Stochastic Thermodynamics of a Particle in a Box

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The piston system (particles in a box) is the simplest paradigmatic model in traditional thermodynamics. However, the recently established framework of stochastic thermodynamics (ST) fails to apply to this model system due to the embedded singularity in the potential. In this Letter, we study the ST of a particle in a box by adopting a novel coordinate transformation technique. Through comparing with the exact solution of a breathing harmonic oscillator, we obtain analytical results of work distribution for an arbitrary protocol in the linear response regime and verify various predictions of the fluctuation-dissipation relation. When applying to the Brownian Szilard engine model, we obtain the optimal protocol $\lambda_t = \lambda_0 2^{t/\tau}$ for a given sufficiently long total time τ. Our study not only establishes a paradigm for studying ST of a particle in a box but also bridges the long-standing gap in the development of ST.

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Introduction.—When opening any textbook of thermodynamics [1], the piston system [2], or the classical ideal gas inside a rigid-wall potential, is the simplest archetypal model used to illustrate various thermodynamic processes and cycles. In the context of traditional thermodynamics, due to the macroscopic size of the system, fluctuations are usually vanishingly small. There, work and heat are phenomenological variables and the microscopic equation of motion (EOM) is not directly relevant.

When considering a small system, however, fluctuations become important and the EOM becomes essential [3]. In recent years, substantial developments in the field of nonequilibrium thermodynamics in small systems [4,5] have been made. One of them is the formulation of the so-called stochastic thermodynamics (ST) [6–8], where stochastic dynamics is incorporated into thermodynamics. For small systems, e.g., a Brownian particle in a controllable potential, a coherent framework of thermodynamics at the trajectory level is constructed. Fluctuating thermodynamic variables, such as work, heat, and entropy production, are identified as functionals of individual trajectories [9–12], based on which one can, in principle, calculate their distributions in arbitrary driven processes [13,14] and thus go beyond the traditional thermodynamics. In the linear response regime, the work distribution is Gaussian and satisfies the fluctuation-dissipation relations (FDRs) [13,15]. What is more, even in arbitrarily far-from-equilibrium processes, some exact fluctuation relations concerning work, heat, and entropy production are discovered [11,16–21]. Experimentally, these fluctuation relations have been verified in various systems, including a Brownian particle in a soft-wall potential [22–25], exemplified by a charged colloidal particle trapped by optical tweezers. The essential point of these developments in thermodynamics is the microscopic definition of work, heat, and entropy at the trajectory level.

However, the usual microscopic definition of work $W[x_t] = \int dt \partial_t V_t(x_t)$ [11,12] (see Refs. [6,21,26–32] for discussions and debates) is not applicable to the piston system, due to singularities in the rigid-wall potential, where work is done during discrete collisions of the particle with the moving piston [33,34]. Previously, there are studies about work distributions of piston systems in nonequilibrium processes, but either with no contact with a heat bath [33–35] or with no relevance to Brownian dynamics [36–39]. The solution to the piston system becomes a "missing puzzle piece" in ST. Possibly for lack of efficient ways of studying ST in a piston system, finite-time thermodynamics of the famous Brownian Szilard engine (BSE) [36,39–43] remains unexplored so far. Hence, how to extend the framework of ST to the piston system becomes one of the most challenging problems in this field.

In this Letter, we try to extend the previous framework of ST to include the rigid-wall potential. We introduce a novel approach of coordinate transformation to study the ST in an isothermal piston. In this way, under certain conditions, the isothermal piston model is found to be highly similar to an isothermal breathing harmonic oscillator (HO) [44,45], one of the very few models whose work distribution in an arbitrary process can be calculated analytically [45]. Since exactly solvable models play an important role in statistical mechanics, considering the special role and the ubiquity of piston systems in thermodynamics, we believe that our work not only significantly extends the applicability of ST but also has pedagogical value. We also note that the rigid-wall potential is accessible in current experiments [46,47], so our findings could possibly be tested.

Model setup.—Consider a single Brownian particle confined in a one-dimensional piston with its left boundary fixed while the right one movable. The mass of the particle is denoted by m, and the left and right boundaries are at the origin $x = 0$ and $x = \lambda_t$ $(0 \le t \le \tau)$, respectively. The piston system is coupled to a heat bath with inverse temperature β, so the motion of the Brownian particle can be described by the following underdamped Kramers-Langevin equation [6]

$$\dot{x} = \frac{p}{m}, \qquad \dot{p} = -\gamma \frac{p}{m} + \sqrt{\frac{2\gamma}{\beta}}\eta_t + I_c, \tag{1}$$

where $(x, p) \equiv \Gamma$ is the particle's position-momentum coordinate in the phase space, γ is the viscous friction coefficient that characterizes the coupling strength between the piston system and the heat bath, η_t is the standard Wiener process satisfying $\langle \eta_t \eta_{t'} \rangle = \delta(t - t')$ and $\eta_t dt \sim N(0, dt)$ (normal distribution with mean zero and variance dt), and I_c is the collision term responsible for the collisions with the two boundaries, which are necessary to keep the particle inside the piston, namely, $x_t \in [0, \lambda_t]$. Explicitly, I_c suddenly changes p into $2m\dot{\lambda}_t - p$ (or $-p$) once a collision at the right (or left) boundary occurs at time t. We emphasize that since the change of the momentum is essential in collision processes, our starting point is the underdamped [45,48,49] EOM (1) instead of the overdamped Langevin equation, which is simpler and is more frequently adapted in calculating work distributions in ST.

Provided that the collisions are elastic, the work functional in terms of a trajectory $\Gamma_t \equiv (x_t, p_t)$ in the phase space can be evaluated as [33]

$$W[\Gamma_t] = -\sum_{t \in C[x_t]} 2\dot{\lambda}_t (p_{t^-} - m\dot{\lambda}_t), \tag{2}$$

where $C[x_t] \equiv \{t : x_t = \lambda_t, 0 \le t \le \tau\}$ is the set of collision time points for a trajectory x_t in real space; p_{t^-} is the momentum value at the time point immediately prior to t. One can see that the above work expression differs significantly from the usual one $W[x_t] = \int dt \partial_t V_t(x_t)$ [11,12] in both the momentum dependence and the discrete summation rather than an integration.

To be specific, in the following we will focus on calculating the work distribution for the expansion process starting from a canonical ensemble, where the initial distributions of x and p are, respectively, $U(0, \lambda_0)$ (uniform distribution) and $N(0, m/\beta)$ (normal distribution). During the course, the right boundary is driven according to an arbitrary protocol λ_t and ends at $\lambda_\tau = 2\lambda_0$. Actually, this is the model used in the famous BSE [36,39–43].

Coordinate transformation and the Feynman-Kac equation.—While the numerical simulation based on Eqs. (1) and (2) is straightforward, a direct analytical treatment seems to be hopeless, due to the difficulties caused by the time-dependent boundary condition and the collision term I_c. To eliminate these difficulties, we perform the following coordinate transformation [50]

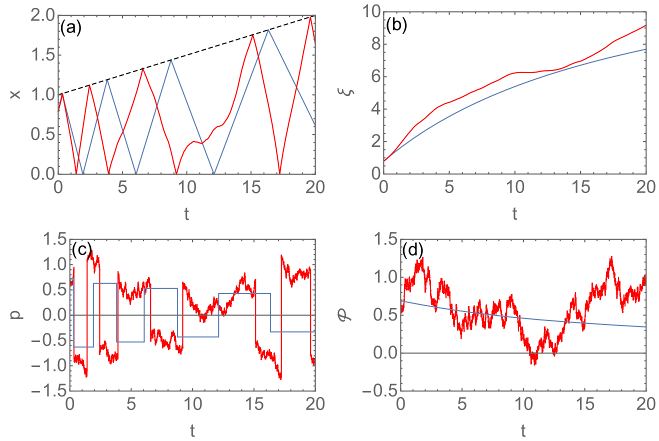

FIG. 1. Typical trajectories of (a) position x and (c) momentum p, as well as the new variables (b) ξ and (d) $\mathcal{P}$ after transformation (3). The expansion protocol is the linear one, i.e., $\lambda_t = \lambda_0(1 + t/\tau)$, where $\lambda_0 = 1$ and $\tau = 20$, presented as the dashed black line in (a). All the blue curves correspond to the adiabatic process ($\gamma = 0$), while the red ones correspond to the isothermal process with $\gamma = 0.05$ and $\beta = 1$.

$$(-)^{\lfloor \xi \rfloor + 1} h(\xi) \equiv \frac{x}{\lambda_t}, \qquad \mathcal{P} \equiv (-)^{\lfloor \xi \rfloor} p + m\dot{\lambda}_t h(\xi), \tag{3}$$

where $h(\xi) \equiv 2\lfloor (\xi + 1)/2 \rfloor - \xi$ with $\lfloor \ldots \rfloor$ being the Gauss floor function; the dimensionless quantity ξ can be any value on the real axis. From Eq. (3), it seems that the new coordinate ξ can hardly be uniquely determined by x, but a one-to-one mapping between them can be indeed unambiguously established as long as we add the information of collision to ξ. We stipulate that ξ crosses an integer every time a collision occurs. In particular, ξ crosses an odd (even) integer once the particle collides with the right (left) boundary. Such a correspondence relation (3) is illustrated schematically in Fig. 1. It is found that both $\dot{\xi}$ and $\mathcal{P}$ are continuous functions of time, in the sense that they never jump. Thus, we expect to construct a collision-free EOM with respect to the new variables $\tilde{\Gamma} \equiv (\xi, \mathcal{P})$, since they are continuous functions of time. After some calculations, we obtain the following new EOM in terms of ξ and $\mathcal{P}$

$$\dot{\xi} = \frac{\mathcal{P}}{m\lambda_t},$$
$$\dot{\mathcal{P}} = (\gamma\dot{\lambda}_t + m\ddot{\lambda}_t)h(\xi) - \left(\frac{\gamma}{m} + \frac{\dot{\lambda}_t}{\lambda_t}\right)\mathcal{P} + \sqrt{\frac{2\gamma}{\beta}}\eta_t. \tag{4}$$

Correspondingly, the work functional in terms of the new variables reads

$$W[\tilde{\Gamma}_t] = -\int_0^\tau dt \frac{\mathcal{P}_t^2 \dot{\lambda}_t}{m\lambda_t}[h'(\xi_t) + 1], \tag{5}$$

where $h'(\xi) + 1$ is a compact form of $2\sum_{k\in\mathbb{Z}} \delta(\xi - 2k - 1)$, and obviously this work functional (5) cannot be directly

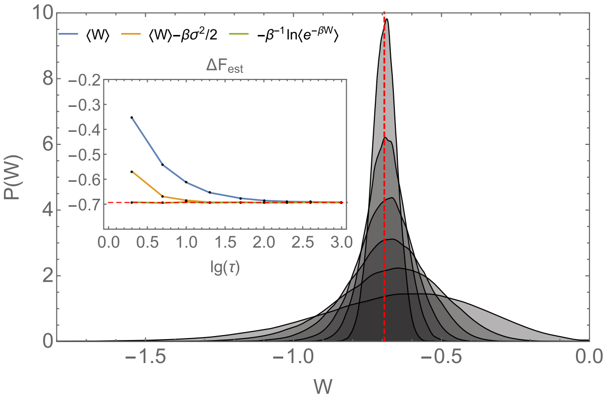

FIG. 2. Work distribution functions for the uniform expansion protocol with $\tau = 20$, 50, 100, 200, 400, 1000 obtained from stochastic simulations, where the $P(W)$ curve with sharper peak corresponds to larger τ (similar results were obtained for a breathing HO in Ref. [53]). The work distribution for $\tau = 20$ is clearly non-Gaussian, and thus beyond the linear response regime. The vertical red dashed line marks the position of $\Delta F = \beta^{-1} \ln 2$. The inset shows the numerical estimation of the free-energy difference ΔF_{est} based, respectively, on the mean work $\langle W \rangle$ (blue line), the linear response correction $\langle W \rangle - \beta\sigma^2/2$ (orange line), and the Jarzynski equality $-\beta^{-1} \ln\langle e^{-\beta W}\rangle$ [15] for nine different uniform expansion processes, with $\tau = 2, 5, 10, 20, 50, 100, 200, 400, 1000$. The horizontal red dashed line is the theoretical free-energy difference, while the dots are the simulation results. Here, $\lambda_0 = 1$, $\beta = 1$, and $\gamma = 1$ are all fixed.

obtained from the usual microscopic definition of work $W[x_t] = \int dt \partial_t V_t(x_t)$ [11,12].

To check the correctness of such a coordinate transformation, we carry out numerical simulations based on the new EOM (4) and the work functional (5). The results are presented in Fig. 2, which strongly suggest the validity of the Jarzynski equality and the asymptotic Gaussian type of work distribution for large τ, which has been analytically demonstrated for generic overdamped Langevin systems with smooth potentials [13]. Further examinations confirm the validity of the coordinate transformation [50].

With these relations, we can write down the Feynman-Kac equation (FKE) [44,45,54], which determines the time evolution of the phase point distribution weighted by a parametric exponential work factor. The FKE is obtained as [50]

$$\partial_t \rho_s = \mathcal{L}[\lambda_t]\rho_s + s\frac{\mathcal{P}^2 \dot{\lambda}_t}{m\lambda_t}[h'(\xi) + 1]\rho_s, \tag{6}$$

where $\rho_s = \rho_s(\xi, \mathcal{P}, t)$ is related to the joint distribution function $\rho(\xi, \mathcal{P}, W, t)$ by a Laplace transform $\rho_s \equiv \int_{-\infty}^{+\infty} dW \rho(\xi, \mathcal{P}, W, t) e^{-sW}$ and the linear operator $\mathcal{L}[\lambda_t]$ is defined as

$$\mathcal{L}[\lambda_t] \equiv -\frac{\mathcal{P}}{m\lambda_t}\partial_\xi + \left[(\gamma\dot{\lambda}_t + m\ddot{\lambda}_t)h(\xi)\partial_{\mathcal{P}} + \partial_{\mathcal{P}}\left(\frac{\gamma}{m} + \frac{\dot{\lambda}_t}{\lambda_t}\right)\mathcal{P}\right] + \frac{\gamma}{\beta}\partial_{\mathcal{P}}^2. \tag{7}$$

Once we solve Eq. (6), we can immediately obtain the generating function $\psi_s(t)$ of the work distribution by integrating out ξ and $\mathcal{P}$, namely, $\psi_s(t) \equiv \langle e^{-sW}\rangle = \int d\xi d\mathcal{P} \rho_s(\xi, \mathcal{P}, t)$. The generating function $\psi_s(t)$ provides an alternative way to get access to the properties of the work distribution function [44], so the central problem is to solve the FKE (6).

Frequent-collision approximation and the reduced Feynman-Kac equation.—Unfortunately, a general exact solution of the FKE (6) is difficult to obtain, due to the complexities arising from both the number of variables and the nonanalyticity of the expressions $[h(\xi)]$. In fact, besides the driven overdamped Brownian HO [55,56], the V potential [57], and the logarithmic-harmonic potential [57,58], the only analytically solvable model in ST so far seems to be the breathing overdamped Brownian HO [44,45]. Even for such a model, an exact solution is usually unavailable unless the initial distribution is Gaussian.

Accordingly, we need to make further approximations to obtain analytic results in certain interesting regimes. Remember that one of the difficulties comes from the discreteness of collisions, and the work accumulates more and more continuously as the collision frequency increases. This is the case in the high temperature limit for a given protocol, or equivalently, in the slow limit of the protocol at any finite temperature. A paradigmatic example to illustrate this subtlety is the work distribution for the quasistatic adiabatic expansion processes of an ideal gas [59], which can be exactly reproduced by the universal work distribution function in Ref. [33] via smoothing out the local oscillations caused by the discreteness of collisions. Inspired by this, we can similarly try to flatten the rapidly oscillating parts $h(\xi)$ in the FKE (6). In fact, it is feasible to construct a reduced partial differential equation only in terms of $\mathcal{P}$ via integrating out the positionlike variable ξ under this approximation, which is completely in contrast to the conventional overdamped Langevin dynamics where the position instead of the momentum is kept. The reduced Feynman-Kac equation (RFKE) in this case is

$$\partial_t \varrho_s = \partial_{\mathcal{P}}\left[\left(\frac{\gamma}{m} + \frac{\dot{\lambda}_t}{\lambda_t}\right)\mathcal{P} + \frac{\gamma}{\beta}\partial_{\mathcal{P}}\right]\varrho_s + s\frac{\mathcal{P}^2\dot{\lambda}_t}{m\lambda_t}\varrho_s, \tag{8}$$

where $\varrho_s = \varrho_s(\mathcal{P}, t) \equiv \int d\xi \rho_s(\xi, \mathcal{P}, t)$ is the $\mathcal{P}$ marginal distribution function weighted by a parametric exponential work factor. The validity of the RFKE can be checked self-consistently [50]. We emphasize that the RFKE (8) is merely an approximated equation valid for sufficiently slow expanding.

Asymptotic behavior and protocol optimization in the linear response regime.—Thanks to the similarity between the RFKE (8) (as well as its associated work functional) and the overdamped FKE for a breathing HO [44,45], we can further simplify Eq. (8) into a set of ordinary differential equations by utilizing the technique developed in dealing with the breathing HO model [44,45]. The key point of the technique is the Gaussian ansatz that the solution takes the form $\varrho_s(\mathcal{P},t) = \sqrt{\{[\psi_s(t)]^3\}/[2\pi\phi_s(t)]}e^{-[\mathcal{P}^2\psi_s(t)]/[2\phi_s(t)]}$ [60]. In this manner, the RFKE (8) is equivalent to

$$\dot{\psi}_s = \frac{s\dot{\lambda}_t}{m\lambda_t}\phi_s,$$
$$\dot{\phi}_s = -2\left(\frac{\gamma}{m} + \frac{\dot{\lambda}_t}{\lambda_t}\right)\phi_s + \frac{2\gamma}{\beta}\psi_s + \frac{3s\dot{\lambda}_t}{m\lambda_t}\frac{\phi_s^2}{\psi_s}, \qquad (9)$$

with the initial conditions $\psi_s(0) = 1$ and $\phi_s(0) = m/\beta$.

To proceed analytically, we further confine ourselves in the linear response regime, where $\alpha \equiv m\dot{\lambda}_t/\gamma\lambda_t \ll 1$ and Eq. (9) can be solved perturbatively. To perform perturbative analysis, we introduce another function $g_s(t) \equiv (\beta/s)(d\ln\psi_s/d\ln\lambda_t)$; thus, ψ_s can be evaluated in terms of g_s through $\psi_s(\tau) = \exp[(s/\beta)\int_0^\tau dt(\dot{\lambda}_t/\lambda_t)g_s(t)]$. Now, the problem is to solve for $g_s(t)$. The nonlinear ordinary differential equation that governs the time evolution of $g_s(t)$ is found to be a Riccati equation

$$\dot{g}_s = \frac{2\dot{\lambda}_t}{\lambda_t}g_s\left(\frac{s}{\beta}g_s - 1\right) - \frac{2\gamma}{m}(g_s - 1), \qquad g_s(0) = 1. \quad (10)$$

In the sense of perturbation, g_s should be expanded as $1 + g_s^{(1)} + g_s^{(2)} + \ldots$, where the magnitude of $g_s^{(k)}$ is $O(\alpha^k)$. In the linear response regime, we have $g_s \approx 1 + g_s^{(1)}$, according to which we expect the system to obey the FDR. In fact, we obtain $g_s^{(1)} = (m\dot{\lambda}_t/\gamma\lambda_t)[(s/\beta) - 1]$; thus, the generating function should be

$$\psi_s(\tau) = \exp\left[\frac{s}{\beta}\ln\frac{\lambda_\tau}{\lambda_0} + \frac{s}{\beta}\left(\frac{s}{\beta} - 1\right)\frac{\gamma}{m}\int_0^\tau dt\alpha^2 + O(\alpha^2)\right]. \qquad (11)$$

This expression indicates that the corresponding work distribution is Gaussian with the mean $\langle W\rangle = -\beta^{-1}\ln(\lambda_\tau/\lambda_0) + (\gamma/\beta m)\int_0^\tau dt\alpha^2$ and the variance $\sigma_W^2 = (2\gamma/\beta^2 m)\int_0^\tau dt\alpha^2$. Since the free-energy difference is $\Delta F = -\beta^{-1}\ln(\lambda_\tau/\lambda_0)$, we verify the first prediction of the FDR [15]: $\langle W\rangle - \Delta F = \frac{1}{2}\beta\sigma_W^2$. If we define the protocols $\lambda_t = \Lambda(t/\tau)$ with different τ as one class, then for a given class $\Lambda(u)$ $(0 \le u \le 1)$, the deviation of the mean work from the free-energy difference will be inversely proportional to τ [61]

$$\langle W\rangle - \Delta F = K\tau^{-1}, \qquad (12)$$

where the coefficient $K = (m/\beta\gamma)\int_0^1 du[\chi'(u)]^2$, $\chi(u) \equiv \ln[\Lambda(u)/\Lambda(0)]$. For a linear (sine) protocol $\chi(u) = \ln(1+u)$ $[\chi(u) = \ln[2\sin(\pi/3)(u+\frac{1}{2})]]$, we have $K = (m/2\beta\gamma)$ $[K = [(3\sqrt{3}-\pi)\pi m/9\beta\gamma]]$. This is another prediction of FDR in the linear response regime and is numerically verified (see Fig. 3). So far, we have analytically demonstrated that all these asymptotic behaviors of the work distribution of the expanding isothermal piston system share the same features

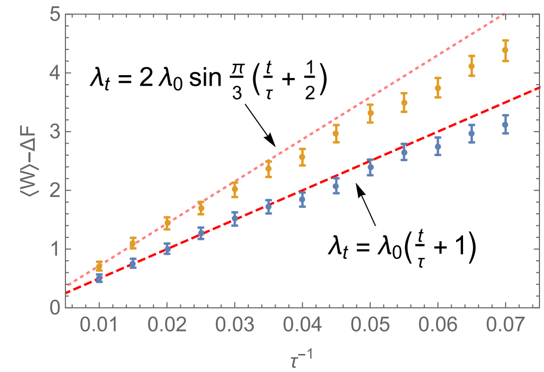

FIG. 3. $\langle W\rangle - \Delta F$ versus τ^{-1} for the uniform and the sine expansion protocols in the linear response regime, obtained by numerical stochastic simulations based on the original EOM (1) as well as the original work expression (2) (blue and yellow dots) and the theoretical prediction (12) (red dashed and dotted lines). The parameters are $\gamma = 1$ and $\beta^{-1} = 100$, and the error bar denotes twice the standard deviation of the mean. One can see good agreement for sufficiently small τ^{-1}.

with those of conventional overdamped Langevin systems [13,15,53] and obey FDRs. However, we again emphasize that the approaches used to deal with the systems with smooth potentials are essentially inapplicable to the piston system. So, a distinct method for the piston system is developed here.

Since we have obtained the mean work expression (12) analytically, we can also investigate the optimization problem in the linear response regime. Particularly, we are interested in the maximum mean work extraction from the heat bath for a given time interval $[0,\tau]$ [62–64] because the optimal work protocol of the BSE is a very important but unsolved problem. For the expansion process in a BSE cycle, the boundary condition can be rewritten as $\chi(0) = 0$ and $\chi(1) = \ln 2$. To maximize the mean work extraction, we only have to minimize the coefficient K as a functional of $\chi(u)$. The variation of K in terms of $\chi(u)$ gives a simple equation $\chi''(u) = 0$, implying that $\chi(u) = u\ln 2$ or $\lambda_t = \lambda_0 2^{t/\tau}$ is the optimal protocol that makes K reach its minimum $(m/\beta\gamma)\ln^2 2$. Starting from Eq. (8), the same result can be obtained from the thermodynamic length $\mathcal{L}$ via $K = \mathcal{L}^2$ [65], where $\mathcal{L} = \int_{\lambda_0}^{\lambda_\tau} d\lambda\sqrt{\zeta}$ with $\zeta = (m/\beta\gamma\lambda^2)$ being the thermodynamic metric for the piston system.

It is worth mentioning that we may also analyze the optimization problem based on Eq. (8) without doing perturbative expansions. The optimal protocol turns out to be similar to that of the breathing HO [62], and in the linear response regime, the exponential optimal protocol $\lambda_t = \lambda_0 2^{t/\tau}$ can be reproduced.

Conclusion.—Previously, nonequilibrium thermodynamics in the isothermal piston system can only be studied numerically and few insights can be gained from the numerical results [66]. In this Letter, by performing a coordinate transformation, we find that the EOM in the new coordinate corresponds to a collision-free stochastic diffusive system in the full space. We have derived the exact FKE and simplified it into a single-variable RFKE under the frequent-collision approximation. By solving the RFKE perturbatively, we not only demonstrate the Gaussian asymptotic behavior of the work distribution and the validity of the FDRs in the piston system but also obtain the optimal work extraction protocol $\lambda_t = \lambda_0 2^{t/\tau}$ of the BSE in the linear response regime. Our study is complementary to previous studies of ST in systems with smooth potentials. By extending the studies of ST to the conceptually simplest and paradigmatic model in traditional thermodynamics, the isothermal piston system, we bridge the long-standing gap in the development of ST.

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