Nonequilibrium corrections to gradient flow

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The force on a probe induced by a nonequilibrium medium is in general nongradient. We detail the mechanism of that feature via nonequilibrium response theory. The emergence of nongradient forces is due to a systematic “twist” of the excess frenesy with respect to the entropy flux, in response to changes in the coupling or in the position of the probe in the nonequilibrium medium.

I. INTRODUCTION

Today there is much interest in understanding what survives or gets modified of standard thermodynamics when dealing with active matter or with nonequilibrium media more generally. The present paper addresses the nongradient nature of the net induced force on a probe coupled to a steady nonequilibrium. That probe may represent a colloidal particle in the medium or may even be macroscopic such as a container wall holding a nonequilibrium fluid or it could be a slow collective variable defined from the microscopic nonequilibrium degrees of freedom. For reversible transformations, the gradient structure of the force is relevant for a great number of thermodynamic relations and for the very existence of certain state functions [1]. For example, return to equilibrium follows steepest descent on the landscape of thermodynamic free energy [2, 3]. That “mechanical” picture breaks down for

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quasistatic transformations in contact with nonequilibria, \cite{4, 5}. The present paper gives general characterizations under which the systematic (net) force becomes nongradient, and what physics (and quantities) determine that. The main ingredient is nonequilibrium response theory and to follow the role of the frenetic contribution in the response of the nonequilibrium medium on the probe \cite{6}.

Gradient flow is a characteristic feature of dissipative relaxational behavior towards equilibrium \cite{7}. One essential aspect is the gradient nature of thermodynamic forces as first described by Onsager \cite{8}. If e.g. we consider a probe with position \(x\) in contact with an equilibrium bath, then the induced force on the probe is simply the gradient \(-\nabla_x F_{eq}\) of the appropriate thermodynamic potential \(F_{eq}\). More specifically, the pressure \(P\) in a fluid in volume \(V\) in thermal contact with a heat bath at temperature \(T\) can be calculated via the formula

\[
P = -\frac{\partial F_{eq}}{\partial V} = k_B T \frac{\partial \log Z}{\partial V}
\]

where \(Z = Z(V, T)\) is the equilibrium partition function appearing in the statistical mechanical expression for the Helmholtz free energy \(F_{eq}\). The basic calculation that obtains that gradient structure comes from equilibrium statistical mechanics. One assumes a quasistatic probe, moving on a time-scale which is much longer than the relevant relaxation time of the equilibrium bath. The latter has degrees of freedom denoted by \(\eta\) so that by integrating over canonical equilibrium the mean (also called, statistical) force equals

\[
f_{eq}(x) = -\frac{1}{Z(x, T)} \int \mathrm{d}\eta \nabla_x U(x, \eta) e^{-\beta U(x, \eta)}
\]

\[= -\nabla_x F_{eq}(x), \quad F_{eq}(x) = -k_B T \log Z(x, T)
\]
The probe makes thermal contact here with the medium via the interaction \( U(x, \eta) \). As the force (1) is gradient, the work

\[
\int_{\gamma:x_i \rightarrow x_f} f_{\text{eq}}(y) \cdot dy = \mathcal{F}_{\text{eq}}(x_i) - \mathcal{F}_{\text{eq}}(x_f)
\]

just depends on the final and initial positions \( x_f, x_i \) in the probe trajectory \( \gamma \). For isothermal changes as above, that reproduces the reversible expression for the work done as the difference in free energy.

Stationary nonequilibria are not simply characterized by thermodynamic quantities like (free) energy or temperature. For a general stationary distribution \( \rho_x \) over the bath degrees of freedom \( \eta \), the force on the probe \( x \in \mathbb{R}^d \) is

\[
f(x) = -\langle \nabla_x U(x, \eta) \rangle_x = -\int \nabla_x U(x, \eta) \rho_x(d\eta)
\]

where the microscopic interaction \( U(x, \eta) \) between probe and medium is given. We keep the assumption of infinite time-scale separation between probe and medium, and for physical realizations it is good to imagine also a (third) family of particles that constitute an equilibrium environment for example to thermostat the nonequilibrium medium. In that case we also know precisely what we mean by the entropy flux for trajectories of the medium.

It should not be very surprising that (3) delivers non-conservative forces. The presence of rotational forces can already be checked in the simplest cases; see the next Section. Similarly, the pressure for a nonequilibrium medium may have a component which renders the work for moving a container wall to depend on the trajectory, quite in contrast with the situation of (2). Nonequilibrium media do not in general yield a path-independent
expression for the compression or expansion work $\int P \, dV$ even under isothermal quasistatic conditions. To be more precise, when the volume $V = Ax$ is changed with fixed area $A$ by changing the linear dimension $x \in \mathbb{R}$, then, of course, the pressure $P(x)$ remains a gradient (as $x$ is one-dimensional). If however the changes are multi-dimensional with a pressure $P(x, y, z)$ involving all three dimensions of the box so that the three-dimensional shape of the volume is being changed via some specific protocol $\gamma$, then the work done will depend on $\gamma$ in general. In fact, because the stationary distribution in (3) may depend on detailed kinetic aspects (e.g. in the probe-medium interaction) it is very well possible that pressure is not a state variable at all; see e.g. [9].

In what follows we go beyond the mere observations above to uncover the rotational component in nonequilibrium statistical forces. The notion of frenesy and how it appears in response theory is formally reviewed in Appendix A and B. We will see that the changes in frenesy of the medium by moving the probe position is proportional to the rotational component in the statistical force. In fact, in Section IV we show that the curl of the statistical force is given in terms of an external product between entropy flux and excess frenesy. After the presentation of a toy-model in the next section, we study the problem in a weak coupling expansion in Section III. It is the nontrivial dependence of the frenesy on the coupling that makes the statistical force nongradient. When the medium is in equilibrium, these rotational components disappear of course. In Section V we investigate the appearance of nongradient forces up to second order around equilibrium,
comparing also the response theory of the Appendix [3] with an approach introduced by Komatsu and Nakagama [10].

II. AN EXAMPLE

Let us start with a toy model to illustrate in a simple setting the main phenomenon. We have a probe moving diffusively on the ring, $x \in S^1$, and coupled to a driven system with two states $\eta = 0, 1$ connected by two different transition channels $0 \leftrightarrow 1$. The transition rates have the general form,

$$
k_{L,R}(0, 1) = a_{L,R}(x) e^{-\frac{\beta}{2} [u(x) \pm \varepsilon]}
$$

$$
k_{L,R}(1, 0) = a_{L,R}(x) e^{\frac{\beta}{2} [u(x) \pm \varepsilon]} , \quad u(x) = U(x, 1) - U(x, 0)
$$

The parameter $\varepsilon$ reads the work of driving forces along the cycle $0 \xrightarrow{R} 1 \xrightarrow{L} 0$. The energy $U(x, \eta)$ and the kinetic factors $a_{L,R}(x)$ depend on the position of the probe. The environment is a thermal bath at inverse temperature $\beta \neq 0$.

The statistical force $f(x)$ on the probe as defined in (3) is the mean force in the quasistatic limit where the probe is fixed at position $x$: here,

$$
f(x) = -U'(x, 1) \rho_x(1) - U'(x, 0) \rho_x(0)
$$

where $\rho_x(\eta)$ is the stationary occupation of the driven two-level system. Everything is explicit here as the stationary occupations satisfy

$$
\frac{\rho_x(1)}{\rho_x(0)} = \frac{k_L(0, 1) + k_R(0, 1)}{k_L(1, 0) + k_R(1, 0)} = \zeta(x) e^{-\beta u(x)}
$$

where

$$
\zeta(x) = \frac{a_R(x) + a_L(x) e^{-\beta \varepsilon}}{a_L(x) + a_R(x) e^{-\beta \varepsilon}}
$$

Hence, the statistical force (5) on the probe equals

$$
f(x) = -U'(x, 0) - \frac{u'(x)}{1 + \zeta^{-1}(x) e^{\beta u(x)}}, \quad x \in S^1
$$
It is easy to check that the statistical force is derived from the free energy
\[ f(x) = \frac{1}{\beta} \frac{d}{dx} \log \left( e^{-\beta U(x,0)} + e^{-\beta U(x,0)} \right) \]
whenever \( \zeta(x) \equiv 1 \) (which is the usual equilibrium formula for the statistical force) when \( \varepsilon = 0 \) (detailed balance) or for \( a_L = a_R \) (channel symmetry). Those are however not the only cases here for which the statistical force is a gradient. Indeed, when the kinetic factors in (7) are “energetic” in the sense that they depend on the position \( x \) entirely via the energy gap, i.e., \( \zeta(x) = z(u(x)) \) for some function \( z(\cdot) \), then the statistical force is also gradient, \( f(x) = -\tilde{F}'(x) \) with respect to the “free energy” (up to any constant),
\[
\tilde{F}(x) = U(x,0) + \int u(x) \frac{d\nu}{1 + z^{-1}(v) e^{\beta v}}
\]
Therefore to obtain nongradient forces it is necessary that, loosely speaking, the positions with the same energy gap are “resolved” via distinct kinetic factors. Note that the issue of “being gradient or not being gradient” is here directly related to what we may suppose to be the induced motion on the probe in the quasistatic and overdamped limit, \( \dot{x}_t = f(x_t) + \sqrt{2T} \xi_t \), where \( T = \beta^{-1} \) is the temperature of the environment giving white noise \( \xi_t \). When the force \( f \) is purely gradient, \( \oint f = 0 \), no probe current can arise.

In order to find a sufficient condition for a nongradient contribution we can be more explicit via an expansion in a small probe-medium coupling constant \( \lambda \),
\[
u(x) = u_0 + \lambda u_1(x) + \ldots \quad \text{and} \quad \zeta(x) = \zeta_0 + \lambda \zeta_1(x) + \ldots
\]
To second order in the coupling strength \( \lambda \), the formula (8) yields
\[
\oint f \, dx = \frac{\lambda^2}{(e^{\beta u_0/2} + \zeta_0 e^{-\beta u_0/2})^2} \oint u_1(x) \zeta_1'(x) \, dx + O(\lambda^3)
\]
For example, if the kinetic factor of the L-channel is harmonically modulated around a symmetric uncoupled reference,

\[ a_L(x) = a + \lambda b \cos(2\pi x), \quad a_R(x) \equiv a > 0 \]

then the nonequilibrium factor reads

\[ \zeta(x) = 1 - \lambda \frac{b}{a \tanh \frac{\beta \varepsilon}{2}} \cos(2\pi x) + O(\lambda^2) \]

and assuming a (shifted) harmonic modulation also in the level spacing,

\[ u(x) = u_0 + \lambda \hat{u}_1 \cos(2\pi x - \phi), \quad \hat{u}_1 \neq 0 \]

the nongradient part in the force equals

\[ \oint f \, dx = \lambda^2 \frac{\hat{u}_1 b}{8a \cosh^2 \left( \frac{\beta u_0}{2} \right)} \tanh \left( \frac{\beta \varepsilon}{2} \right) \sin \phi + O(\lambda^3) \]  

(10)

We observe that for a nonzero gradient force we need not only that the (fast) two-level system is driven ($\varepsilon \neq 0$) or the channel is asymmetric ($b \neq 0$), but also that there is a phase shift (or “twist”) ($\phi \neq 0$) between the spatial modulations in the level spacing and in the kinetic factor, respectively. We will see that effect again and discussed more generally in the following section.

### III. WEAK COUPLING EXPANSION

Assume that the coupling potential between probe and medium has the form

\[ U_\lambda(x, \eta) = U_0(\eta) + \lambda U_I(x, \eta). \]

Expanding the force \( f(x) \) in the coupling parameter $\lambda$, the leading term is of gradient form,

\[ f(x) = -\lambda \nabla_x \langle U_I \rangle^{\lambda=0} + O(\lambda^2). \]

We apply response theory [11], see Appendix [3] to find the second order correction in the weak coupling expansion. In contrast with equilibrium we need here also the excess in frenesy $D$, defined for each trajectory of the
medium. See Appendix [A] for an introduction and the necessary tools for what follows.

Let us make the assumption that the probe does not directly interfere with a nonequilibrium driving of the medium in the sense that the (path-wise) work \( W(\omega) \) of driving forces is independent of \( \lambda \) or \( x \). Here, \( \omega = [\eta_s]_0^t \) denotes the trajectory in the nonequilibrium medium. Then the entropy flux per \( k_B \),

\[
S(\omega) = \beta [U(\lambda, x, \eta_0) - U(\lambda, x, \eta_t) + W(\omega)]
\]  

(11)
satisfies \( S'(\omega) = \beta [U_I(\lambda, x, \eta_0) - U_I(\lambda, x, \eta_t)] \) with the shorthand \( ' \equiv d/d\lambda|_{\lambda=0} \).

We now use formula (B2) with process \( P_2 \) corresponding to coupling \( \lambda \) and process \( P_1 \) with coupling \( \lambda = 0 \). We start both processes from the stationary distribution \( \rho^0 \) of the medium for the uncoupled case. The stationary distribution at coupling \( \lambda \) can then be evaluated as in (B2), for \( t \to \infty \),

\[
\frac{d\rho^\lambda_x}{d\rho^0}(\eta) = \left\langle e^{(S^\lambda-S^0)/2-(D^\lambda-D^0)} \right| \eta_t = \eta \rangle^0
\]

\[
= 1 + \lambda \left\langle \frac{S'}{2} - D' \right| \eta_t = \eta \rangle^0 - \lambda \left\langle \frac{S'}{2} - D' \right| \eta_0 = \eta \rangle^0 + O(\lambda^2)
\]

(12)

We have used relation (B3) for adding \( \left\langle \frac{S'}{2} - D' \right| \eta_0 = \eta \rangle^0 = 0 \), and that

\[
\lim_{t \to \infty} \langle U_I(x, \eta_0) \mid \eta_t = \eta \rangle^0 = \langle U_I \rangle^0
\]

We denote

\[
H'_x(\eta) = \lim_{t \to \infty} \left[ \langle D'_x \mid \eta_0 = \eta \rangle^0 - \langle D'_x \mid \eta_t = \eta \rangle^0 \right]
\]

See (A2) for an explicit formula for \( D \). Per consequence the force on the
probe is
\[
f_{\lambda}(x) = -\lambda \left\langle \frac{d\rho_{\lambda}^x}{d\rho_{0}^x} \nabla_x U_I \right\rangle^0
\]
\[
\quad = -\lambda \nabla_x \langle U_I \rangle^0 + \frac{\lambda^2 \beta}{2} \nabla_x [\langle U_I^2 \rangle^0 - (\langle U_I \rangle^0)^2] - \lambda^2 \langle H' \nabla_x U_I \rangle^0 + O(\lambda^3)
\]
\[
\quad = -\nabla_x \Psi_{\lambda}(x) + f_{\lambda}^{\text{neq}}(x)
\] (13)

with the potential defined in the decoupled medium
\[
\Psi_{\lambda}(x) = -\frac{1}{\beta} \log \left\langle e^{-\beta \lambda U_I} \right\rangle^0
\] (14)

which obviously reduces to the equilibrium free energy (difference) under detailed balance, and the second contribution is generally nonconservative,
\[
f_{\lambda}^{\text{neq}}(x) = -\lambda^2 \langle H' \nabla_x U_I \rangle^0 + O(\lambda^3)
\]
\[
\quad = -\frac{1}{\beta} \left\langle (D_{\lambda} - D_0) \nabla_x (S_{\lambda} - S_0) \right\rangle^0 + O(\lambda^3)
\] (15)

As suggested by the last (formal) expression the latter originates from correlations between the (gradient of) entropy flux and the freneisy. (Note that the $S_0$ is redundant there.)

The decomposition of the induced force into conservative and nonconservative components is of course not unique (unless imposing some extra condition like, e.g., that the latter component is to be divergence-free as in the Helmholtz decomposition). An alternative representation would be, for example,
\[
f_{\lambda}(x) = -\nabla_x \tilde{\Psi}_{\lambda}(x) + \tilde{f}_{\lambda}^{\text{neq}}(x)
\] (16)

with the modified potential (now in the coupled medium)
\[
\tilde{\Psi}_{\lambda}(x) = \frac{1}{\beta} \log \left\langle e^{\beta \lambda U_I} \right\rangle^\lambda
\] (17)
and the modified nonconservative force
\[ \tilde{f}_\lambda(x) = \lambda^2 \langle U_I \nabla_x H' \rangle^0 + O(\lambda^3) \]
\[ = \frac{1}{\beta} \langle (S_\lambda - S_0) \nabla_x (D_\lambda - D_0) \rangle^0 + O(\lambda^3) \]  
(18)

We see that it is the position dependence of the medium’s freeness that delivers the nongradient contribution.

The above is easily checked by using the response formula (B2) or (12) directly for the averaged interaction potential
\[ \langle U_I \rangle^\lambda = \langle U_I \rangle^0 - \lambda \beta \left[ \langle U_I^2 \rangle^0 - \langle \langle U_I \rangle^0 \rangle^2 \right] + \lambda \langle H' U_I \rangle^0 + O(\lambda^2) \]  
(19)

Finally, observe that by adding the two expressions (13) and (16) we get the induced force as
\[ 2\beta f_\lambda(x) = -\nabla_x \log \frac{\langle e^{\beta \lambda U_I} \rangle^\lambda}{\langle e^{-\beta \lambda U_I} \rangle^0} \]
\[ + \langle (S_\lambda - S_0) \nabla_x (D_\lambda - D_0) - (D_\lambda - D_0) \nabla_x (S_\lambda - S_0) \rangle^0 + O(\lambda^3) \]
where the nongradient part (in the second line) contains the “bracket” \( \partial_\lambda S \nabla_x D - \partial_\lambda D \nabla_x S \).

**IV. STIFFNESS**

We can also apply the linear response formalism to establish local properties of the mean force (3) in the “thermodynamic space” of probe coordinates \( x = (x_1, \ldots, x_d) \). More specifically, we can study the (differential) stiffness of the probe in terms of the linear response matrix
\[ M_{jk}(x) = -\nabla_j f_k(x) = \nabla_j \langle \nabla_k U \rangle_x, \quad \nabla_j \equiv \frac{\partial}{\partial x_j} \]  
(21)
We remind that $\langle \cdot \rangle_x$ denotes expectation over the nonequilibrium medium with probe fixed at $x$. Note also that under equilibrium conditions and as a continuation from (1) that matrix is

$$M_{jk}^{\text{eq}}(x) = -k_B T \partial_{jk} \log Z(x) = \langle \partial_{jk} U \rangle_x^{\text{eq}} - \beta \text{Cov}(\nabla_j U; \nabla_k U)_x^{\text{eq}}$$

(22)

where the first term represents an inherent (mechanical) stiffness of the probe, which is diminished by fluctuations in the medium (the second term). It always satisfies the Maxwell symmetry relations $M_{jk}^{\text{eq}}(x) = M_{kj}^{\text{eq}}(x)$, obviously a direct consequence of the existence of a potential for the thermodynamic force.

Out of equilibrium the matrix $M(x)$ generally decomposes into a symmetric part, $M^{(s)}(x)$, corresponding to locally conservative forces, and an antisymmetric part, $M^{(a)}(x)$, representing rotational forces.

The differential stiffness (21) is easily computed via noticing

$$M_{jk}(x) = \langle \partial_{jk} U \rangle_x + \langle \nabla_j \log \rho \nabla_k U \rangle_x$$

(23)

where $\rho = \rho_x$ is the stationary distribution of the medium. We apply now the response formula (B2) for fixed coupling $\lambda$ and with initial condition given by $\rho_x$. For $t \to \infty$,

$$\rho_{x+dx}(\eta) = \langle \delta(\eta_t - \eta) \rangle_{x+dx} = \rho_x(\eta) \left\{ 1 + \frac{\text{d}S_x}{2} - \text{d}D_x |_{\eta_t = \eta} - \frac{\text{d}S_x}{2} - \text{d}D_x |_{\eta_0 = \eta} \right\}$$

$$= \rho_x(\eta) \left\{ 1 - \beta [\text{d}U(x, \eta) - \langle \text{d}U \rangle_x] + \text{d}H(x, \eta) \right\}$$

(24)

where $\text{d}H(x, \eta) := \lim_t \langle \text{d}D_x |_{\eta_0 = \eta} - \langle \text{d}D_x |_{\eta_t = \eta} \rangle_x$, and we have again used (B3) for $\langle \frac{\text{d}S_x}{2} - \text{d}D_x |_{\eta_0 = \eta} \rangle_x = 0$ and $\text{d}S_x(\omega) = \beta [\text{d}U(x, \eta_0) - \langle \text{d}U \rangle_x] \right\}$.
\[ dU(x, \eta_t) \] due to our assumption that the driving contribution to the entropy flux does not (explicitly) depend on \( x \). Equivalently,

\[ d \log \rho_x(\eta) = -\beta [dU(x, \eta) - \langle dU \rangle_x] + dH(x, \eta) \quad (25) \]

We can insert that in (23). Writing \( dH(x, \eta) = H_j \, dx_j \), the differential stiffness (21) equals

\[ M_{jk}(x) = \langle \partial_{jk} U \rangle_x - \beta \text{Cov}(\nabla_j U; \nabla_k U)_x + \text{Cov}(\nabla_k U; H_j)_x \quad (26) \]

Comparing that with (22) we see that the last term makes the typical nonequilibrium contribution. It can equivalently be written as

\[ \text{Cov}(\nabla_j U; H_k)_x = \langle [\nabla_j U(x, \eta_0) - \nabla_j U(x, \eta_\tau)] \nabla_k D \rangle_x \]

\[ = k_B T \langle \nabla_j S \nabla_k D \rangle_x \quad (27) \]

In particular, the antisymmetric part violating the Maxwell relations is, formally,

\[ M^{(a)}_{jk}(x) = k_B T \langle \nabla_j S \nabla_k D - \nabla_k S \nabla_j D \rangle_x \quad (28) \]

which can also be expressed more elegantly by employing the external form calculus (with \( X \wedge Y = -Y \wedge X \) and \( d^2 = 0 \)) in the form

\[ d \langle dU \rangle^x = M^{(a)}_{jk} \, dx_j \wedge dx_k \]

\[ = k_B T \langle dS \wedge dD \rangle_x \quad (29) \]

Note that \( dS \wedge dD \) is the volume form of a parallelogram demarcated by (co-)vectors \( dS \) and \( dD \) (pathwise).

V. NOT-SO-CLOSE-TO-EQUILIBRIUM REGIME

Statistical forces can also be investigated in an expansion near equilibrium. Via the condition of local detailed balance it is mostly possible to speak about
a driving amplitude $\varepsilon$, as present in the irreversible work $W$ in (11). Linear order (in $\varepsilon$) corrections have been given in [12]. Here we add the second order correction, for which we employ the Komatsu-Nakagawa formula, [10], and which, to be self-contained, is derived in Appendix C from the response formalism of Appendix B.

The expression for the stationary distribution obtained in [10] (formula C6 in Appendix B) reads

$$\log \frac{d\rho}{d\rho^{\text{eq}}}(\eta) = \beta\Omega - \frac{1}{2} \left[ \langle S_i \rangle_{\eta} - \langle S_i \rangle_{\eta \rightarrow \eta} \right] + O(\varepsilon^3) \quad (30)$$

with $\varepsilon$ the driving amplitude and where the difference in the square bracket reads the difference between the irreversible entropy production $S_i = \beta W$ (linear in $\varepsilon$) along the process started from $\eta$ and the process conditioned on ending at $\eta$. The expectations are denoted by $\langle \cdot \rangle_{\eta}$, respectively $\langle \cdot \rangle_{\eta \rightarrow \eta}$, and the limit $t \uparrow \infty$ is understood. Furthermore,

$$\beta\Omega = S(\rho | \rho^{\text{eq}}) = \beta \left[ F(\rho) - F(\rho^{\text{eq}}) \right] + O(\varepsilon^3) \quad (31)$$

which is the difference between the “nonequilibrium free energy” $F^{\text{neq}} := F(\rho) = \langle U + \beta^{-1} \log \rho \rangle$ and the equilibrium free energy $F^{\text{eq}} := F(\rho^{\text{eq}}) = -\beta^{-1} \log Z$. Within the second order approximation it is also explicitly given as $\Omega = \frac{1}{2\beta} \langle \langle S_i \rangle_{\eta}^{\text{eq}} \rangle_{\eta}^{\text{eq}} = \frac{1}{2} \langle \langle W \rangle_{\eta}^{(\text{ex})} \rangle_{\eta}^{\text{eq}}$, i.e., one half of the excess work done when the medium starts from equilibrium.

This formalism can directly be applied to statistical forces. Assuming $\rho^{\text{eq}}_{x}(\eta) = \frac{1}{Z_x} e^{-\beta U(x,\eta)}$, then we have

$$f(x) = -\langle \nabla_x U \rangle_{x}^{x} = -\nabla_x F^{\text{eq}}(x) - \frac{1}{\beta} \left\langle \nabla_x \log \frac{d\rho_x}{d\rho^{\text{eq}}_x} \right\rangle_{x}^{x}$$

$$= -\nabla_x F^{\text{neq}}(x) + \frac{1}{2} \left\langle \nabla_x \left[ \langle W \rangle_{\eta}^{x} - \langle W \rangle_{\eta \rightarrow \eta}^{x} \right] \right\rangle_{x}^{x} + O(\varepsilon^3) \quad (32)$$
or
\[
\int f(x) \cdot dx = -d\mathcal{F}^{\text{neq}} + \frac{1}{2} [dW(x) - dW^-(x)] + O(\varepsilon^3)
\]
where \(dW(x) = \int \langle W \rangle_{\eta}^{x+dx} \rho^x(\eta)d\eta\) is the usual work of driving forces along the thermodynamic transformation \(x \mapsto x + dx\), whereas \(dW^-(x) = \int \langle W \rangle_{\eta \to \eta}^{x+dx} \rho^x(\eta)d\eta\) can be interpreted as the work along a reversed spontaneous process \(x + dx \mapsto x\) (more precisely: within an ensemble interpretation it reads the work done along a typical excitation path realizing the empirical occupations given by \(\rho_x\) in the steady state described by \(\rho_{x+dx}\)).

VI. CONCLUSION

The notions of thermodynamic landscape and potential are at the core of many thermodynamic considerations and heuristics. For a probe in a nonequilibrium medium the work done by or on the probe may be path-dependent even under quasistatic conditions. It allows for a greater phenomenology in statistical forces, avoiding gradient flow and enabling oscillatory motion. That forces obtain a rotational component when induced by nonequilibrium media is not surprising, but it is important and interesting to see the explicit nature and mechanism.

From response theory we have obtained a general characterization of how that picture arises. The rotational component can be expressed via the dependencies on the probe of the entropy flux and the frenesy in the nonequilibrium medium. A certain “twist” between the entropic and the frenetic contributions induces the nongradient nature of the force.

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Appendix A: Frenesy

At various places in the main text appears the frenesy $D$ of the medium, either as function of the coupling or as function of the probe position. Let us explain here where it stands for.

Suppose for simplicity that the medium in contact with the static probe $x$ undergoes a Markov jump process $(\eta_s, 0 \leq s \leq t)$ with transition rates

$$k(\eta, \eta') = \Phi_{x, \lambda}(\eta, \eta') \exp[\beta U_\lambda(x, \eta)] \exp[\beta W(\eta, \eta')/2]$$  \hspace{1cm} (A1)

for symmetric prefactor $\Phi_{x, \lambda}(\eta, \eta') = \Phi_{x, \lambda}(\eta', \eta)$ and with work $W(\eta, \eta') = -W(\eta', \eta)$ done by the driving forces in the transition $\eta \to \eta'$. We are here under the condition of local detailed balance and we take the isothermal set-up at inverse temperature $\beta$ thermostated by an imagined equilibrium bath, and $U_\lambda$ is the coupling energy between (nonequilibrium) medium and probe. For $W \equiv 0$ there is (global) detailed balance with potential $U_\lambda$.

Frenesy is a (time-extensive) path-quantity $D = D_{x, \lambda, \text{driving}}(\omega)$, where $\omega$ is the medium trajectory during $[0, t]$, which complements the variable entropy flux $S(\omega)$ and they both together uniquely determine the plausibility of a trajectory $\omega$. In particular, $D(\omega) = D(\theta \omega)$ is time-symmetric with time-reversal $(\theta \omega)_s = \eta_{t-s}$. The frenesy $D$ gets always expressed relative to some other process, changing some physical parameters in (A1). Let us here however keep the nonequilibrium driving and the environment temperature fixed but we suppose changing the probe position $x$ or the coupling $\lambda$. 
There are two parts in $D$, one related to the log-reactivities,

$$r(\eta, \eta') := -\log \Phi_{x,\lambda}(\eta, \eta') - \frac{\beta}{2} [U_{\lambda}(x, \eta) + U_{\lambda}(x, \eta')]$$

and one obtained from the escape rate

$$\xi(\eta) = \exp [\beta U_{\lambda}(x, \eta)] \sum_{\eta'} \Phi_{x,\lambda}(\eta, \eta') \exp[\beta W(\eta, \eta')/2]$$

Then, the frenesy equals

$$D(\omega) = \sum_s r(\eta_s^-, \eta_s) + \int_0^t ds \xi(\eta_s) \quad \text{(A2)}$$

where the first sum is over the jump times in the trajectory $\omega$. The important point is that the medium responds to changes in these parameters through the frenesy $D$ and through the entropy flux $S$, as we briefly review next.

**Appendix B: Response formulæ**

Response theory out-of-equilibrium is reviewed in [13]. We compare two processes, $P_1$ and $P_2$, both corresponding to (A1) but for different $\lambda$ or $x$. The initial state at time zero is supposed to be the same for both. The processes can be compared via expectations of observables $f(\omega)$,

$$\langle f(\omega) \rangle_1 = \int f(\omega) dP_1(\omega) \quad \text{versus} \quad \langle f(\omega) \rangle_2 = \int f(\omega) dP_2(\omega)$$

and $dP_2 = dP_1 e^{-A}$ where

$$A(\omega) = D_2(\omega) - D_1(\omega) - \frac{1}{2} [S_2(\omega) - S_1(\omega)]$$

where $D$ (the frenesy) is given in (A2) and $S(\omega) = \beta [U_{\lambda}(x, \eta_0) - U_{\lambda}(x, \eta_T) + W(\omega)]$ is the entropy flux over the path $\omega$. Let us apply that now in the
spirit of [10] for the probability to find state $\eta$ at time $t$, by choosing $f(\omega) = \delta(\eta_t - \eta)$,

$$p_2'(\eta) = \langle \delta(\eta_t - \eta) \rangle_2 = \int e^{-A(\omega)} \delta(\eta_t - \eta) \, dP_1(\omega) \quad (B1)$$

and dividing that by $\langle \delta(\eta_t - \eta) \rangle_1$ we get for all times $t$, including those far beyond the relaxation time of the medium, that

$$\frac{p_2'(\eta)}{p_1'(\eta)} = \langle e^{-A(\omega)} | \eta_t = \eta \rangle_1$$

$$= \langle e^{D_1(\omega) - D_2(\omega) + \frac{1}{2}[S_2(\omega) - S_1(\omega)]} | \eta_t = \eta \rangle_1 \quad (B2)$$

For a small change from the first to the second process we obviously need the derivatives of $D$ and $S$ with respect to coupling $\lambda$ and probe position $x$, to write

$$e^{-A(\omega)} = 1 - (\lambda_2 - \lambda_1) \left[ \frac{\partial D}{\partial \lambda} - \frac{1}{2} \frac{\partial S}{\partial \lambda} \right] - (x_2 - x_1) \cdot \nabla_x (D - \frac{S}{2}) + \ldots$$

where the $[\cdot]$ must be evaluated at $\lambda_1, x_1$. That can be plugged into (B2) for obtaining the small changes in the statistics at time $t$. That is what is done under (12) and (24).

At the same time, e.g. from (B1) by summing over $\eta$ we always have the normalization

$$\int e^{-A(\omega)} \, dP_1(\omega) = 1$$

and hence

$$\langle \frac{\partial D}{\partial \lambda} \rangle_1 = \frac{1}{2} \langle \frac{\partial S}{\partial \lambda} \rangle_1, \quad \langle \nabla_x (D - \frac{S}{2}) \rangle_1 = 0 \quad (B3)$$

for no matter what initial condition.
Appendix C: Komatsu-Nakagawa formula

Here we sketch here how the results in [10] that we have used in Section V can be recovered within the framework of the previous Appendix B. The process $P_1$ now refers to equilibrium and the process $P_2$ to the nonequilibrium process. We will however drop the subscripts 1, 2 and e.g. write $P^{eq}$ and $\rho^{eq}$ for the reference equilibrium path-space and stationary distributions. Similarly, the $S_2 - S_1 = S_1 = \beta W$ is the associated entropy flux linear in the driving amplitude $\varepsilon$, and $D_i = D_2 - D_1$. Then, as in [12] or via [14], one finds for $\tau \uparrow \infty$,

$$
\frac{d\rho}{d\rho^{eq}}(\eta) = \left\langle e^{\frac{S_1}{2} - D_i} \left| \eta_\tau = \eta \right. \right \rangle^{eq} \quad (\text{C1})
$$

Time-reversal allowed to change the conditioning in the future to specifying an initial condition. The last line is however formal with entropy flux and excess frenesy over an infinite time-interval. That formal expression can be renormalized by using excess quantities. The excess entropy flux along relaxation to stationarity from an initial $\eta$ equals

$$
\langle S_i \rangle^{(\text{ex})}_{\eta} = \langle S_i \rangle_{\eta} - \langle S_i \rangle
$$

$$
= \left\langle \left(1 - D_i + \frac{S_i}{2}\right) S_i \right \rangle_{\eta}^{eq} - \left\langle \rho^{eq}(\eta_0) \left(1 - D_i + \frac{S_i}{2}\right) S_i \right \rangle_{\eta}^{eq} + O(\varepsilon^3) \quad (\text{C2})
$$

Substituting the first-order approximation (C1) for $\rho$, we get

$$
\langle S_i \rangle^{(\text{ex})}_{\eta} = \langle S_i \rangle_{\eta}^{eq} - \langle D_i S_i \rangle_{\eta}^{eq} + \left\langle \frac{S_i^2}{2} \right \rangle_{\eta}^{eq} - \left\langle \frac{S_i^2}{2} \right \rangle^{eq} + \left\langle \left(\langle S_i \rangle_{\eta}^{eq} \right)^2 \right \rangle^{eq} + O(\varepsilon^3) \quad (\text{C3})
$$
By taking the expectation with respect to $\rho_{eq}(\eta)$ of (C3) we check that the last (constant) term

$$\left\langle \left( \langle S_i \rangle_{eq}^{\eta} \right)^2 \right\rangle_{eq} = \left\langle \langle S_i \rangle^{(ex)}_{\eta} \right\rangle_{eq}$$

coincides with the mean excess entropy flux when started from equilibrium.

Analogously as in (C3) we can calculate the excess entropy flux but now conditioned on ending at $\eta$. A tedious but straightforward calculation gives

$$\langle S_i \rangle^{(ex)}_{\eta} := \langle S_i | \eta_T = \eta \rangle - \langle S_i \rangle = -\langle S_i \rangle_{eq} + \langle D_i S_i \rangle_{eq} + \left\langle \frac{S_i^2}{2} \right\rangle_{eq} - \left\langle \frac{S_i^2}{2} \right\rangle_{eq} - \left\langle \langle S_i \rangle_{eq} \right\rangle^2 + O(\varepsilon^3) \quad (C4)$$

Hence, subtracting (C4) from (C3), we get

$$\langle S_i \rangle_{\eta} - \langle S_i \rangle_{\eta} = 2\langle S_i \rangle_{eq} - 2\langle D_i S_i \rangle_{eq} + \left\langle \langle S_i \rangle_{eq} \right\rangle^2 + \left\langle \langle S_i \rangle^{(ex)}_{\eta} \right\rangle_{eq} + O(\varepsilon^3) \quad (C5)$$

We now compare with (C1) and obtain

$$\frac{d\rho}{d\rho_{eq}}(\eta) = 1 - \frac{1}{2} \left[ \langle S_i \rangle_{\eta} - \langle S_i \rangle_{\eta} \right] + \frac{1}{2} \left\langle \langle S_i \rangle_{eq} \right\rangle^2 + \frac{1}{2} \left\langle \langle S_i \rangle^{(ex)}_{\eta} \right\rangle_{eq} + O(\varepsilon^3) \quad (C6)$$

Finally we take the logarithm of that expression and expand it to second order around equilibrium. Observe that the only linear term in (C6) comes from the first term in the right-hand side of (C5). That delivers immediately the Komatsu-Nakagawa formula (30) of [10], from which we start in Section V.

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