

Finite-time adiabatic processes: Derivation and speed limitCarlos A. Plata,¹ David Guéry-Odelin,² Emmanuel Trizac,³ and Antonio Prados ⁴¹*Dipartimento di Fisica e Astronomia “Galileo Galilei,” Istituto Nazionale di Fisica Nucleare, Università di Padova, Via Marzolo 8, 35131 Padova, Italy*²*Laboratoire Collisions, Agrégats, Réactivité, IRSAMC, Université de Toulouse, CNRS, UPS, Toulouse, France*³*LPTMS, CNRS, Université Paris-Saclay, 91405 Orsay, France*⁴*Física Teórica, Universidad de Sevilla, Apartado de Correos 1065, E-41080 Sevilla, Spain*

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Obtaining adiabatic processes that connect equilibrium states in a given time represents a challenge for mesoscopic systems. In this paper, we explicitly show how to build these finite-time adiabatic processes for an overdamped Brownian particle in an arbitrary potential, a system that is relevant at both the conceptual and the practical level. This is achieved by jointly engineering the time evolutions of the binding potential and the fluid temperature. Moreover, we prove that the second principle imposes a speed limit for such adiabatic transformations: there appears a minimum time to connect the initial and final states. This minimum time can be explicitly calculated for a general compression or decompression situation.

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Adiabatic processes are a cornerstone in the thermodynamics of macroscopic systems. Therein, energy is solely exchanged as work—there is no heat—and the large system size makes fluctuations mostly irrelevant. If, in addition, the system always sweeps equilibrium states, i.e., the process is reversible, there is no entropy change. These processes played a central conceptual role in laying the foundations of thermodynamics, culminating with the works of Carathéodory and Planck (see Ref. [1]). Also, such processes are essential to build thermal engines. The Carnot cycle indeed consists of two reversible isothermal and two reversible adiabatic branches [1,2].

The relevance of mesoscopic systems spreads out across a wide range of fields in physics and technology, such as nanodevices [3,4], biomolecules [5–7], or active matter [8,9]. Statistical methods are typically applicable to mesoscopic systems, but their smallness entails that fluctuations play an important role [10,11]. It is thus challenging but also compelling to extend macroscopic concepts to the mesoscale because new physics often emerges, like the fluctuation theorems or transient violations of the second law [12–16].

At the mesoscale, defining and characterizing adiabatic processes is crucial, e.g., to build a mesoscopic version of the Carnot engine. But this is far from trivial: it is meaningless to imagine an inherently fluctuating Brownian particle thermally isolated from its environment for each of its trajectories; over them, both work and heat contribute to the energy change [17,18]. However, one can think of processes in which the average heat vanishes, not only between the initial and final states, but along the whole dynamics; thus the average work yields the average energy increment. This is the concept of adiabatic process that we employ throughout.

Finite-time adiabatic processes have not been devised so far. In fact, adiabatic processes have been only analyzed in simple limiting cases: vanishing or infinite-time operation. In the overdamped regime, *instantaneous* processes in which the position distribution does not change have been termed adiabatic [19–22] because the configurational contribution to the heat vanishes. However, these processes are not actually adiabatic, since there is a contribution to the heat—and to the entropy change—coming from the velocity degree of freedom: the temperature varies in such instantaneous processes [19,23]. For underdamped dynamics, only quasistatic *reversible adiabatic processes* have been analyzed, mainly for the harmonic case. Therein, this has led to the condition $T^2/k = \text{const}$, where T is the bath temperature and k is the stiffness of the trap [18,24,25].

Engineering adiabatic processes requires the joint time control of both the bath temperature and the confining potential, which can be implemented in experiments with micron-size colloids manipulated by laser tweezers in a suspending fluid [26,27]. Optical confinement makes it possible to control the time dependence of the effective temperature seen by the Brownian particle [26]. The dynamics is neatly overdamped for the broad class of systems consisting of mesoscopic objects suspended in a solvent [28]. We shall thus carry our analysis in this framework (see Appendix A).

Hereafter, we answer two physically relevant questions. First, we show how *finite-time adiabatic* processes can be built for a colloidal particle driven by an arbitrary potential. This has not only theoretical importance but also practical consequences. For example, shortening the duration of the adiabatic branches of a Brownian Carnot engine—like the one investigated in Ref. [18]—increases the delivered power. Second, we show that there appears a fundamental speed limit for such adiabatic processes. This is at variance with

the isothermal case, where equilibration can be arbitrarily accelerated [29]. The emergence of such speed limits is also of fundamental interest, with relevance in control theory and the foundations of nonequilibrium statistical mechanics [30–35].

The paper is organized as follows. In Sec. II, we rigorously show the feasibility of finite-time adiabatic processes in the context of stochastic thermodynamics. Section III is devoted to the optimization of such processes, either minimizing the connecting time or optimizing the target temperature. Finally, we summarize the conclusions of this paper in Sec. IV, along with a discussion of future perspectives. The Appendices deal with some technical aspects and complementary discussions that are not essential for the understanding of our results, and thus are omitted in the main text.

II. ENGINEERING FINITE-TIME ADIABATIC PROCESSES AND SPEED LIMIT

We consider a Brownian particle immersed in a heat bath at temperature $T(t)$ and trapped in a generic potential $U(X, t)$. The particle position obeys the Langevin equation

$$\lambda \frac{dX}{dt} = -\partial_X U(X, t) + \sqrt{2\lambda k_B T(t)} \xi(t), \quad (1)$$

with λ the friction coefficient and $\xi(t)$ a unit-variance Gaussian white noise. The Fokker-Planck (FP) equation for the probability density function (PDF) $P(X, t)$ of finding the particle at position X at time t thus reads

$$\lambda \partial_t P(X, t) = \partial_X [\partial_X U(X, t) P(X, t)] + k_B T(t) \partial_X^2 P(X, t). \quad (2)$$

We are interested in processes that connect two given equilibrium states in a running time t_f . Dimensionless variables are introduced with the definitions $\tau = t/t_f$ ($0 \leq \tau \leq 1$), $x = X/\sigma_{X,i}$, $\theta = T/T_i$, $u = U/(k_B T_i)$, and $p(x, \tau) = \sigma_{X,i} P(\sigma_{X,i} x, t_f \tau)$. For any physical quantity Y , we denote throughout the paper derivatives by $\dot{Y} \equiv \partial_\tau Y$ and $Y' \equiv \partial_x Y$, the initial (final) value by Y_i (Y_f), the difference between final and initial values by $\Delta Y \equiv Y_f - Y_i$, and the variance by σ_Y^2 . The FP equation is then

$$\dot{p}(x, \tau) = -j'(x, \tau), \quad (3a)$$

$$\frac{j(x, \tau)}{t_f^*} = -[u'(x, \tau)p(x, \tau) + \theta(\tau)p'(x, \tau)], \quad (3b)$$

where $t_f^* = k_B T_i t_f / (\lambda \sigma_{X,i}^2)$ is the dimensionless connecting time [36].

Energy has two contributions: a kinetic one and a configurational one coming from the potential $u(x, \tau)$. Within the overdamped description, the average kinetic energy always has the equilibrium value $\theta/2$, which is time dependent. Thus, the average energy is $\bar{E} = \theta/2 + \bar{u}(x, \tau)$, where $\bar{u}(x, \tau) = \int dx u(x, \tau) p(x, \tau)$. Work and heat exchange rates are $\dot{W} = \int dx \dot{u} p$ and $\dot{Q} = \dot{\theta}/2 + \dot{Q}_x$, with $\dot{Q}_x \equiv \int dx u \dot{p} = \int dx u' j$ the configurational heat rate. The first principle then holds: $\dot{E} = \dot{Q} + \dot{W}$ [10].

Entropy is introduced as [10] $S = S_{\text{kin}} + S_x$, where $S_{\text{kin}} = \frac{1}{2} \ln \theta$ and $S_x(\tau) = -\int dx p(x, \tau) \ln p(x, \tau) + K$. We choose the constant K to make $S_{x,i} = 0$ and simplify some formulas.

From the FP equation, extended forms of the second principle have been derived, $\dot{S} = \dot{S}_{\text{irr}} + \dot{Q}/\theta$, where $\dot{S}_{\text{irr}} \geq 0$ is the entropy production rate [10,11,37]. For adiabatic processes, \dot{S}_{irr} only contributes to the entropy change and one gets in dimensionless variables

$$\dot{S} = \dot{S}_{\text{irr}} = \frac{1}{t_f} \frac{1}{\theta(\tau)} \int dx \frac{j^2(x, \tau)}{p(x, \tau)}. \quad (4)$$

Let us consider given equilibrium initial and final states, corresponding to temperature and potential pairs $(\theta_i, u_i(x))$ and $(\theta_f, u_f(x))$, respectively. Our first aim is to show the feasibility of connecting these states adiabatically, i.e., find solutions of Eq. (3) that (i) have the canonical form at both the initial and final times

$$p_i(x) = Z_i^{-1} e^{-u_i(x)/\theta_i}, \quad p_f(x) = Z_f^{-1} e^{-u_f(x)/\theta_f}, \quad (5)$$

with $Z_{i,f}$ ensuring the normalization of the distributions, and (ii) make the total heat exchange rate $\dot{Q} = 0$ for all times. We show below how this can be done by tuning the temperature $\theta(\tau)$ and the potential $u(x, \tau)$. Note that $\bar{W} = \Delta \bar{E}$, regardless of the process duration.

We build explicitly these adiabatic processes by an *inverse-engineering* procedure. Starting from any $p(x, \tau)$ connecting these two fixed states, Eq. (3a) gives $j(x, \tau) = \int_x^{+\infty} d\xi \dot{p}(\xi, \tau)$. If we knew $\theta(\tau)$ (we do not yet), integration of Eq. (4) from $\tau = 0$ to 1 would yield the value of t_f and Eq. (3b) would finally give the force field $u'(x, \tau)$. This remark suggests to get rid of $\theta(\tau)$ by introducing the change of variable $\Xi(\tau) = e^{2S_x(\tau)}$, with $\Xi_i = 1$. Then, Ξ evolves according to

$$\Xi(\tau) = \theta(\tau) e^{2S_x(\tau)} = 1 + \frac{2}{t_f} \int_0^\tau d\zeta e^{2S_x(\zeta)} \int dx \frac{j^2(x, \zeta)}{p(x, \zeta)}. \quad (6)$$

Starting again from a PDF $p(x, \tau)$ verifying Eq. (5), $j(x, \tau)$ and also $S_x(\tau)$ follow. Thus, we know $\Xi(\tau)$ for all times and we can complete the inverse-engineering procedure.

(i) Particularizing Eq. (6) for $\tau = \tau_f = 1$, we obtain the value of the connecting time:

$$t_f = \frac{2}{\Delta \Xi} \int_0^1 d\tau e^{2S_x(\tau)} \int dx \frac{j^2(x, \tau)}{p(x, \tau)}. \quad (7)$$

(ii) Turning to Eq. (6), we get the temperature program $\theta(\tau)$. Note that $\theta(\tau) > 0$ for all times.

(iii) Equation (3b) provides us with the force $u'(x, \tau)$ that does the job.

Equation (6) shows that two arbitrary states cannot be connected with an adiabatic transformation. The positiveness of the right hand side ensures that $\Delta \Xi \geq 0$ or $\Xi_f \geq \Xi_i = 1$. The equality only holds for the quasistatic case: if $\Delta \Xi = 0$, we have that t_f diverges [38] and $\Xi(\tau) = 1$. With the exception of the quasistatic case, the adiabatic process cannot be reversed in time because that would violate the second principle.

Moreover, the second principle imposes a speed limit for finite-time adiabatic processes: there appears a minimum nonvanishing value for the connecting time t_f , except for a trivial “configurationally static” case. Starting from Eq. (6), this can be proved by a *reductio ad absurdum* argument. Let

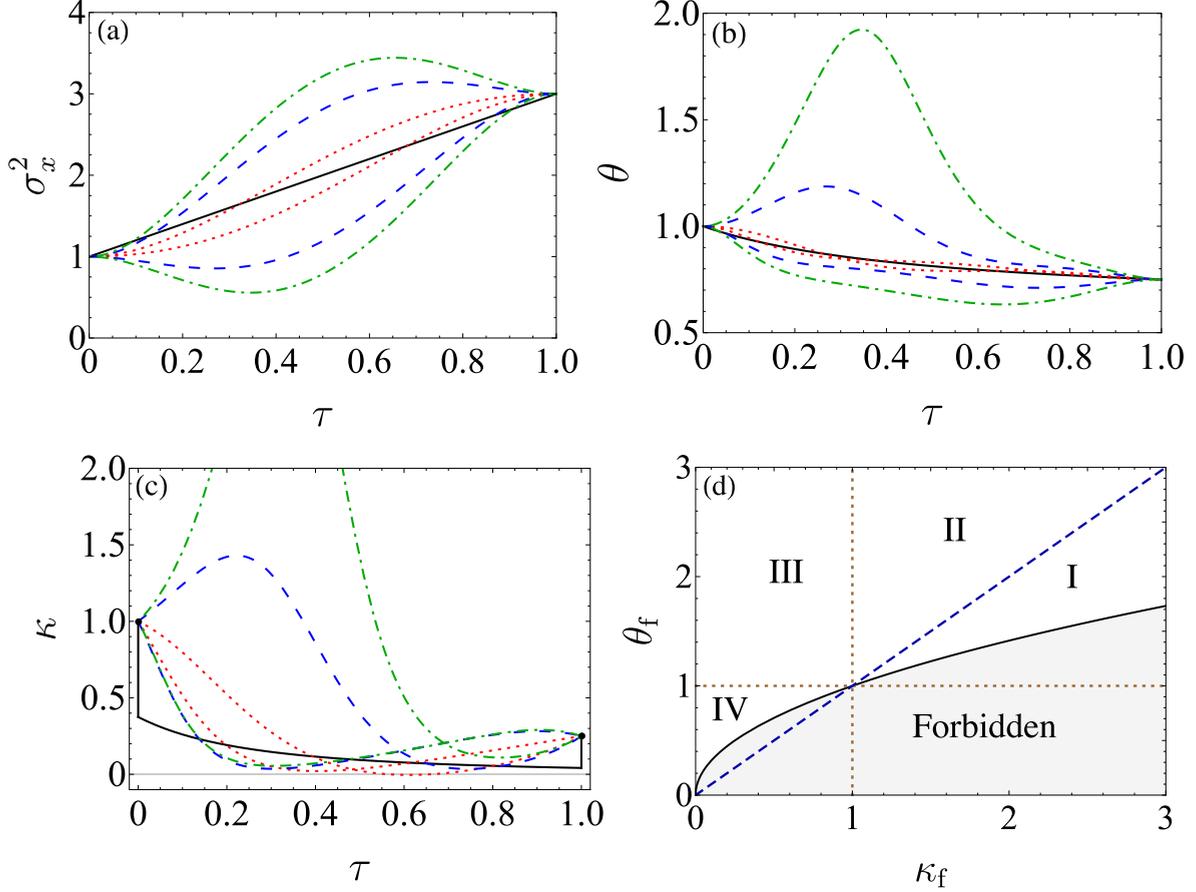


FIG. 1. Time evolution of $(\sigma_x^2, \theta, \kappa)$ in an adiabatic process (a–c) and phase diagram in the (κ_f, θ_f) plane (d). The target point in panels (a)–(c) is $(\sigma_{x,f}^2 = 3, \theta_f = 0.75, \kappa_f = 0.25)$. Optimal evolutions (solid lines) give the shortest connecting time $\tilde{t}_f = 1.6$. Nonoptimal evolutions correspond to longer connecting times $t_f = r\tilde{t}_f$, with $r = 1.25$ (dotted red), $r = 2$ (dashed blue), and $r = 3$ (dot-dashed green). In panel (d), the solid curve $\theta_f = \theta_f^\infty = \sqrt{\kappa_f}$ demarcates the gray region, which cannot be reached with an adiabatic process (“Forbidden”). Reachable points lie in four regions, labeled from I to IV. The diagonal line $\theta_f = \kappa_f$ separates compression ($\sigma_{x,f} < 1$, I) and expansion ($\sigma_{x,f} > 1$, II–IV) regions. The horizontal line separates heating ($\theta_f > 1$, I–III) and cooling ($\theta_f < 1$, IV), whereas the vertical one separates stiffening ($\kappa_f > 1$, I and II) from loosening ($\kappa_f < 1$, III and IV).

us assume that there is no lower bound for t_f and thus an instantaneous adiabatic process with $t_f = 0$ is possible. The right hand side of Eq. (7) then vanishes and $j(x, \tau) = 0$ everywhere. This entails that the FP equation must have a time-independent solution $p(x, \tau)$, but $p_i(x) \neq p_f(x)$ in general. This contradiction completes the argument. If $p_i(x) = p_f(x)$, i.e., $u'_i(x)/\theta_i = u'_f(x)/\theta_f$ as follows from Eq. (5), we deal with a configurationally static situation and t_f may vanish (see below). In that case, the system cannot cool since $\Xi(\tau)$ is nondecreasing, and thus so is $\theta(\tau)$.

III. COMPRESSION AND DECOMPRESSION PROCESSES: OPTIMAL CONNECTION

Let us analyze a generic and physically relevant case: the compression or decompression of a system around a fixed average value \bar{x} (the axis origin for convenience). We take $p(x, \tau) = [Z\sigma_x(\tau)]^{-1} \exp\{-u_i[x/\sigma_x(\tau)]\}$, thus of shape-preserved form, where σ_x is the variance of the distribution and the normalization constant $Z = \int dy \exp[-u_i(y)]$ does not depend on σ_x . The system is being decompressed (compressed) for $\dot{\sigma}_x > 0$ ($\dot{\sigma}_x < 0$) [39]. The corresponding current

and entropy follow immediately as $j = (\dot{\sigma}_x/\sigma_x)xp$ and $\Xi = \theta\sigma_x^2$. The adiabatic inequality simplifies to $\theta_f\sigma_{x,f}^2 \geq 1$.

For each choice of the function $\sigma_x(\tau)$ obeying $\sigma_x(0) = 1$, $\sigma_x(1) = \sigma_{x,f}$, the initial and final states are connected. Herein, explicit expressions for the connecting time t_f , the temperature program $\theta(\tau)$, and the binding potential $u(x, \tau)$ can be given. Indeed, Eqs. (6) and (7) reduce to

$$\theta(\tau)\sigma_x^2(\tau) - 1 = \frac{1}{2t_f} \int_0^\tau d\zeta \left[\frac{d}{d\zeta} \sigma_x^2(\zeta) \right]^2, \quad (8a)$$

$$t_f = \frac{J[\sigma_x]}{2\Delta(\theta\sigma_x^2)} \quad \text{with} \quad J[\sigma_x] \equiv \int_0^1 d\tau \left[\frac{d}{d\tau} \sigma_x^2(\tau) \right]^2 \quad (8b)$$

and the potential stems from Eq. (3b):

$$u(x, \tau) = -\frac{1}{2t_f} \frac{\dot{\sigma}_x(\tau)}{\sigma_x(\tau)} x^2 + \theta(\tau) u_i\left(\frac{x}{\sigma_x(\tau)}\right). \quad (9)$$

The speed limit for the adiabatic process can be explicitly worked out as well. Since the denominator of t_f in Eq. (8b) is fixed, the minimum time \tilde{t}_f corresponds to the variance profile

$\tilde{\sigma}_x$ that minimizes $J[\sigma_x]$. We get

$$\tilde{\sigma}_x(\tau) = \sqrt{1 + \tau \Delta(\sigma_x^2)} \quad \text{and} \quad \tilde{t}_f = \frac{[\Delta(\sigma_x^2)]^2}{2 \Delta(\theta \sigma_x^2)}. \quad (10)$$

Note that $\tilde{t}_f > 0$ unless $\Delta\sigma_x = 0$: consistently, the connection time cannot vanish except for the configurationally static case. The optimal temperature evolution follows from Eq. (8a):

$$\tilde{\theta}(\tau) = \frac{1 + \tau \Delta(\theta \sigma_x^2)}{1 + \tau \Delta(\sigma_x^2)}. \quad (11)$$

Equations (10) and (11) are valid in the whole time interval $t \in [0, \tilde{t}_f]$ or $0 \leq \tau \leq 1$. Both $\tilde{\sigma}_x$ and $\tilde{\theta}$ are monotonic functions of time, the sign of their derivatives being those of $\Delta\sigma_x$ and $\Delta\theta$, respectively. The optimal potential $\tilde{u}(x, \tau)$ is obtained after inserting $\tilde{\sigma}_x$ and $\tilde{\theta}$ into Eq. (9). This expression holds only for $t \in (0, \tilde{t}_f)$ because $\dot{\tilde{\sigma}}_x \neq 0$ for $t = 0, t_f$ [40].

We complement the study above with the analysis of the harmonic case having time-dependent stiffness $u(x, \tau) = \frac{1}{2}\kappa(\tau)x^2$, a standard experimental situation. Therein, $p(x, \tau)$ remains Gaussian for all times, which guarantees shape preservation as shown in Appendix B. With our choice of units, $\kappa_i = 1$ and $\kappa_f = \theta_f/\sigma_{x,f}^2$. The adiabatic inequality is $\theta_f^2/\kappa_f \geq 1$. Equation (9) gives the relation between $\kappa(\tau)$ and $\sigma_x(\tau)$, which reduces to [46]

$$\kappa(\tau) = -\frac{1}{t_f} \frac{d \ln \sigma_x(\tau)}{d\tau} + \frac{\theta(\tau)}{\sigma_x^2(\tau)}. \quad (12)$$

After some simple algebra, we obtain the optimal stiffness

$$\tilde{\kappa}(\tau) = \frac{C}{\tilde{\sigma}_x^4(\tau)}, \quad C = \frac{\Delta\theta}{\Delta(\sigma_x^{-2})} = \frac{\Delta\theta}{\Delta(\kappa/\theta)}. \quad (13)$$

Time evolutions of the state point $(\sigma_x^2(\tau), \theta(\tau), \kappa(\tau))$, in both optimal (solid lines) and nonoptimal adiabatic processes, are illustrated in Figs. 1(a)–1(c). Optimal evolutions are obtained by particularizing Eqs. (10), (11), and (13) for each case. Nonoptimal evolutions are obtained starting from a fourth-order polynomial for the variance $\sigma_x^2(\tau) = 1 + b\tau + c\tau^2 + d\tau^3 + e\tau^4$, similarly to the approach in Ref. [29] for isothermal processes. The values (b, c, d, e) are chosen to fulfill the boundary conditions for $(\sigma_x^2, \theta, \kappa)$ and the desired connecting time $t_f = r\tilde{t}_f$. For each r value, there are two paths that connect the initial and final states (see Appendix C).

Figure 1(d) shows a phase diagram in the plane of final states (κ_f, θ_f) —recall that $\sigma_{x,f}^2 = \theta_f/\kappa_f$. Over the reversible line $\theta_f = \theta_f^{\text{qs}} = \sqrt{\kappa_f}$, the denominator \tilde{t}_f in Eq. (10) vanishes and the minimum time \tilde{t}_f diverges. The bath always must be heated to get compression (region I), whereas the trap must be loosened to allow for cooling (IV). However, at odds with the isothermal case, the signs of $\Delta\kappa$ and $\Delta\sigma_x^2$ are not univocally related in an adiabatic process: stiffening the trap may lead to expansion (II). Loosening entails expansion but the bath may need to be heated (III).

We turn to the characterization of the minimum time. For both loosening and stiffening, \tilde{t}_f is a nonmonotonic function of θ_f for fixed κ_f ; \tilde{t}_f decreases from infinity for the quasistatic value $\theta_f = \theta_f^{\text{qs}}$ to its minimum $\tilde{t}_{\min}^{d \text{ or } c}$ at $\theta_f = \theta_f^{d \text{ or } c}$ and increases therefrom to $t_f^{(1)} = (2\kappa_f)^{-1}$ at large θ_f (see Fig. 2). For

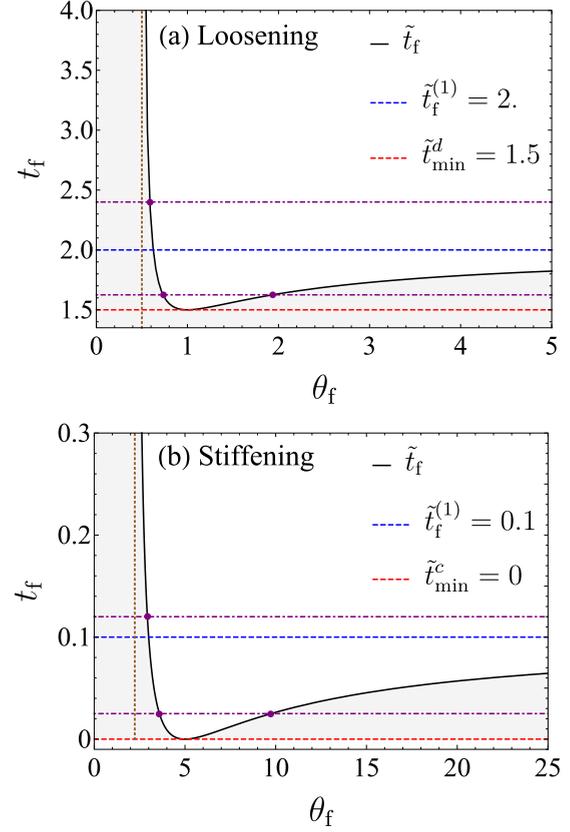


FIG. 2. Minimum connecting time as a function of the target temperature, as given by Eq. (10). Two values of the target stiffness are considered: (a) $\kappa_f = 0.25$ and (b) $\kappa_f = 5$. The greyed area corresponds to the forbidden region $t_f < \tilde{t}_f$. On both panels, \tilde{t}_f is nonmonotonic and displays an absolute minimum $\tilde{t}_{\min}^{d \text{ or } c}$ at temperatures $\theta_f^d = 1$ and $\theta_f^c = \kappa_f$. Note that $\tilde{t}_{\min}^d \neq 0$ whereas $\tilde{t}_{\min}^c = 0$: it is impossible to engineer an instantaneous adiabatic process when loosening.

loosening, $\theta_f^d = 1$ ($\Delta\theta = 0$) and $\tilde{t}_{\min}^d = (2\kappa_f)^{-1} - 1/2 > 0$. For stiffening, $\theta_f^c = \kappa_f$ and $\tilde{t}_{\min}^c = 0$. The horizontal dashed red line marks the minimum time $\tilde{t}_{\min}^{d \text{ or } c}$, the horizontal blue dashed line the asymptotic value $t_f^{(1)}$, and the dotted vertical asymptote the minimum temperature θ_f^{qs} .

Instead of fixing the final temperature θ_f , we can fix the connecting time t_f and investigate the range of reachable final temperatures. For instance, a question of experimental relevance for stiffening is the following: what is the minimum final fluid temperature for a given t_f ? Interestingly, Fig. 2 yields the answer, if read “horizontally” rather than “vertically” as before. A fresh look at either panel shows that for “long” connecting times $t_f \geq t_f^{(1)}$ temperatures below the only one verifying $\tilde{t}_f(\theta_f, \kappa_f) = t_f$ are inaccessible, because they demand a longer t_f . This is illustrated with the horizontal dot-dashed line above $t_f^{(1)}$, where $\tilde{\theta}_f$ is marked with a purple circle. For “short” connecting times, $\tilde{t}_{\min}^{d \text{ or } c} \leq t_f < t_f^{(1)}$, there are two temperatures verifying $\tilde{t}_f(\theta_f, \kappa_f) = t_f$, as exemplified by the horizontal dot-dashed line below $t_f^{(1)}$: only the temperatures between the two purple circles can be reached. Both the minimum time for fixed final state and the extremal temperature(s) for fixed connection time can be obtained by means of a variational approach, as shown in Appendix D.

For a quasistatic—not necessarily adiabatic—process, the PDF of the work is delta peaked around its average value. The heat distribution is more complex and has been explicitly obtained for the harmonic potential, being asymmetric around its mean [25]. For finite-time operation, calculating these PDFs is far more challenging because position values at different times are correlated. Yet, the dominant (up to order of $1/t_f$) contributions to the variance of work and heat can be obtained for slow driving. Work is Gaussian distributed with variance

$$\sigma_W^2 \sim \frac{1}{2t_f} \int_0^1 d\tau \dot{\kappa}^2(\tau) \frac{\theta^2(\tau)}{\kappa^3(\tau)}. \quad (14)$$

The change in the heat PDF is also more complex: shape is not conserved and the variance shift is

$$\sigma_Q^2 - (\sigma_Q^{\text{qs}})^2 \sim \sigma_W^2 - \frac{1}{2t_f} \Delta \left(\dot{\kappa} \frac{\theta^2}{\kappa^2} \right). \quad (15)$$

The last term in σ_Q^2 stems from the cross correlation between work and heat. For a detailed derivation of work and heat fluctuations, see Appendix E.

IV. CONCLUSION

The reported results are very general, being applicable to an overdamped Brownian particle bound by an arbitrary nonlinear potential. We have shown how two equilibrium states can be connected with an adiabatic—zero heat—process in a finite time, by explicitly building such a transformation. The second principle entails the existence of (i) a forbidden region, i.e., the impossibility of reaching certain final states from a given initial one, and (ii) a speed limit for the adiabatic connection, when it is indeed possible: in general, an instantaneous adiabatic process does not exist.

For compression or decompression of the Brownian particle, further characterization of these adiabatic transformations can be done. Both the physical discussion and the conclusions stemming from Figs. 1 and 2 remain valid for any nonlinear potential, by defining a final “effective” stiffness $\kappa_f = \theta_f/\sigma_{x,f}^2$ in the nonlinear case. Specifically, the emergence of a speed limit—for fixed final state—or a range of reachable temperatures—for fixed connecting time—in adiabatic transformations are robust features of our theory. Also, the phase diagram in Fig. 1(d) applies to the general nonlinear case [47].

In the underdamped case, building finite-time adiabatic processes remains an open problem. We may surmise though that they cannot be instantaneous, which would point to the robustness of finite speed limits. An instantaneous process requires again that the initial and target PDFs be coincident, but now for the joint position-velocity PDF. Thus $\theta_f = \theta_i$ and $u_f(x) = u_i(x)$: there would be no room for the entropy to increase, a scenario we can dismiss.

Perspectives concern the stability of the optimal solutions found here with respect to small perturbations in the trap stiffness, bath temperature, or other constraints. Also, our paper paves the way for a theory of control in statistical physics, based on stochastic thermodynamics. Such optimal solutions clarify the role of fluctuations and identify a fundamental bottleneck with, for instance, the existence of a speed limit. The extension of such ideas to quantum thermodynamics is a promising perspective [48–50].

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APPENDIX A: REASON FOR THE OVERDAMPED FORMALISM

We are interested in the dynamics of a mesoscopic object in a suspending fluid (solvent), driven by a time-dependent force field stemming from the potential $U(X, t)$. The fluid is at equilibrium at temperature T . For simplicity, we investigate a one dimensional situation, without loss of generality. The position X of a “particle” of mass m (a colloid such as a macromolecule, or, at a much smaller scale, a large molecule) obeys the Langevin equation

$$m \frac{d^2 X}{dt^2} = -\lambda \frac{dX}{dt} - U'(X, t) + \lambda \sqrt{2D} \xi(t) \quad (A1)$$

where $D = kT/\lambda$ is the diffusion coefficient, and $\xi(t)$ stands for Gaussian white noise of zero mean and unit variance. The drag coefficient λ originates from viscous friction and reads

$$\lambda = 6\pi\eta r, \quad (A2)$$

where η is the fluid dynamic viscosity and r the particle radius. The associated time scale m/λ governs the equilibration of velocity degrees of freedom; it depends on particle size: explicitly through r , and also through $m \propto r^3$. For a micron-size particle in water at room temperature, we find m/λ in the range of 10^{-7} s. This largely exceeds the microscopic solvent correlation time, which justifies the Langevin description with white noise. A third important scale in the problem is the time t_r needed to diffuse over a particle diameter (hence, $r^2 \sim Dt_r$). It sets the scale of position evolution; on the other hand, m/λ is the time scale ruling velocity relaxation. While $m/\lambda \propto r^2$, $t_r \propto r^3$, and we have $t_r \gg m/\lambda$. For instance, $t_r \simeq 1$ s for the above micron-size colloid. The scale separation $t_r \gg m/\lambda$ holds down to small dimensions, being still true for r in the nanometer range. This gap makes it possible to simplify Eq. (A1): as far as positional degrees of freedom are concerned, inertial terms are irrelevant and we have

$$\lambda \frac{dX}{dt} = -\partial_X U(X, t) + \lambda \sqrt{2D} \xi(t). \quad (A3)$$

This yields the overdamped framework, of much relevance for practical applications, and the starting point of our treatment. Protocols that would require consideration of the inertial term in (A1) would need to involve time scales below $0.1 \mu\text{s}$ for micron-size particles.

APPENDIX B: EVOLUTION EQUATION FOR THE VARIANCE OF THE POSITION

1. From Langevin to Fokker-Planck

We now address external driving through a harmonic potential with stiffness k . Both the temperature and the stiffness,

which are externally controlled, may be time dependent. The Langevin equation (A3) for the particle position reads

$$\lambda \frac{dX(t)}{dt} = -kX(t) + \sqrt{2\lambda k_B T} \xi(t). \quad (\text{B1})$$

The dynamics of the system can be studied using the probability density function $P(X, t)$ for finding the Brownian particle at position X at time t . Its time evolution is governed by the Fokker-Planck equation

$$\lambda \partial_t P(X, t) = k \partial_X [XP(X, t)] + k_B T \partial_X^2 P(X, t). \quad (\text{B2})$$

The Langevin equation (B1) and the Fokker-Planck equation (B2) are equivalent; both completely characterize the time evolution of the Brownian particle position—mathematically, the stochastic process [51].

In light of the above, we can obtain the time evolution of all the moments or, alternatively, all the cumulants of the position from either Eq. (B1) or Eq. (B2). If the initial condition $P(X, 0)$ is Gaussian, as is the case if the system starts from the corresponding equilibrium state, $P(X, t)$ remains Gaussian for all times: the two first cumulants, i.e., position average $\langle X \rangle$ and variance $\sigma_X^2 = \langle X^2 \rangle - \langle X \rangle^2$, completely characterize the evolution of the Brownian particle. This can be readily understood from the Fokker-Planck equation by going to Fourier space. This is the route we take in the following.

2. Evolution of moments

First, we define the Fourier transform of $P(X, t)$ as

$$G(s, t) \equiv \langle e^{isX} \rangle = \int_{-\infty}^{+\infty} dX e^{isX} P(X, t). \quad (\text{B3})$$

Therefore, taking the Fourier transform in Eq. (B2) leads to

$$\lambda \partial_t G(s, t) = -k s \partial_s G(s, t) - k_B T s^2 G(s, t). \quad (\text{B4})$$

On the one hand, the expansion of $G(s, t)$ generates the moments $\mu_n(t) \equiv \langle X^n \rangle(t)$, since $G(s, t) = \sum_{n=0}^{\infty} (is)^n \mu_n(t)/n!$. On the other hand, the expansion of $\ln G(s, t)$ generates the cumulants $\chi_n(t)$:

$$\ln G(s, t) = \sum_{n=1}^{\infty} \frac{(is)^n}{n!} \chi_n(t). \quad (\text{B5})$$

We have $\chi_1 = \mu_1$ (the mean) and $\chi_2 = \mu_2 - \mu_1^2$ (the variance).

Equation (B4) can be rewritten as

$$\lambda \partial_t \ln G(s, t) = -k s \partial_s \ln G(s, t) - k_B T s^2. \quad (\text{B6})$$

Introducing the expansion (B5) into (B6) and equating the coefficients sharing the same power of s , the equations for the cumulants are obtained as

$$\lambda \frac{d\chi_n(t)}{dt} = -nk \chi_n(t) + 2k_B T \delta_{n,2}, \quad n \geq 1. \quad (\text{B7})$$

First, we consider the equation for $n = 1$. Its solution is

$$\mu_1(t) \equiv \langle X \rangle(t) = \langle X \rangle(0) \exp\left[-\frac{1}{\lambda} \int_0^t dt' k(t')\right]. \quad (\text{B8})$$

Then, the average position remains zero for all times if it is so initially. Second, the equation for $n = 2$ gives the time

evolution of the variance $\chi_2 \equiv \sigma_X^2$:

$$\lambda \frac{d}{dt} \sigma_X^2 = -2k \sigma_X^2 + 2k_B T. \quad (\text{B9})$$

Third, the equations for $n \geq 2$ entail that an initially Gaussian distribution remains Gaussian for all times: if $\chi_n(0) = 0$ for all $n \geq 2$, we have that $\chi_n(t) = 0$ for all $n \geq 2$. Equation (B9) can be solved, with the result

$$\sigma_X^2(t) = \sigma_{X,\text{eq}}^2(t) + \left[\sigma_X^2(0) - \sigma_{X,\text{eq}}^2(0) \right] \exp\left[-\frac{2}{\lambda} \int_0^t dt' k(t')\right] - \int_0^t dt' \frac{d\sigma_{X,\text{eq}}^2(t')}{dt'} \exp\left[-\frac{2}{\lambda} \int_{t'}^t dt'' k(t'')\right], \quad (\text{B10})$$

$$\sigma_{X,\text{eq}}^2(t) \equiv \frac{k_B T(t)}{k(t)}. \quad (\text{B11})$$

If the stiffness of the trap k and the temperature of the fluid T are time independent, the third term on the right hand side is not present and $\sigma_X^2(t)$ decays exponentially towards its equilibrium value $\sigma_{X,\text{eq}}^2$.

For the discussion that follows, we introduce dimensionless variables as in the main text,

$$\kappa = \frac{k}{k_i}, \quad \theta = \frac{T}{T_i}, \quad x = \frac{X}{(\sigma_{X,\text{eq}})_i}, \quad (\text{B12})$$

except for dimensionless time, which is defined as

$$t^* = k_i t / \lambda. \quad (\text{B13})$$

Note that, consistently with our notation in the paper, t_i^* is the connection time in the t^* variable. Therefore, $\tau = t^*/t_i^*$ is the dimensionless time scale that we have employed throughout the main text. In these Appendices, we will make use of both time scales, t^* and τ , depending on which is most useful for each situation. In agreement with the notation followed in the paper, we drop the asterisk for simplicity. Also, for the sake of consistency, $\equiv d/d\tau$ and thus we explicitly write d/dt for derivatives in the time scale t .

In dimensionless variables, the evolution equation of the variance is given by

$$\frac{d\sigma_x^2}{dt} = -2\kappa(t)\sigma_x^2 + 2\theta(t). \quad (\text{B14})$$

The equilibrium variance of the position is

$$\sigma_{x,\text{eq}}^2(t) = \frac{\theta(t)}{\kappa(t)}, \quad (\text{B15})$$

and the time evolution of the mean and variance of the position are

$$\langle x \rangle(t) = \langle x \rangle(0) e^{-\varphi(t,0)}, \quad (\text{B16})$$

$$\sigma_x^2(t) = \sigma_{x,\text{eq}}^2(t) + \left[\sigma_x^2(0) - \sigma_{x,\text{eq}}^2(0) \right] e^{-2\varphi(t,0)} - \int_0^t dt' \frac{d\sigma_{x,\text{eq}}^2(t')}{dt'} e^{-2\varphi(t,t')}, \quad (\text{B17})$$

where we have defined

$$\varphi(t_2, t_1) = \int_{t_1}^{t_2} dt \kappa(t). \quad (\text{B18})$$

APPENDIX C: NONOPTIMAL ADIABATIC PROCESSES WITH A FOURTH-ORDER POLYNOMIAL IN THE VARIANCE

Herein, we describe the nonoptimal adiabatic protocols considered in Figs. 1(a)–1(c) of the paper. For a general compression or decompression, the adiabaticity condition $\dot{Q} = 0$ reduces to $\sigma_x^2 d\theta + \langle xu' \rangle d\sigma_x^2 = 0$, where u is the binding potential. For the harmonic case, $u' = \kappa x$ and $\langle xu' \rangle = \kappa \sigma_x^2$, so that adiabaticity is further simplified to $d\theta + \kappa d\sigma_x^2 = 0$ or $\kappa = -\dot{\theta}/(2\sigma_x \dot{\sigma}_x)$, which provides us with the stiffness.

The construction of these protocols follows the recipe described in the main text: starting from a given time dependence for the variance, we compute first the time duration for the process, second the temperature protocol, and finally the stiffness protocol. Specifically, our starting point here is a fourth-order polynomial for the time evolution of the variance,

$$\sigma_x^2(\tau) = 1 + b\tau + c\tau^2 + d\tau^3 + e\tau^4, \quad (\text{C1})$$

which satisfies the initial condition $\sigma_x^2(0) = 1$. The set of parameters (b, c, d, e) is chosen as explained in the following.

(1) We impose a given final value for the variance, $\sigma_x^2(\tau = 1) = \sigma_{x,f}^2$, which leads to

$$1 + b + c + d + e = \sigma_{x,f}^2. \quad (\text{C2})$$

This constraint (i) reduces the degrees of freedom of our polynomial from 4 to 3 and (ii) is necessary for the consistency of the proposed protocol, which connects the initial and final states.

(2) We impose a fixed value of the connecting time t_f , which we give in terms of the minimum time \tilde{t}_f as $t_f = r\tilde{t}_f$. For our specific shape of $\sigma_x^2(\tau)$, the functional $J[\sigma_x]$ in Eq. (8b) reduces to a function $J(b, c, d, e)$ of the polynomial parameters. Thus, Eq. (8b) with the condition $t_f = r\tilde{t}_f$ entails that

$$J(b, c, d, e) = r(\Delta\sigma_x^2)^2. \quad (\text{C3})$$

Note that this condition ensures that the temperature protocol $\theta(\tau)$ obtained from Eq. (8a) verifies the boundary conditions for both the initial and final times, $\theta(\tau = 0) = 1$ and $\theta(\tau = 1) = \theta_f$.

(3) We impose continuity in the stiffness protocol at both the initial and the final times, i.e., $\kappa(0) = 1$ and $\kappa(\tau = 1) = \kappa_f$. Following our discussion above,

$$-\frac{\dot{\theta}}{2\dot{\sigma}_x} \Big|_{\tau=0} = 1, \quad -\frac{\dot{\theta}}{2\dot{\sigma}_x} \Big|_{\tau=1} = \frac{\theta_f}{\sigma_{x,f}}. \quad (\text{C4})$$

The system of equations Eqs. (C2)–(C4) can be exactly solved and provides us with two sets of parameters:

$$b = 0, \quad c = \frac{1}{2}(6\Delta\sigma_x^2 \pm \Gamma), \quad d = -2\Delta\sigma_x^2 \mp \Gamma, \\ e = \pm \frac{1}{2}\Gamma \quad (\text{C5})$$

where the up and down signs correspond to the first and second solutions, respectively, and we have introduced

$$\Gamma = \sqrt{42(5r - 6)(\Delta\sigma_x^2)^2}. \quad (\text{C6})$$

Thus, these nonoptimal protocols are limited to $r \geq 6/5$ and allow us to obtain connection times that are, at least, 20%

longer than the minimum time \tilde{t}_f . This restriction stems from our imposing of continuous stiffness at the boundaries, as given by Eq. (C4). Had we relaxed this condition, we would have obtained a larger set of solutions for the parameters (b, c, d, e) including the optimal solution $(\Delta y, 0, 0, 0)$ for $r = 1$, the associated optimal stiffness of which has finite jumps at the boundaries, as discussed in the main text.

APPENDIX D: OPTIMIZATION PROBLEMS

1. Optimal (extremal) temperature for fixed running time

a. Statement of the variational problem

We would like to minimize the final temperature in an adiabatic process for the trapped Brownian particle. Therefore, consider the temperature increment

$$\Delta\theta \equiv \theta_f - \theta_i = \int_0^{t_f} dt \frac{d\theta}{dt}. \quad (\text{D1})$$

This is a “constrained” minimization problem, since we seek the minimization of $\Delta\theta$ that is compatible with (i) the time evolution of the variance of the Brownian particle, Eq. (B9), and (ii) the adiabaticity condition, $d\theta + \kappa d\sigma_x^2 = 0$, i.e.,

$$\frac{d\sigma_x^2}{dt} = -2\kappa\sigma_x^2 + 2\theta, \quad \kappa \frac{d\sigma_x^2}{dt} + \frac{d\theta}{dt} = 0. \quad (\text{D2})$$

Therefore, we have to introduce Lagrange multiplier functions $\lambda(t)$ and $\mu(t)$ ensuring that the above conditions hold for all times, as explained in Ref. [52] for minimization problems with “auxiliary conditions”—or in Ref. [53] for minimization problems with “subsidiary conditions.”

Throughout this section, we use the abbreviation $y \equiv \sigma_x^2$ to simplify the notation. Then, we look for functions that make

$$\mathcal{S}[y, \kappa, \theta, \lambda, \mu] = \int_0^{t_f} dt \frac{d\theta}{dt} + \int_0^{t_f} dt \lambda(t) \left(\frac{dy}{dt} + 2\kappa y - 2\theta \right) \\ + \int_0^{t_f} dt \mu(t) \left(\kappa \frac{dy}{dt} + \frac{d\theta}{dt} \right) \quad (\text{D3})$$

stationary. We have to minimize the “action”

$$\mathcal{S}[y, \kappa, \theta, \lambda, \mu] = \int_0^{t_f} dt \mathcal{L} \left(\kappa, y, \frac{dy}{dt}, \theta, \frac{d\theta}{dt}, \lambda, \mu \right), \quad (\text{D4})$$

in which we have the “Lagrangian”

$$\mathcal{L} \left(\kappa, y, \frac{dy}{dt}, \theta, \frac{d\theta}{dt}, \lambda, \mu \right) = \frac{d\theta}{dt} + \lambda \left(\frac{dy}{dt} + 2\kappa y - 2\theta \right) \\ + \mu \left(\kappa \frac{dy}{dt} + \frac{d\theta}{dt} \right). \quad (\text{D5})$$

Note that the Lagrangian does not depend on $d\kappa/dt$. This means that the corresponding Euler-Lagrange equations for κ can be used to eliminate κ in favor of the remainder of the variables [54].

The boundary conditions for the minimization problem are the following.

(i) Given the initial equilibrium state, i.e., given values of κ_i, y_i , and θ_i ,

$$\kappa(t = 0) = \kappa_i, \quad y(t = 0) = y_i, \quad \theta(t = 0) = \theta_i = \kappa_i y_i. \quad (\text{D6})$$

(ii) Given the value of the final stiffness κ_f and equilibrium condition at the final time, $\kappa_f y_f = \theta_f$,

$$\kappa(t = t_f) = \kappa_f, \quad \kappa(t = t_f)y(t = t_f) = \theta(t = t_f). \quad (\text{D7})$$

By taking an infinitesimal variation of \mathcal{S} and equating it to zero, we get not only the Euler-Lagrange equations for the minimization problem, but also the adequate boundary conditions—as discussed in Ref. [52], Sec. II.15. The boundary term in $\delta\mathcal{S}$ must vanish:

$$p_\kappa \delta\kappa + p_y \delta y + p_\theta \delta\theta|_0^{t_f} = 0. \quad (\text{D8})$$

We have here introduced the canonical momenta, which for our problem read

$$p_\kappa \equiv \frac{\partial \mathcal{L}}{\partial (d\kappa/dt)} = 0, \quad (\text{D9a})$$

$$p_y \equiv \frac{\partial \mathcal{L}}{\partial (dy/dt)} = \lambda + \mu\kappa, \quad (\text{D9b})$$

$$p_\theta \equiv \frac{\partial \mathcal{L}}{\partial (d\theta/dt)} = 1 + \mu. \quad (\text{D9c})$$

Since κ_i , y_i , and θ_i are fixed, there is no boundary contribution coming from $t = 0$. For $t = t_f$, however, we have a different situation, $\delta\kappa_f = 0$, but y_f and θ_f are simply linked by the equilibrium condition, which entails that $\kappa_f \delta y_f = \delta\theta_f$. Therefore, we have that

$$p_{\kappa_f} \delta\kappa_f + p_{y_f} \delta y_f + p_{\theta_f} \delta\theta_f = (p_{y_f} + p_{\theta_f} \kappa_f) \delta y_f = 0, \quad (\text{D10})$$

so that

$$p_y(t = t_f) + p_\theta(t = t_f)\kappa(t = t_f) = 0, \quad (\text{D11})$$

since δy_f is arbitrary. By employing the expressions for p_y and p_θ found above, we get

$$\lambda_f + \mu_f \kappa_f + (1 + \mu_f)\kappa_f = \kappa_f + \lambda_f + 2\mu_f \kappa_f = 0 \quad (\text{D12})$$

for the lacking boundary condition, i.e.,

$$\kappa(t = t_f) + \lambda(t = t_f) + 2\mu(t = t_f)\kappa(t = t_f) = 0. \quad (\text{D13})$$

b. Euler-Lagrange equations

Now, we write the Euler-Lagrange equations for the minimization problem. First, taking into account Eq. (D9a) and $\partial_\kappa \mathcal{L} = 2\lambda y + \mu dy/dt$,

$$0 = 2\lambda y + \mu \frac{dy}{dt}. \quad (\text{D14})$$

Second, we bring to bear Eq. (D9b) and $\partial_y \mathcal{L} = 2\kappa\lambda$:

$$\frac{d}{dt}(\lambda + \mu\kappa) = 2\kappa\lambda. \quad (\text{D15})$$

Third, we make use of Eq. (D9c) and $\partial_\theta \mathcal{L} = -2\lambda$ to write

$$\frac{d\mu}{dt} = -2\lambda. \quad (\text{D16})$$

In addition, since by construction the Lagrangian does not depend on the time derivatives of the Lagrange multipliers λ and μ , the Euler-Lagrange equations for λ and μ reduce to the constraints or auxiliary conditions (D2).

It is straightforward to get rid of the Lagrange multipliers by first inserting Eq. (D16) into (D14), which gives

$$\mu \frac{dy}{dt} - y \frac{d\mu}{dt} = 0 \quad \Rightarrow \quad \mu = c_1 y, \quad (\text{D17})$$

where c_1 is an arbitrary constant, to be determined later by imposing the boundary conditions. Moreover, Eq. (D16) yields

$$\lambda = -\frac{c_1}{2} \frac{dy}{dt}. \quad (\text{D18})$$

These expressions for the multipliers in terms of y and dy/dt allow us to work out the solution, as detailed below. The constant c_1 should be nonzero because its vanishing leads to $\lambda(t) = \mu(t) = 0$, i.e., the situation without constraints.

Inserting Eqs. (D17) and (D18) into Eq. (D15), we get

$$\frac{d^2 y}{dt^2} - 4\kappa \frac{dy}{dt} - 2 \frac{d\kappa}{dt} y = 0, \quad (\text{D19})$$

after taking into account that $c_1 \neq 0$. By employing Eq. (D2) to take the time derivative of the evolution equation for y and make use of the adiabatic condition, it is also shown that

$$\frac{d^2 y}{dt^2} + 4\kappa \frac{dy}{dt} + 2 \frac{d\kappa}{dt} y = 0. \quad (\text{D20})$$

Combining Eqs. (D19) and (D20), we obtain

$$2\kappa \frac{dy}{dt} + \frac{d\kappa}{dt} y = 0 \quad \Rightarrow \quad \kappa y^2 = c_2, \quad (\text{D21})$$

where c_2 is an arbitrary constant.

Finally, taking into account Eq. (D21), we find the expressions for the variance and the temperature. The adiabatic condition is now simplified to

$$c_2 \frac{1}{y^2} \frac{dy}{dt} + \frac{d\theta}{dt} = 0 \quad \Rightarrow \quad \theta = \frac{c_2}{y} + \frac{c_3}{2}, \quad (\text{D22})$$

in which c_3 is another arbitrary constant—the factor $1/2$ on the right hand side is convenient later. Substituting Eqs. (D21) and (D22) into the evolution equation for the variance y gives

$$\begin{aligned} \frac{dy}{dt} + 2 \frac{c_2}{y^2} - 2 \left(\frac{c_2}{y} + \frac{c_3}{2} \right) &= 0 \quad \Rightarrow \quad \frac{dy}{dt} = c_3, \\ \Rightarrow y &= c_3 t + c_4. \end{aligned} \quad (\text{D23})$$

Once more, c_4 is an arbitrary constant.

c. Solution of the problem

Equations (D21)–(D23) provide the solution to the minimization problem. The constants (c_1, c_2, c_3, c_4) have to be written in terms of physical quantities by imposing the boundary conditions. It may seem odd at first sight that there are four constants but six boundary conditions. The reason is the same as in other problems in stochastic thermodynamics: κ may have jumps at the boundaries. In the present context, this peculiar behavior is readily understood: the conjugate moment $p_\kappa = \partial_\kappa \mathcal{L}$ identically vanishes and therefore $\delta\kappa(t = 0)$ and $\delta\kappa(t = t_f)$ are in fact arbitrary when imposing the extremality condition $\delta\mathcal{S} = 0$. This means that κ can indeed have finite-jump discontinuities at the initial and final times: $\kappa(t = 0^+)$ and $\kappa(t = t_f^-)$ do not coincide in general with κ_i and κ_f .

Following the discussion above, we now impose the four relevant boundary conditions

$$(t = 0) = y_i, \quad (\text{D24a})$$

$$\theta(t = 0) = \theta_i, \quad (\text{D24b})$$

$$\kappa_f y(t = t_f) = \theta(t = t_f), \quad (\text{D24c})$$

$$\kappa_f + \lambda(t = t_f) + 2\kappa_f \mu(t = t_f) = 0. \quad (\text{D24d})$$

The constants c_3 and c_4 are directly obtained as

$$c_3 = \frac{y_f - y_i}{t_f}, \quad c_4 = y_i. \quad (\text{D25})$$

Note that y_f does not have a definite value but is related to θ_f by the equilibrium condition; this will be brought to bear later. The optimal time evolution for the variance is then

$$y(t) = y_i + \frac{y_f - y_i}{t_f} t. \quad (\text{D26})$$

Now, particularizing Eq. (D22) for $t = 0$ makes it possible to obtain c_2 :

$$\theta_i = \frac{c_2}{y_i} + \frac{c_3}{2} \Rightarrow c_2 = y_i \left(\theta_i - \frac{y_f - y_i}{2t_f} \right). \quad (\text{D27})$$

Using again Eq. (D22) but for an arbitrary time t , one gets after some simple algebra

$$\theta(t) = \frac{y_i \theta_i + \frac{(y_f - y_i)^2}{2t_f^2} t}{y_i + \frac{y_f - y_i}{t_f} t}. \quad (\text{D28})$$

Substituting $t = t_f$ into this equation, we obtain

$$\theta_f = \frac{y_i \theta_i}{y_f} + \frac{(y_f - y_i)^2}{2t_f y_f}, \quad (\text{D29})$$

so that

$$\theta_f \geq \frac{y_i \theta_i}{y_f}, \quad (\text{D30})$$

with the equality holding in the limit as $t_f \rightarrow \infty$.

We have yet to impose the boundary condition $y_f = \theta_f / \kappa_f$. We do so in Eq. (D29):

$$\theta_f = \frac{\kappa_f y_i \theta_i}{\theta_f} + \frac{\kappa_f \left(\frac{\theta_f}{\kappa_f} - y_i \right)^2}{2t_f \theta_f} \quad (\text{D31a})$$

$$\Rightarrow \theta_f^2 = \kappa_f y_i \theta_i + \frac{\kappa_f}{2t_f} \left(\frac{\theta_f}{\kappa_f} - y_i \right)^2. \quad (\text{D31b})$$

This is a quadratic equation for θ_f in terms of the fixed parameters κ_f , y_i , θ_i , and t_f . Solving it for t_f , we find

$$t_f = \frac{\left(\frac{\theta_f}{\kappa_f} - \frac{\theta_i}{\kappa_i} \right)^2}{2 \left(\frac{\theta_f^2}{\kappa_f} - \frac{\theta_i^2}{\kappa_i} \right)}, \quad (\text{D32})$$

which is equivalent to Eq. (10) in the main text, particularized for the harmonic potential.

It is worth noting that the constant c_1 has not been necessary to obtain the solution for the physical quantities, the stiffness $\kappa(t)$, the variance $y(t)$, and the temperature $\theta(t)$. It is

only needed to derive the final expressions for the Lagrange multipliers $\lambda(t)$ and $\mu(t)$. For the sake of completeness, we give the expression for c_1 that follows from Eq. (D13):

$$\kappa_f - \frac{c_1 c_3}{2} + 2c_1 y_f \kappa_f = 0 \Rightarrow c_1 = \frac{2\kappa_f}{c_3 - 4\theta_f}. \quad (\text{D33})$$

2. Minimum time for fixed initial and final states

We turn our attention to another optimization problem: that of obtaining the minimum time to connect two given equilibrium states with an adiabatic process. This problem has been solved in the paper by an *ad hoc* procedure, but it can be addressed in a way similar to the one employed in the previous section. In this case, we would like to minimize

$$t_f = \int_0^{t_f} dt \, 1, \quad (\text{D34})$$

submitted again to the constraints given by Eq. (D2). Therefore, we have to minimize a new action

$$\hat{\mathcal{S}}[y, \kappa, \theta, \lambda, \mu] = \int_0^{t_f} dt \, \hat{\mathcal{L}} \left(\kappa, y, \frac{dy}{dt}, \frac{d\theta}{dt}, \lambda, \mu \right), \quad (\text{D35})$$

in which we have the new Lagrangian

$$\begin{aligned} \hat{\mathcal{L}} \left(\kappa, y, \frac{dy}{dt}, \theta, \frac{d\theta}{dt}, \lambda, \mu \right) &= \mathcal{L} \left(\kappa, y, \frac{dy}{dt}, \theta, \frac{d\theta}{dt}, \lambda, \mu \right) \\ &+ \frac{d}{dt} (t - \theta). \end{aligned} \quad (\text{D36})$$

Since $\hat{\mathcal{L}}$ and \mathcal{L} differ by the total derivative of a function that depends only on the ‘‘coordinates’’—and not on the velocities, we know that the Euler-Lagrange equations for both minimization problems will be the same. At any rate, we cannot yet conclude that the solutions to both problems are the same, since the boundary conditions for them are not [55].

In this case, the boundary conditions are simpler than those addressed in Sec. D, because (κ, y, θ) have prescribed values at the initial and final times, although the latter is not fixed; it is the quantity that we want to minimize. Specifically, Eqs. (D6) and (D7) remain valid but Eq. (D13) must be substituted with

$$\theta(t = t_f) = \theta_f. \quad (\text{D37})$$

Therefore, we deal with a ‘‘standard’’ variational problem, for which $\delta\kappa$, δy , and $\delta\theta$ vanish at the boundaries, similarly to the situation found in classical mechanics. Nonetheless, once more we have that κ may have finite jump discontinuities at the boundaries: recall that its corresponding canonical momentum verifies $\hat{p}_\kappa \equiv 0$.

Since the Euler-Lagrange equations are unchanged, Eqs. (D17), (D18), and (D21)–(D23) still hold. In principle, we should have to reobtain the constants (c_2, c_3, c_4) with the new boundary conditions. However, it is readily realized that the substitution of Eq. (D13) with Eq. (D37) leaves their expressions unchanged, because Eq. (D13) was not employed in their derivation for the optimal temperature problem. The only difference is that θ_f is now fixed and t_f is the variable being minimized, instead of the other way around. In light of the previous discussion, it appears that the same function relates the optimal values θ_f and t_f for both physical situations, as argued in the main text on physical grounds.

APPENDIX E: FLUCTUATIONS OF THE ENERGY INCREMENT, WORK, AND HEAT

In the quasistatic limit, the PDFs for the increment of potential energy Δu , work W , and heat Q have been obtained for the harmonic potential [25]. The calculations rely on the values of $x(t)$ and $x(t')$ being uncorrelated for all times, which is strictly true only for an infinite connecting time. Here, we consider how these results are changed by a finite time but slow driving, i.e., the situation when the dimensionless connecting time $t_f \gg 1$ and both the stiffness and the temperature are slowly varied, with their time derivatives in the “fast” scale t being of the order of t_f^{-1} .

1. Time correlations

For slow drivings, it is convenient to go to the time scale $\tau = t/t_f$, over which the evolution equation of the variance of the position is given by

$$t_f^{-1} \frac{d\sigma_x^2}{d\tau} = -2\kappa(\tau)\sigma_x^2(\tau) + 2\theta(\tau). \quad (\text{E1})$$

Therefore, the lowest order approximation for the variance is

$$\sigma_x(\tau) \sim \sigma_{x,\text{eq}}(\tau). \quad (\text{E2})$$

This expression is uniformly valid in time: it verifies both boundary conditions in Eq. (5) of the main text. Therefore, the one-time PDF for the position at time t is Gaussian with

$$p(x, t|x_i, 0) \sim \frac{1}{\sqrt{2\pi[\sigma_{x,\text{eq}}^2(t) - \sigma_{x,i}^2 e^{-2\varphi(t,0)}]}} \exp\left\{-\frac{(x - x_i e^{-\varphi(t,0)})^2}{2[\sigma_{x,\text{eq}}^2(t) - \sigma_{x,i}^2 e^{-2\varphi(t,0)}]}\right\}, \quad t \geq 0. \quad (\text{E3})$$

This equation can be readily generalized to a given initial condition x' at any time t' as

$$p(x, t|x', t') \sim \frac{1}{\sqrt{2\pi[\sigma_{x,\text{eq}}^2(t) - \sigma_{x,\text{eq}}^2(t') e^{-2\varphi(t,t')}]}} \exp\left\{-\frac{(x - x' e^{-\varphi(t,t')})^2}{2[\sigma_{x,\text{eq}}^2(t) - \sigma_{x,\text{eq}}^2(t') e^{-2\varphi(t,t')}]}\right\}, \quad t \geq t'. \quad (\text{E4})$$

The lowest order approximation given by Eqs. (E3) and (E7) is consistent; these PDFs obey the Chapman-Kolmogorov conditions $\int dx' p(x, t|x', t') p(x', t'|x'', t'') = p(x, t|x'', t'')$ and $\int dx' p(x, t|x', t') p(x', t') = p(x, t)$.

For calculating the probability distributions of energy increment, work, and heat, we will need to calculate correlation functions of the form

$$C(t, t') \equiv \overline{x^2(t)x^2(t')} - \overline{x^2(t)} \overline{x^2(t')} = \overline{[x^2(t) - \overline{x^2(t)}][x^2(t') - \overline{x^2(t')}]}. \quad (\text{E5})$$

In our lowest order approximation, we have that $\overline{x(t)} = 0$ and

$$\overline{x^2(t)} \sim \sigma_{x,\text{eq}}^2(t) \quad (\text{E6})$$

for all times. Then, the two-time correlations reduce to

$$C(t, t') \sim \overline{[x^2(t) - \sigma_{x,\text{eq}}^2(t)][x^2(t') - \sigma_{x,\text{eq}}^2(t')]} = \int dx \int dx' [x^2 - \sigma_{x,\text{eq}}^2(t)][x'^2 - \sigma_{x,\text{eq}}^2(t')] p(x, t|x', t') p(x', t'). \quad (\text{E7})$$

zero mean and this variance, i.e.,

$$p(x, t) \sim \frac{1}{\sqrt{2\pi\sigma_{x,\text{eq}}^2(t)}} \exp\left[-\frac{x^2}{2\sigma_{x,\text{eq}}^2(t)}\right]. \quad (\text{E8})$$

The situation is more subtle for two-time objects. Indeed, let us consider the same equation but for a given initial condition, i.e., when we are interested in the transition probability $p(x, \tau|x_i, 0)$, such that $p(x, \tau|x_i, 0)|_{\tau=0} = \delta(x - x_i)$ and $x(t=0) = x_i$. Over the “slow” time scale τ , Eq. (E2) again holds but it does not verify the initial condition $\sigma_{x,i} = 0$. Note that over the time scale τ

$$\varphi(t, 0) = \int_0^t dt' \kappa(t') \quad \rightarrow \quad \varphi(\tau, 0) = t_f \int_0^\tau d\tau' \kappa(\tau'). \quad (\text{E9})$$

Therefore, the “external” approximation Eq. (E2)—using the terminology in Ref. [56]—holds for $\tau = O(1)$, such that $\varphi = O(t_f) \gg 1$, but not for short times, such that $\varphi = O(1)$, where a boundary layer emerges. In the boundary layer, we obtain the “internal” solution

$$\sigma_x^2(t) \sim \sigma_{x,\text{eq}}^2(t) - \sigma_{x,i}^2 e^{-2\varphi(t,0)}. \quad (\text{E10})$$

This can be justified either by a dominant balance argument in the differential equation (B14) or by showing that the last term on the right hand side of Eq. (B17) is subdominant against the first one. Consistently with the notation employed in the main text, $\sigma_{x,i}^2$ stands for the initial value of the variance $\sigma_{x,\text{eq}}^2(t=0)$. A uniform solution in time is obtained by adding Eqs. (E2) and (E5) and subtracting their common limit for $\varphi(t, 0) \gg 1$ and $\tau \ll 1$, which is $\sigma_{x,\text{eq}}^2(t)$. Therefore, Eq. (E5) gives the uniform solution and $p(x, t|x_i, 0)$ is the Gaussian distribution with that variance and mean $x_i \exp[-\varphi(t, 0)]$, as predicted by Eq. (B16):

Therefore, we first evaluate the conditioned average

$$\int dx [x^2 - \sigma_{x,\text{eq}}^2(t)] p(x, t | x', t') = [x'^2 - \sigma_{x,\text{eq}}^2(t')] e^{-2\varphi(t, t')}, \quad t \geq t', \quad (\text{E11})$$

which inserted into Eq. (E10) leads to

$$C(t, t') \sim e^{-2\varphi(t, t')} \int dx' [x'^2 - \sigma_{x,\text{eq}}^2(t')]^2 p(x', t') = 2\sigma_{x,\text{eq}}^4(t') e^{-2\varphi(t, t')}, \quad t \geq t'. \quad (\text{E12})$$

Correlations are relevant over the fast time scale t , as long as $\varphi(t, t') = O(1)$, but become exponentially small over the slow time scale τ because, consistently with Eq. (E4),

$$\varphi(t, t') = \int_{t'}^t dt'' \kappa(t'') \rightarrow \varphi(\tau, \tau') = t_f \int_{\tau'}^{\tau} d\tau'' \kappa(\tau''), \quad (\text{E13})$$

and $\varphi(\tau, \tau') = O(t_f) \gg 1$. In the quasistatic limit $t_f \rightarrow \infty$, $C(t, t') \rightarrow 0$ because $p(x, t | x', t') \rightarrow p(x, t)$ and time correlations are “instantaneously” killed.

2. Fluctuations of the energy increment

Since the increment of kinetic energy is for a given protocol fixed and equal to $\Delta\theta/2$ (in dimensionless variables), we focus on the fluctuations of the increment of the potential energy:

$$\Delta u = \frac{1}{2} (\kappa_f x_f^2 - \kappa_i x_i^2). \quad (\text{E14})$$

The average value is straightforward, $\overline{\Delta u} = \Delta\theta/2$. Fluctuations are also easy to calculate, since

$$\Delta u - \overline{\Delta u} = \frac{1}{2} [\kappa_f (x_f^2 - \sigma_{x,f}^2) - \kappa_i (x_i^2 - \sigma_{x,i}^2)] \quad (\text{E15})$$

and the variance is readily written in terms of the correlation function as

$$\begin{aligned} \sigma_{\Delta u}^2 &\equiv \overline{(\Delta u - \overline{\Delta u})^2} \\ &= \frac{1}{4} [\kappa_f^2 C(t_f, t_f) + \kappa_i^2 C(0, 0) - 2\kappa_f \kappa_i C(t_f, 0)]. \end{aligned} \quad (\text{E16})$$

Employing Eq. (E12), we get

$$\sigma_{\Delta u}^2 = \frac{1}{2} [\kappa_f^2 \sigma_{x,f}^4 + \kappa_i^2 \sigma_{x,i}^4 - 2\kappa_f \kappa_i \sigma_{x,i}^4 e^{-2\varphi(t_f, 0)}]. \quad (\text{E17})$$

For slow driving, the last term on the right hand side is exponentially small in the connecting time t_f , since

$$e^{-2\varphi(t_f, 0)} = e^{-\hat{\kappa} t_f}, \quad \hat{\kappa} \equiv \int_0^1 d\tau \kappa(\tau) = O(1). \quad (\text{E18})$$

Neglecting this exponentially decreasing term (EDT), we have that

$$\sigma_{\Delta u}^2 \sim \frac{1}{2} (\theta_f^2 + \theta_i^2). \quad (\text{E19})$$

In conclusion, $\sigma_{\Delta u}$ coincides with that of the quasistatic limit, except for EDT. In fact, the whole distribution $\mathcal{P}(\Delta u)$,

$$\begin{aligned} \mathcal{P}(\Delta u) &= \int dx_i \int dx_f \delta\left(\Delta u - \frac{1}{2} \kappa_f x_f^2 + \frac{1}{2} \kappa_i x_i^2\right) \\ &\times p(x_f, t_f | x_i, 0) p(x_i, 0), \end{aligned} \quad (\text{E20})$$

coincides with that for the quasistatic limit except for EDT, because

$$\begin{aligned} p(x_f, t_f | x_i, 0) &\sim \frac{1}{\sqrt{2\pi (\sigma_{x,f}^2 - \sigma_{x,i}^2 e^{-2\hat{\kappa} t_f})}} \\ &\times \exp\left[-\frac{(x - x_i e^{-\hat{\kappa} t_f})^2}{2(\sigma_{x,f}^2 - \sigma_{x,i}^2 e^{-2\hat{\kappa} t_f})}\right] \\ &= p(x_f, t_f) + \text{EDT}. \end{aligned} \quad (\text{E21})$$

Then,

$$\begin{aligned} \mathcal{P}(\Delta u) \sim \mathcal{P}_{\text{qs}}(\Delta u) &= \int dx_i \int dx_f \delta\left(\Delta u - \frac{1}{2} \kappa_f x_f^2 + \frac{1}{2} \kappa_i x_i^2\right) \\ &\times p(x_f, t_f) p(x_i, 0). \end{aligned} \quad (\text{E22})$$

This integration has been carried out in Ref. [25]:

$$\mathcal{P}(\Delta u) = \frac{1}{\pi \sqrt{\theta_i \theta_f}} \exp\left[-\frac{\Delta\theta}{2\theta_i \theta_f} \Delta u\right] K_0\left(\frac{\theta_i + \theta_f}{2\theta_i \theta_f} |\Delta u|\right), \quad (\text{E23})$$

where K_0 is the zeroth-order modified Bessel function of the second kind. The above results are valid for slow—not necessarily adiabatic—driving between two equilibrium states. In fact, adiabaticity does not play any role here.

3. Fluctuations of the work

In dimensionless variables, work is given by

$$W = \frac{1}{2} \int_0^{t_f} dt \frac{d\kappa(t)}{dt} x^2(t), \quad (\text{E24})$$

so that

$$\begin{aligned} W - \overline{W} &= \frac{1}{2} \int_0^{t_f} dt \frac{d\kappa(t)}{dt} [x^2(t) - \overline{x^2(t)}] \\ &\sim \frac{1}{2} \int_0^{t_f} dt \frac{d\kappa(t)}{dt} [x^2(t) - \sigma_{x,\text{eq}}^2(t)]. \end{aligned} \quad (\text{E25})$$

Therefore, the work variance is

$$\begin{aligned} \sigma_W^2 &\equiv \overline{(W - \overline{W})^2} = \frac{1}{4} \int_0^{t_f} dt \frac{d\kappa(t)}{dt} \int_0^{t_f} dt' \frac{d\kappa(t')}{dt'} C(t, t') \\ &= \frac{1}{2} \int_0^{t_f} dt \frac{d\kappa(t)}{dt} \int_0^t dt' \frac{d\kappa(t')}{dt'} C(t, t'), \end{aligned}$$

where we have used that $C(t, t')$ and thus the integrand is symmetric under the exchange $t \leftrightarrow t'$.

Now, we insert Eq. (E12) into (E26) and go to the slow τ variable to write

$$\sigma_W^2 \sim \int_0^1 d\tau \dot{\kappa}(\tau) \int_0^\tau d\tau' \dot{\kappa}(\tau') \sigma_{x,\text{eq}}^4(\tau') \exp \left[-2t_f \int_{\tau'}^\tau d\tau'' \kappa(\tau'') \right]. \quad (\text{E26})$$

For $t_f \gg 1$, only a narrow region of width t_f^{-1} contributes to the second integral. Thus, to the lowest order we can (i) substitute τ' with τ in both $\dot{\kappa}(\tau')$ and $\sigma_{x,\text{eq}}(\tau')$; (ii) approximate $\int_{\tau'}^\tau d\tau'' \kappa(\tau'') \sim \kappa(\tau)\Delta$, with $\Delta = \tau - \tau'$; and (iii) extend the integral over Δ to the interval $[0, +\infty)$. Then, we have that

$$\int_0^\tau d\tau' \dot{\kappa}(\tau') \sigma_{x,\text{eq}}^4(\tau') \exp \left[-2t_f \int_{\tau'}^\tau d\tau'' \kappa(\tau'') \right] \sim \dot{\kappa}(\tau) \sigma_{x,\text{eq}}^4(\tau) \int_0^\infty d\Delta \exp[-2t_f \kappa(\tau)\Delta] = \frac{\dot{\kappa}(\tau) \sigma_{x,\text{eq}}^4(\tau)}{2t_f \kappa(\tau)}, \quad (\text{E27})$$

and finally the variance for the work reads

$$\sigma_W^2 \sim \frac{1}{2t_f} \int_0^1 d\tau \dot{\kappa}^2(\tau) \frac{\sigma_{x,\text{eq}}^4(\tau)}{\kappa(\tau)} = \frac{1}{2t_f} \int_0^1 d\tau \dot{\kappa}^2(\tau) \frac{\theta^2(\tau)}{\kappa^3(\tau)}. \quad (\text{E28})$$

Corrections of the order of t_f^{-2} have been neglected.

In the quasistatic limit $t_f \rightarrow \infty$, the variance vanishes and work becomes delta distributed around its mean. For long but not infinite t_f , work becomes Gaussian distributed with the variance given by Eq. (E28) to the lowest order. Adiabaticity only enters the picture by restricting the stiffness and temperature profiles in Eq. (E28). In addition, for adiabatic processes $\bar{Q} = 0$ and the mean work $\bar{W} = \Delta E = \Delta\theta$.

4. Fluctuations of the heat

We now turn our attention to the fluctuations of the heat. Since the kinetic contribution is fixed in the overdamped description, this is equivalent to considering the fluctuations of its configurational contribution $Q_x = \Delta u - W$. Therefore, the deviation from the mean value is given by

$$Q - \bar{Q} = Q_x - \bar{Q}_x = \Delta u - \bar{\Delta u} - (W - \bar{W}) = \frac{1}{2} \kappa_f (x_f^2 - \sigma_{x,f}^2) - \frac{1}{2} \kappa_i (x_i^2 - \sigma_{x,i}^2) - \frac{1}{2} \int_0^{t_f} dt \frac{d\kappa(t)}{dt} [x^2(t) - \overline{x^2(t)}]. \quad (\text{E29})$$

The n th central moment is defined by

$$\mu_{Q,n} \equiv \overline{(Q_x - \bar{Q}_x)^n}, \quad n \in \mathbb{N}. \quad (\text{E30})$$

To calculate such moments, we will need to evaluate n -time correlation functions. For the variance, this means that it suffices to know the two-time correlations introduced in Eq. (E8), as has already been the case for the work fluctuations. More specifically,

$$\sigma_Q^2 \equiv \mu_{Q,2} = \sigma_{\Delta u}^2 + \sigma_W^2 - 2 \overline{(W - \bar{W})(\Delta u - \bar{\Delta u})}, \quad (\text{E31})$$

and we focus in the following on the last term, i.e., on the calculation of the energy-work cross correlation.

From the definitions of Δu and W , it is straightforward that

$$\overline{(W - \bar{W})(\Delta u - \bar{\Delta u})} = \frac{1}{4} \int_0^{t_f} dt \frac{d\kappa(t)}{dt} [\kappa_f C(t_f, t) - \kappa_i C(t, 0)], \quad (\text{E32})$$

and making use of Eq. (E12) we have that

$$\overline{(W - \bar{W})(\Delta u - \bar{\Delta u})} \sim \frac{1}{2} \int_0^{t_f} dt \frac{d\kappa(t)}{dt} [\kappa_f \sigma_{x,\text{eq}}^4(t) e^{-2\varphi(t_f,t)} - \kappa_i \sigma_{x,i}^4 e^{-2\varphi(t,0)}]. \quad (\text{E33})$$

Again, going to the slow variable τ ,

$$\overline{(W - \bar{W})(\Delta u - \bar{\Delta u})} \sim \frac{1}{2} \int_0^1 d\tau \dot{\kappa}(\tau) \left\{ \kappa_f \sigma_{x,\text{eq}}^4(\tau) \exp \left[-2t_f \int_\tau^1 d\tau' \kappa(\tau') \right] - \kappa_i \sigma_{x,i}^4 \exp \left[-2t_f \int_0^\tau d\tau' \kappa(\tau') \right] \right\}. \quad (\text{E34})$$

Similarly to the calculation for σ_W^2 , both terms contribute in a narrow τ interval, namely, that close to $\tau = 1$ ($\tau = 0$) for the first (second) one. Thus we obtain

$$\overline{(W - \bar{W})(\Delta u - \bar{\Delta u})} \sim \frac{1}{4t_f} [\dot{\kappa}_f \sigma_{x,f}^4 - \dot{\kappa}_i \sigma_{x,i}^4] = \frac{1}{4t_f} \left[\dot{\kappa}_f \frac{\theta_f^2}{\kappa_f^2} - \dot{\kappa}_i \frac{\theta_i^2}{\kappa_i^2} \right], \quad (\text{E35})$$

neglecting once more $O(t_f^{-2})$ corrections. Finally, we get for the variance of the heat

$$\sigma_Q^2 = \sigma_{\Delta u}^2 + \frac{1}{2t_f} \int_0^1 d\tau [\dot{\kappa}(\tau)]^2 \frac{\theta^2(\tau)}{\kappa^3(\tau)} - \frac{1}{2t_f} \left[\dot{\kappa}_f \frac{\theta_f^2}{\kappa_f^2} - \dot{\kappa}_i \frac{\theta_i^2}{\kappa_i^2} \right] + O(t_f^{-2}). \quad (\text{E36})$$

Integration by parts simplifies this into

$$\sigma_Q^2 = \sigma_{\Delta u}^2 - \frac{1}{2t_f} \int_0^1 d\tau \kappa(\tau) \frac{d}{d\tau} \left[\dot{\kappa}(\tau) \frac{\theta^2(\tau)}{\kappa^3(\tau)} \right] + O(t_f^{-2}). \quad (\text{E37})$$

This expression is also valid for slow driving, regardless of being adiabatic or not. Similarly to the case of the work distribution, adiabaticity only enters the picture by restricting the stiffness and temperature profiles that can be substituted into Eq. (E37).

Therefore, in the limit of slow driving we find a small change in the variance of the heat—recall that it is nonzero and equal to $\sigma_{\Delta u}^2$ for the quasistatic case. For slow but not quasistatic driving, work is no longer delta distributed around the mean and then the fluctuations of heat and energy increment are not equivalent: the corrections are of the order of t_f^{-1} for the former but exponentially small for the latter. A relevant question thus arises: whether or not the heat distribution conserves its shape, i.e., if all the change of the distribution can be encoded in the change of the variance. Although the calculation of the whole heat distribution seems to be a challenging mathematical problem—even for the harmonic case, we show that the situation is more complex in the following, by obtaining the third central moment of the distribution—recall that the distribution of the heat is asymmetric around its mean.

Consistently with the comments above, we consider the third central moment $\mu_{Q,3}$. Making use of Eq. (E29), we have that

$$\mu_{Q,3} = \overline{(\Delta u - \overline{\Delta u})^3} - 3\overline{(\Delta u - \overline{\Delta u})^2(W - \overline{W})} + 3\overline{(\Delta u - \overline{\Delta u})(W - \overline{W})^2} - \overline{(W - \overline{W})^3}. \quad (\text{E38})$$

In order to obtain $\mu_{Q,3}$, we need to evaluate three-time correlations of the kind

$$A(t_1, t_2, t_3) = \overline{[x^2(t_1) - \overline{x^2(t_1)}][x^2(t_2) - \overline{x^2(t_2)}][x^2(t_3) - \overline{x^2(t_3)}]}, \quad t_1 \geq t_2 \geq t_3. \quad (\text{E39})$$

In the same approximation employed throughout these Appendices, i.e., that given by Eqs. (E3) and (E7), this correlation has the asymptotic behavior

$$A(t_1, t_2, t_3) \sim 8\sigma_{x,\text{eq}}^2(t_2)\sigma_{x,\text{eq}}^4(t_3) \exp[-2\varphi(t_1, t_3)]. \quad (\text{E40})$$

In the following, we repeatedly use this expression for $A(t_1, t_2, t_3)$ to calculate all contributions to $\mu_{Q,3}$.

We start by considering

$$\mu_{Q,3}^{(1)} \equiv \overline{(\Delta u - \overline{\Delta u})^3} = \left[\frac{1}{2}\kappa_f(x_f^2 - \sigma_{x,f}^2) - \frac{1}{2}\kappa_i(x_i^2 - \sigma_{x,i}^2) \right]^3. \quad (\text{E41})$$

In this case, there is no integration and any term that mixes $(x_f^2 - \sigma_{x,f}^2)$ and $(x_i^2 - \sigma_{x,i}^2)$ contains an EDT of the form $\exp[-2\varphi(t_f, 0)] = \exp[-2\hat{\kappa}t_f]$. Thus, we recover the quasistatic situation in which $(x_f^2 - \sigma_{x,f}^2)$ and $(x_i^2 - \sigma_{x,i}^2)$ are uncorrelated, except for EDT, i.e.,

$$\mu_{Q,3}^{(1)} \sim \mu_{Q,3}^{\text{qs}} = \frac{1}{8}\kappa_f^3(x_f^2 - \sigma_{x,f}^2)^3 - \frac{1}{8}\kappa_i^3(x_i^2 - \sigma_{x,i}^2)^3 = \theta_f^3 - \theta_i^3. \quad (\text{E42})$$

If $\theta_f \neq \theta_i$, this contribution is different from zero, in accordance with the heat fluctuations being asymmetric around its mean in the quasistatic limit.

Now, we turn our attention to

$$\mu_{Q,3}^{(2)} \equiv -3\overline{(\Delta u - \overline{\Delta u})^2(W - \overline{W})} \sim -\frac{3}{2} \overline{\left[\frac{1}{2}\kappa_f(x_f^2 - \sigma_{x,f}^2) - \frac{1}{2}\kappa_i(x_i^2 - \sigma_{x,i}^2) \right]^2 \int_0^{t_f} dt \frac{d\kappa(t)}{dt} [x^2(t) - \sigma_{x,\text{eq}}^2(t)]}, \quad (\text{E43})$$

i.e.,

$$\mu_{Q,3}^{(2)} \sim -\frac{3}{8} \int_0^{t_f} dt \frac{d\kappa(t)}{dt} [\kappa_f^2 A(t_f, t_f, t) - 2\kappa_f \kappa_i A(t_f, t, 0) + \kappa_i^2 A(t, 0, 0)]. \quad (\text{E44})$$

The term containing the correlation $A(t_f, t, 0)$ is exponentially decreasing, $A(t_f, t, 0) \sim 8\sigma_{x,\text{eq}}^2(t)\sigma_{x,i}^4 \exp[-2\varphi(t_f, 0)]$. Then, we only need to consider the other two terms. We start with the analysis of the first one, specifically

$$\int_0^{t_f} dt \frac{d\kappa(t)}{dt} A(t_f, t_f, t) \sim 8 \int_0^{t_f} dt \frac{d\kappa(t)}{dt} \sigma_{x,f}^2 \sigma_{x,\text{eq}}^4(t) \exp[-2\varphi(t_f, t)] = 8\sigma_{x,f}^2 \int_0^1 d\tau \dot{\kappa}(\tau) \sigma_{x,\text{eq}}^4(\tau) \exp \left[-2t_f \int_\tau^1 d\tau' \kappa(\tau') \right]. \quad (\text{E45})$$

In the limit $t_f \gg 1$, we can once more use Watson's lemma to estimate the integral to the lowest order, with the result

$$\int_0^{t_f} dt \frac{d\kappa(t)}{dt} A(t_f, t_f, t) \sim 8\sigma_{x,f}^6 \dot{\kappa}_f \frac{1}{2\kappa_f t_f} = \frac{1}{t_f} \frac{4\sigma_{x,f}^6}{\kappa_f} \dot{\kappa}_f. \quad (\text{E46})$$

An analogous calculation yields

$$\int_0^{t_f} dt \frac{d\kappa(t)}{dt} A(t, 0, 0) \sim 8\sigma_{x,i}^6 \dot{\kappa}_i \frac{1}{2\kappa_i t_f} = \frac{1}{t_f} \frac{4\sigma_{x,i}^6}{\kappa_i} \dot{\kappa}_i. \quad (\text{E47})$$

Then, up to order t_f^{-1} we have that

$$\mu_{Q,3}^{(2)} \sim -\frac{3}{2t_f} \left(\dot{\kappa}_f \frac{\theta_f^3}{\kappa_f^2} - \dot{\kappa}_i \frac{\theta_i^3}{\kappa_i^2} \right). \quad (\text{E48})$$

Let us analyze the following contribution:

$$\begin{aligned} \mu_{Q,3}^{(3)} &\equiv \overline{3(\Delta u - \overline{\Delta u})(W - \overline{W})^2} \\ &= \frac{3}{4} \overline{\left[\frac{1}{2} \kappa_f (x_f^2 - \sigma_{x,f}^2) - \frac{1}{2} \kappa_i (x_i^2 - \sigma_{x,i}^2) \right] \int_0^{t_f} dt \frac{d\kappa(t)}{dt} [x^2(t) - \overline{x^2(t)}] \int_0^{t_f} dt' \frac{d\kappa(t')}{dt'} [x^2(t') - \overline{x^2(t')}] } \\ &= \frac{3}{2} \overline{\left[\frac{1}{2} \kappa_f (x_f^2 - \sigma_{x,f}^2) - \frac{1}{2} \kappa_i (x_i^2 - \sigma_{x,i}^2) \right] \int_0^{t_f} dt \frac{d\kappa(t)}{dt} [x^2(t) - \overline{x^2(t)}] \int_0^t dt' \frac{d\kappa(t')}{dt'} [x^2(t') - \overline{x^2(t')}] } \\ &= \frac{3}{4} \int_0^{t_f} dt \frac{d\kappa(t)}{dt} \int_0^t dt' \frac{d\kappa(t')}{dt'} [\kappa_f A(t_f, t, t') - \kappa_i A(t, t', 0)]. \end{aligned} \quad (\text{E49})$$

Note that $t \geq t'$ in the last two lines, making use of the symmetry of the integrand under the exchange $t \leftrightarrow t'$.

Again, we have to calculate three-time correlation functions. We start by analyzing the term stemming from

$$A(t_f, t, t') \sim 8\sigma_{x,\text{eq}}^2(t)\sigma_{x,\text{eq}}^4(t') \exp[-2\varphi(t_f, t')]. \quad (\text{E50})$$

More specifically, we have to find the lowest order contribution to the integral

$$\begin{aligned} \int_0^{t_f} dt \frac{d\kappa(t)}{dt} \int_0^t dt' \frac{d\kappa(t')}{dt'} A(t_f, t, t') &\sim 8 \int_0^{t_f} dt \frac{d\kappa(t)}{dt} \int_0^t dt' \frac{d\kappa(t')}{dt'} \sigma_{x,\text{eq}}^2(t)\sigma_{x,\text{eq}}^4(t') \exp[-2\varphi(t_f, t')] \\ &= 8 \int_0^1 d\tau \dot{\kappa}(\tau)\sigma_{x,\text{eq}}^2(\tau) \int_0^\tau d\tau' \dot{\kappa}(\tau')\sigma_{x,\text{eq}}^4(\tau') \exp\left[-2t_f \int_\tau^1 d\tau'' \kappa(\tau'')\right]. \end{aligned} \quad (\text{E51})$$

Once more, the asymptotic estimate of this integral to the lowest order can be calculated by applying Watson's lemma. First, we integrate over τ' at given τ , and this yields

$$\int_0^{t_f} dt \frac{d\kappa(t)}{dt} \int_0^t dt' \frac{d\kappa(t')}{dt'} A(t_f, t, t') \sim \int_0^1 d\tau \dot{\kappa}^2(\tau)\sigma_{x,\text{eq}}^6(\tau) \frac{1}{2\kappa(\tau)t_f} \exp\left[-2t_f \int_\tau^1 d\tau'' \kappa(\tau'')\right], \quad (\text{E52})$$

because the exponential reaches its maximum value for $\tau' = \tau$, i.e., when τ' is closest to unity. The integral over τ is now dominated by the contribution of a narrow interval close to $\tau = 1$, i.e., by applying again Watson's lemma we get

$$\int_0^{t_f} dt \frac{d\kappa(t)}{dt} \int_0^t dt' \frac{d\kappa(t')}{dt'} A(t_f, t, t') \sim \dot{\kappa}_f^2 \sigma_{x,f}^6 \left(\frac{1}{2\kappa_f t_f} \right)^2. \quad (\text{E53})$$

Therefore, this contribution is of the order t_f^{-2} and thus subdominant to that in $\mu_{Q,2}^{(2)}$, which was of the order of t_f^{-1} .

Now we look into the contribution coming from $A(t, t', 0)$. In this case, it is better to introduce the condition $t \geq t'$ by integrating t' from zero to t_f and restricting t to the interval $[t', t_f]$. By doing so, the calculation follows completely similar lines as those above. The correlation $A(t, t', 0)$ has a term $\exp[-2\varphi(t, 0)] = \exp[-2t_f \int_0^\tau d\tau'' \kappa(\tau'')]$: the first integration over t gives a t_f^{-1} factor and makes $t = t'$ in φ ; the second integration over t' gives a second t_f^{-1} factor and makes $t' = 0$ in φ . Then, we have that this contribution is also proportional to t_f^{-2} , specifically

$$\int_0^{t_f} dt \frac{d\kappa(t)}{dt} \int_0^t dt' \frac{d\kappa(t')}{dt'} A(t, t', 0) \sim \dot{\kappa}_i^2 \sigma_{x,i}^6 \left(\frac{1}{2\kappa_i t_f} \right)^2. \quad (\text{E54})$$

With a similar line of reasoning, it is possible to show that the last contribution to $\mu_{Q,3}$,

$$\mu_{Q,3}^{(4)} = -\overline{(W - \overline{W})^3}, \quad (\text{E55})$$

is also subdominant, i.e., it does not contain t_f^{-1} terms. This can also be qualitatively understood by recalling that work fluctuations are Gaussian in the slow driving limit $t_f \gg 1$: $\overline{(W - \overline{W})^3}$ should vanish to the lowest order.

Finally, we get that

$$\mu_{Q,3} = \theta_f^3 - \theta_i^3 - \frac{3}{2t_f} \left(\dot{\kappa}_f \frac{\theta_f^3}{\kappa_f^2} - \dot{\kappa}_i \frac{\theta_i^3}{\kappa_i^2} \right) + O(t_f^{-2}), \quad (\text{E56})$$

and the correction to the third central moment is a pure boundary term. Interestingly, this means that the heat distribution is not simply being compressed or decompressed around its mean. The heat PDF $\mathcal{P}(Q)$ is such that

$$\mathcal{P}(Q) \neq f\left(\frac{Q - \bar{Q}}{\sigma_Q}\right), \quad (\text{E57})$$

even in the slow driving limit. Had we $\mathcal{P}(Q) = f\left(\frac{Q - \bar{Q}}{\sigma_Q}\right)$, the third central moment would be proportional to σ_Q^3 . In other words, $\mu_{Q,3}/\sigma_Q^3$ would be constant, independent of t_f , to the considered order. It is quite clear that $\mu_{Q,3}/\sigma_Q^3$ does depend on t_f , i.e., the t_f^{-1} corrections coming from $\mu_{Q,3}$ and σ_Q^3 do not cancel out. Thus, the shape of the heat distribution is not preserved when we change the connecting time.

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- [39] All the central moments are $\overline{x^n(\tau)} = (\overline{x^n})_i [\sigma_x(\tau)]^n$; $\sigma_{x,i} = 1$ and $\theta_i = 1$ with our choice of units.
- [40] As found in other problems, the optimal control has finite jumps at $t = 0$ and $t = t_f$ [41–45]. Adiabaticity is not broken: there is no *instantaneous* heat transfer at $t = 0$ and/or $t = t_f$.
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