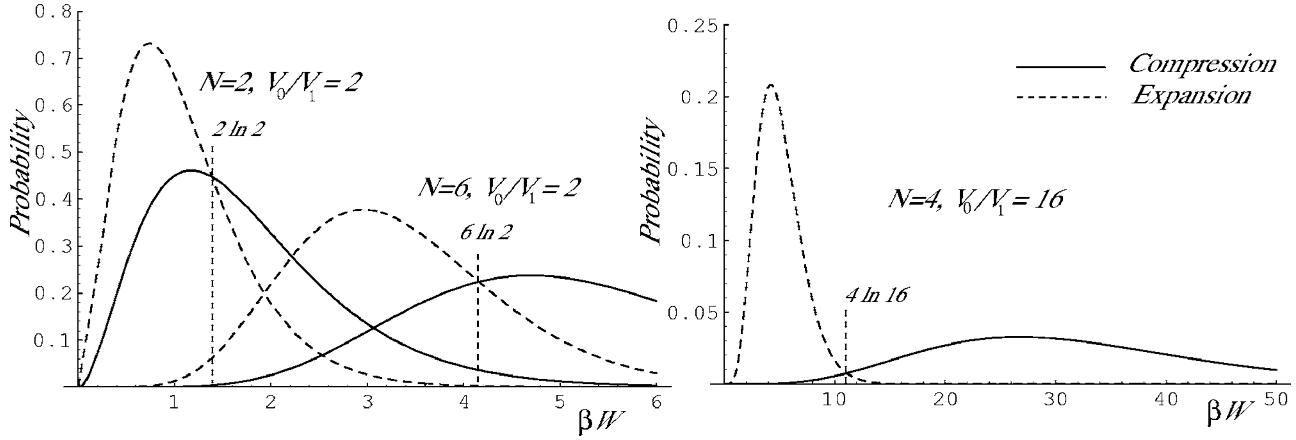

FIG. 2. The work probability density $\rho(W)$ given by Eq. (12). The solid lines are the work of compression, and the dashed lines are the *negative* work of expansion. Note that the magnitude of the work is greater for compression than expansion. Each distribution obeys the nonequilibrium work theorem (1), and each compression-expansion pair are related by the work fluctuation theorem (2). A direct consequence of the latter, illustrated in the figure, is that the corresponding forward and negative reverse work distributions cross at $W=\Delta F$ (13).

$$\rho(W) = \int dE_0 P(E_0;\beta)\,\delta(W-\alpha E_0)$$

$$= \frac{\beta}{|\alpha|\Gamma(k)}\left(\frac{\beta|W|}{\alpha}\right)^{k-1} e^{-\beta|W|/\alpha}\theta(\alpha W). \qquad (12)$$

Here the unit step function $\theta(\cdot)$ guarantees that W is positive for compression $(\alpha>0)$ and negative for expansion $(\alpha<0)$. Note that $\rho(W)$ depends on the ratio V_1/V_0 and not on the absolute volumes. Equation (12), the central result of this paper, shows that the distribution of absolute work values is a gamma distribution with shape parameter $k=dN/2$ and scale $s=|\alpha|/\beta$, as illustrated in Fig. 2. In contrast with previous models [10–24], this non-Gaussian expression is valid for an interacting, many-particle system.

Equation (12) allows us to verify the fluctuation theorem, Eq. (2). Let $\alpha_{\mathrm{F}}=(V_0/V_1)^{2/d}-1$ and $\alpha_{\mathrm{R}}=(V_1/V_0)^{2/d}-1$ denote the values of α for the forward $(V_0\to V_1)$ and reverse $(V_1\to V_0)$ processes. Note that $-\alpha_{\mathrm{R}}/\alpha_{\mathrm{F}}=(V_1/V_0)^{2/d}$ and $\alpha_{\mathrm{F}}^{-1}+\alpha_{\mathrm{R}}^{-1}=-1$. Combining these identities with Eq. (12), we obtain

$$\frac{\rho_{\mathrm{F}}(+W)}{\rho_{\mathrm{R}}(-W)} = \frac{|\alpha_{\mathrm{R}}|}{|\alpha_{\mathrm{F}}|}\left(-\frac{\alpha_{\mathrm{R}}}{\alpha_{\mathrm{F}}}\right)^{k-1}\exp[-\beta W(\alpha_{\mathrm{F}}^{-1}+\alpha_{\mathrm{R}}^{-1})]$$

$$= \left(\frac{V_1}{V_0}\right)^{N} e^{\beta W} = e^{\beta(W-\Delta F)},$$

where

$$\Delta F = F(\beta,V_1) - F(\beta,V_0) = \frac{N}{\beta}\ln\frac{V_0}{V_1} = \frac{1}{\beta}\frac{dN}{2}\ln(1+\alpha), \qquad (13)$$

by Eqs. (7) and (10). This confirms Eq. (2).

The nonequilibrium work relation [Eq. (1)] follows immediately from the work fluctuation theorem [Eq. (2)] [3], though it can also be verified by the direct evaluation of $\int\rho(W)e^{-\beta W}dW$. An alternative approach is to use a cumulant expansion [1]

$$\ln\langle e^{-\beta W}\rangle = \sum_{j=1}^{\infty}(-\beta)^j\frac{\omega_j}{j!}, \qquad (14)$$

where ω_j is the jth cumulant of $\rho(W)$. Using standard properties of the gamma distribution [33], we get

$$\omega_j = \frac{dN}{2}\left(\frac{\alpha}{\beta}\right)^{j}(j-1)!, \qquad (15)$$

hence

$$-\ln\langle e^{-\beta W}\rangle = -\frac{dN}{2}\sum_{j=1}^{\infty}\frac{(-\alpha)^j}{j} = \frac{dN}{2}\ln(1+\alpha), \qquad (16)$$

again confirming Eq. (1) for this model [see Eq. (13)].

The adiabatic invariance of $\Phi(E;V)$ determines the energy of the gas, not only at the end of the process [Eq. (6)] but also at intermediate times: $E(t)=[V_0/V(t)]^{2/d}E_0\equiv q_tE_0$. Combining this result with Eq. (11) to evaluate the time-dependent distribution of gas energies,

$$p(E,t) = \int dE_0 P(E_0;\beta)\,\delta(E-q_tE_0) = P(E;\beta/q_t), \qquad (17)$$

we find that our ensemble remains canonically distributed during the entire process (this is a specific feature of our model) at a slowly changing temperature

$$T(t) = [V_0/V(t)]^{2/d}T_0. \qquad (18)$$

This is in agreement with a macroscopic picture of adiabatic compression. It is important to keep in mind, however, that ΔF in Eqs. (1) and (2) is *not* the free energy difference between the initial and final states of the gas during this *adiabatic* process, but rather between the terminal states of the corresponding *isothermal* process; see Eq. (13), the earlier discussion of local and global equilibrium, and Refs. [34,35].

When $N\gg 1$, we expect a Gaussian distribution of work values, by the central limit theorem. Equation (12) confirms this expectation, as the gamma distribution approaches a Gaussian for large $k=dN/2$ [33]. Since all higher $(j>2)$ cumulants of a Gaussian vanish identically, we might be tempted to conclude that a good approximation is obtained by truncating Eq. (14) after two terms:

$$\Delta F \approx \langle W\rangle - \frac{\beta}{2}\sigma_W^2 = \frac{1}{\beta}\frac{dN}{2}(\alpha - \alpha^2), \qquad (19)$$

where $\langle W\rangle = \omega_1$ and $\sigma_W^2 = \omega_2$ are the mean and variance of $\rho(W)$. However, comparison with the exact result, Eq. (13), reveals that this approximation is valid only for small $|\alpha|$, when $V_1 \approx V_0$. The failure of Eq. (19) for larger $|\alpha|$ illustrates a subtle point: while $\rho(W)$ is indeed very nearly Gaussian in the central region near its mean, the average of $\exp(-\beta W)$ is dominated by work values deep in the lower tail of the distribution [12,36], *precisely where the central limit theorem does not apply*. Thus we cannot use the argument that $\rho(W)$ "becomes Gaussian" to justify neglecting the higher cumulants. Equation (19) is also the linear response prediction for ΔF, which is valid for processes that can be viewed as small excursions away from an isothermal process [37]. However, this condition is not met during the adiabatic process that we have considered: unless $V_1 \approx V_0$, the temperature of the ensemble under adiabatic compression changes substantially [Eq. (18)].

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