First-principles nonequilibrium deterministic equation of motion of a Brownian particle and microscopic viscous drag

P. D. Gujrati*

Department of Physics, Department of Polymer Science, The University of Akron, Akron, Ohio 44325, USA

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We present a *first-principles thermodynamic approach* to provide an alternative to the Langevin equation by identifying the *deterministic* (no stochastic component) microforce $\mathbf{F}_{k,\mathrm{BP}}$ acting on a nonequilibrium Brownian particle (BP) in its kth microstate $\mathfrak{m}_k$. (The prefix "micro" refers to microstate quantities and carry a suffix k.) The deterministic new equation is easier to solve using basic calculus. Being oblivious to the second law, $\mathbf{F}_{k,\mathrm{BP}}$ does *not* always oppose motion but viscous dissipation emerges upon ensemble averaging. The equipartition theorem is always satisfied. We reproduce well-known results of the BP in equilibrium. We explain how the microforce is obtained directly from the mutual potential energy of interaction beween the BP and the medium after we average it over the medium so we only have to consider the particles in the BP. Our approach goes beyond the phenomenological and equilibrium approach of Langevin and unifies nonequilibrium viscous dissipation from mesoscopic to macroscopic scales and provides new insight into Brownian motion beyond Langevin's and Einstein's formulation.

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I. INTRODUCTION

The aim in this study is to introduce a nonequilibrium (NEQ) thermodynamics based exclusively on microstates, which will be called the μNEQT in short (μ for micro-), and apply it to describe viscous dissipation associated with the dynamics of a Brownian particle (BP) as it undergoes a *macroscopic* relative motion with respect to the rest of the system Σ. The system is in a medium $\widetilde{\Sigma}$; see Fig. 1. Due to the above motion, Σ is not in equilibrium (EQ) [1,2]; however, $\widetilde{\Sigma}$ is always assumed to be in EQ. The μNEQT will be an extension of the traditional macroscopic NEQ thermodynamics (MNEQT, M for macro-) [3–9] to the microstate level.

At the simplest level, BP's diffusion and dynamics in EQ are described using Einstein's and Langevin's approaches, respectively [10–13]. The study is motivated by the fact that the dynamics of a BP has received a resurgence of interest mainly due to the current interest in nonequilibrium (NEQ) processes observed at the microstate scale such as by micron- or smaller-sized *active* BPs often encountered in biological or man-made systems [14–17], and in inhomogeneous systems [18]. These processes are strongly influenced by NEQ fluctuations that may be very different from their equilibrium counterpart.

Spontaneous fluctuations close to EQ are Gaussian [1] as in the two approaches above, but *non-Gaussianity* [19,20] seems to be a signature of NEQ states and abounds in Nature when the system is far from equilibrium. In this case, the above two approaches must fail and we need to develop new approaches to study NEQ viscous drag. Several attempts have been made to obtain generalized Langevin equations for the microstate $\mathfrak{m}_k$; see, for example, Ref. [21]. Despite significant attempts to understand Brownian dynamics in a passive or active medium under external driving [13,14,16,22–25] resulting in NEQ conditions, we still lack its comprehensive thermodynamic understanding, gaining which should then allow us to have a systematic enlargement of the NEQ state space $\mathfrak{S}$ (see below) and expansion to higher order than just two in fluctuations. It was Einstein [10] who had first initiated a successful *thermodynamic* approach for a BP in EQ. This should be contrasted with the mechanical *stochastic* approach of Langevin [11]. We will adopt a *hybrid* approach in this work in which we begin with a NEQ thermodynamic from which we derive a mechanical equation of motion. Being associated with microstates, the μNEQT will allow us to capture the thermodynamics of fluctuations and viscous dissipation experienced by a BP under any condition using the state space $\mathfrak{S}$. Within the framework of this theory, the behavior of the system will dictate whether fluctuations are Gaussian or not or whether viscous drag follows Stokes' law or a more complex behavior. Moreover, while most of us are familiar with classical MNEQT, not many are trained in the technical issues of the Wiener process (such as the Itô and Stratonovich integrals) necessary to follow Langevin's *stochastic* approach. In our approach, we will only be dealing with a *deterministic* equation of motion. This should make our approach quite useful.

Einstein assumed that a BP can be simply described by its stochastic *center of mass* (CM) position $\mathbf{r}_k$ for its specification and by ignoring the center of mass momentum $\mathbf{p}_k$, and the specification of its constituent atoms or molecules that identify the BP as a thermodynamic *object*. The interface between the BP and the system causes osmotic pressure that drives the diffusion of its CM. The EQ diffusion of the BP obeys a diffusion equation, the Fokker–Planck equation describing

*pdg@uakron.edu

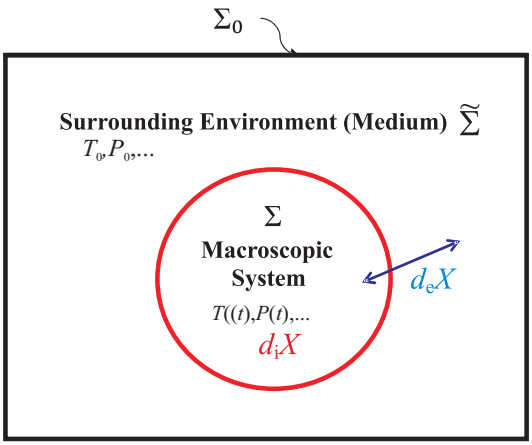

FIG. 1. An isolated system Σ_0 consisting of the system Σ in a surrounding medium $\widetilde{\Sigma}$. The BP, which is not shown here, is embedded within Σ as shown in Fig. 2. The medium and the system are characterized by their fields T_0, P_0, ... and $T(t)$, $P(t)$, ..., respectively, which are different when the two are out of equilibrium. Exchange quantities (d_eX) carry a subscript "e" and irreversibly generated quantities (d_iX) within the system by a subscript "i" by extending the Prigogine notation. Their sum $d_eX + d_iX$ is denoted by dX, which is a system-intrinsic quantity (see text).

stochasticity in terms of conditional probabilities in the ensemble picture [26], which Einstein solved. Langevin [11] later provided a *stochastic* formulation of the same motion by applying Newton's equation

$$M d^2\mathbf{r}_k/dt^2 = \mathbf{F}'_{k,\mathrm{BP}}(t) \tag{1}$$

to the BP of mass M in each *microstate* $\mathfrak{m}_k$ specified by a small cell around $[\mathbf{r}_k(t), \mathbf{v}_k(t)]$, by dividing the stochastic force $\mathbf{F}'_{k,\mathrm{BP}}$ into a *deterministic* (no randomness) force component $\mathbf{F}_{k,\mathrm{f}}(t) \doteq -\gamma \mathbf{v}_k(t) = -\gamma d\mathbf{r}_k(t)/dt$ determined by the microstate k (with $\gamma > 0$), and a *stochastic* Gaussian white force component $\boldsymbol{\xi}(t)$ [27]; see Ref. [12] for an elegant discussion and inherent assumptions. Both γ and the Langevin force $\boldsymbol{\xi}(t)$ are *independent* of the position and velocity of the BP in $\mathfrak{m}_k$ so the two forces are independent despite arising from the interaction of the BP with its surroundings. Chandrasekhar [12] emphasizes $\xi(t)$ as a *characteristic* of a BP, which undergoes *rapid* fluctuations over an interval Δt over which $\mathbf{v}_k(t)$ only undergoes a small variation. Implicit in the above formulation is that (i) $\mathbf{F}_{k,\mathrm{f}}(t)$ opposes motion in *every* $\mathfrak{m}_k(\gamma > 0)$ as if it is a *macroscopic*, i.e., a thermodynamic average force satisfying the second law, (ii) the Langevin force $\boldsymbol{\xi}(t)$ performs no average work, (iii) $\boldsymbol{\xi}(t)$ represents a rapidly fluctuating force (fast-force) and $\mathbf{F}_{k,\mathrm{f}}(t)$ a slowly varying force (slow-force) due to widely separated time scales, and (iv) the separation between the two distinct time scales requires two distinct averages involving a joint probability distribution of initial microstates $[\mathbf{r}_k(0), \mathbf{v}_k(0)]$ and $\boldsymbol{\xi}(t)$; the latter requires its conditional probability distribution corresponding to a Wiener process [26]. The *separation* between $\mathbf{F}_{k,\mathrm{f}}(t)$ and $\boldsymbol{\xi}(t)$ is one of the basic assumptions as discussed by Chandrasekhar [12]; see also Mazur and Bedeaux [27], and Pomeau and Piasecki [28]. The above four assumptions are taken to be valid in any theory of a BP in which a clear separation between fast and slow components of the force are made. For brevity, we will call all of them as following the *Langevin approach*, which also includes the modern theory of stochastic processes [26] and the Mori-Zwanzig approach [29,30].

The distinct approaches by Einstein and Langevin have developed into mathematically distinct but physically equivalent ways to investigate stochastic processes [26]. The approach by Einstein adopts a probabilistic approach to capture thermodynamic stochasticity and results in *ensemble*, i.e., *thermodynamic averages* such as the root-mean-square displacement but dynamics is not a central issue. In contrast, Langevin's approach starts with the dynamical equation in which $\mathbf{F}_{k,\mathrm{f}}(t)$ is related to the instantaneous velocity $\mathbf{v}_k(t)$. The stochasticity due to $\boldsymbol{\xi}(t)$ defines a stationary process because the probability distribution does not change in time [12], a well-known property of white noise so that averaging Eq. (1) over $\boldsymbol{\xi}(t)$ alone results in a deterministic equation.

All quantities associated with $\mathfrak{m}_k$ are called *microquantities* as opposed to their ensemble averages, which we call *macroquantities* or simply quantity in this work. All microquantities will always carry a suffix k [31,32].

The Langevin equation in one dimension is

$$M dv_k(t)/dt = F'_{k,\mathrm{BP}}(t) = -\gamma v_k(t) + \xi(t), \tag{2}$$

with $F_{k,\mathrm{f}}(t) \doteq -\gamma v_k(t)$. The sets $\{v_k(t)\}$ and $\{F'_{k,\mathrm{BP}}(t)\}$ form the set of outcomes of random variables v and F', respectively, over $\{\mathfrak{m}_k\}$.

Stokes' law for a spherical BP of radius a gives $\gamma = 6\pi a\eta > 0$, where η is the viscosity of the surrounding fluid; see Ref. [33] for a microscopic derivation.

It is well known that the Langevin force $\xi(t)$ is central to satisfy the equipartition theorem $\langle v^2(t)\rangle = T_0/M$, where $\langle\bullet\rangle$ refers to the ensemble average over all microstates and T_0 is the temperature of the medium (heat bath) [11]. Therefore, one needs to perform two *distinct* and *independent* averages over initial velocities $\{v_0\}$ and positions $\{x_0\}$, and $\xi(t)$ at each time; see for example Reichl [34] for a clear discussion. However, the equipartition theorem is always fulfilled in the Einstein approach [10] without any ξ. This suggests that our hybrid approach based on a statistical formulation (μNEQT) à la Einstein, from which equations of motion à la Langevin can also be derived, will offer a possible route to study all possible kinds of BPs since it will contain all the information necessary to incorporate the *correct* (Gaussian or non-Gaussian) nature of fluctuations appropriate for the system. No $\xi(t)$ is required. Thus, the μNEQT offers a framework to study all of them within a unified first-principles approach in which only the ensemble average $\langle\bullet\rangle$ is required.

Our approach using the μNEQT is very different from the above two approaches. As various $\mathfrak{m}_k$'s are defined by the Hamiltonian $\mathcal{H}$, we identify the microforce $\mathbf{F}_{k,\mathrm{BP}}(t)$ on $\mathfrak{m}_k$ as the *mechanical* force determined by the microstate energy (microenergy) E_k obtained directly from $\mathcal{H}$. This microforce refers to the system Σ and not to the BP, unless the BP happens to be the system as will be the case in Sec. IV. As $\mathcal{H}$ itself is deterministic, $\mathbf{F}_{k,\mathrm{BP}}(t)$ is *deterministic*, which immediately distinguishes it from the stochastic force $\mathbf{F}'_{k,\mathrm{BP}}(t)$ used by Langevin. In addition, $\mathbf{F}_{k,\mathrm{BP}}(t)$ is not partitioned into *slow* and *fast* components as is required in the Langevin approach. Newton's equation with the deterministic $\mathbf{F}_{k,\mathrm{BP}}(t)$

is different from Eq. (1) and much simpler to solve as we do not need to deal with stochastic integrals [26]. This makes solving the equation of motion straight forward using basic calculus. There is no requirement that $\mathbf{F}_{k,\mathrm{BP}}(t)$ oppose the motion in $\mathfrak{m}_k$ as the second law is applicable to macrostates and not to microstates. Thus, it is distinct from the slow component $\mathbf{F}_{k,\mathrm{f}}(t)$ above. As is normal, $\mathbf{F}_{k,\mathrm{BP}}(t)$ fluctuates over $\{\mathfrak{m}_k\}$. Its ensemble average $\mathbf{F}_{\mathrm{BP}}(t)$ satisfies the second law and opposes the motion, whereas $\mathbf{F}_{k,\mathrm{f}}(t)$ satisfies the law ($\gamma > 0$) for each microstate. We calculate various fluctuations over the statistical ensemble in the μNEQT and reproduce all known results. The probabilities $\{p_k(t)\}$ are determined uniquely in the μNEQT as we will see. We only focus on $\{\mathbf{F}_{k,\mathrm{BP}}(t)\}$ and the consequences here. We describe in detail the computational scheme to show the feasibility and the usefulness of our approach.

The layout of the paper is as follows. We introduce the new thermodynamics in the next section with a focus on the BP problem and give a very general form of viscous dissipation that follows from the second law. In Sec. III, we discuss in depth the microforce that results in the viscous dissipation, the resulting new microstate equation of motion, and calculate various thermodynamic fluctuations. Section IV deals with the feasibility of the new approach for the simple case of a BP in a medium. We consider here the mutual interaction between the BP and the medium and average it over the macrostate of the medium. The resulting potential depends only on the BP-microstate and determines $\mathbf{F}_{k,\mathrm{BP}}(t)$. Thus, we only need to pay attention to the particles in the BP, which simplifies the calculation. The final section deals with discussion and conclusions.

II. A NEW APPROACH USING THE μNEQT

We find it very useful to follow the extension of the Prigogine's notation in this study [35]; see also Fig. 1 caption.

A. The concept of internal equilibrium

The central concept of the NEQT exploited here is that of the *internal equilibrium* (IEQ) according to which the entropy S of a NEQ macrostate is a *state function* of the state variables in the enlarged state space $\mathfrak{S}$ [7–9]; see Sec. II C for details. The enlargement of the space relative to the EQ state space $\mathfrak{S}_0$ is due to independent internal variables [3–8] that are required to describe a NEQ macrostate as we explain below. In EQ, the internal variables are no longer independent of the observables forming the space $\mathfrak{S}_0$. As a consequence, their affinities vanish in EQ. Observables are quantities that can be controlled from the outside but not the internal variables. In general, the temperature T of the system in IEQ is identified in the standard manner by the relation

$$1/T = \partial S/\partial E, \tag{3}$$

using the fact that S is state variable in $\mathfrak{S}$.

An important property of IEQ macrostates is the following that will prove very useful here: It is possible in an IEQ macrostate to have different degrees of freedom or different parts of a system to have different temperatures than T. For example, in a glass, it is well known that the vibrational degrees of freedom have a different temperature than the configurational degrees of freedom [36,37]. In the viscous drag problem, the CM-motion of the BP can be separated out from the motion of its various constituent particles as is well known; see Sec. IV. Then, it is possible for the BP motion to have a different temperature than T introduced above. This observation is easily verified in MNEQT based on the concept of IEQ as done elsewhere [[37], see Sec. 8.1 and Eq. (58)]. The derivation also works when various parts of the system have different temperatures. As this observation will play an important role in this investigation, we rederive it for clarity in a different manner, which supplements the previous demonstration [37] and also shows how an internal variable is required to describe an IEQ macrostate.

1. An example

Consider the case of two identical bodies Σ_1 and Σ_2 in thermal contact at different temperatures $T_1(t)$ and $T_2(t)$ and energies $E_1(t)$ and $E_2(t)$, respectively; we ignore other observables N, V, etc. We assume that each one is in an EQ state of its own at each instant. Together, they form an isolated system Σ, whose entropy $S(E_1, E_2) = S_1(E_1) + S_2(E_2)$ is a function of two variables at each instant t, and can be written as a state function in the enlarged state space formed by $E = E_1 + E_2 = \mathrm{const}$ (the observable) and $\xi(t) = E_1 - E_2$ (the internal variable). (We have neglected the interaction energy E_{12} between Σ_1 and Σ_2 here.) For this IEQ state, it is trivial to show that the temperature is $T(t) = 2T_1T_2/(T_1 + T_2)$ and the affinity $T\partial S/\partial\xi$ is $A(t) = (T_1 - T_2)/(T_1 + T_2)$. At equilibrium, $T_1 = T_2 = T_{\mathrm{eq}}$ and $\xi = 0, A = 0$. Thus, T_1 and T_2 may be very different, yet the system can be treated in IEQ, any temperature difference between its parts not withstanding. The discussion can be extended easily to the case the two bodies are in IEQs and also when they are of different sizes.

2. Microstates

We consider the phase space Γ associated with Σ and partition it completely into countable nonoverlapping cells $\{\delta\mathbf{z}_k\}, k = 1, 2, \ldots$, each of size h^{3N}, around the phase point $\mathbf{z} \in \mathbf{\Gamma}$; here N is the number of particles in Σ and we assume that the volume $|\Gamma|$ of Γ has been divided by $N!$ to account for the permutation symmetry of the N particles. We use the cells to identify the set of microstate $\{m_k\}$ of Σ. Consider Σ to be composed of two distinct bodies Σ_1 and Σ_2, as above in the example. As each cell $\delta\mathbf{z}_k$ is a union of cells $\delta\mathbf{z}_{k_1}^{(1)}$ and $\delta\mathbf{z}_{k_2}^{(2)}$ corresponding to Σ_1 and Σ_2, we can relate the microstate energies as follows:

$$E_k = E_{k_1} + E_{k_2} + E_{k,12}, \tag{4a}$$

where we have also included the interaction energy $E_{k,12}$, which is usually neglected as we did above. These energies are independent of the macrostates and, therefore, independent of quantities such as the temperatures that specify macrostates of various bodies forming the system. The energies corresponding to their macrostates are related by

$$E = E_1 + E_2 + E_{12}. \tag{4b}$$

The interaction energy $E_{k,12}$ and its macroaverage E_{12}, however, will play an important role later in Sec. IV, where

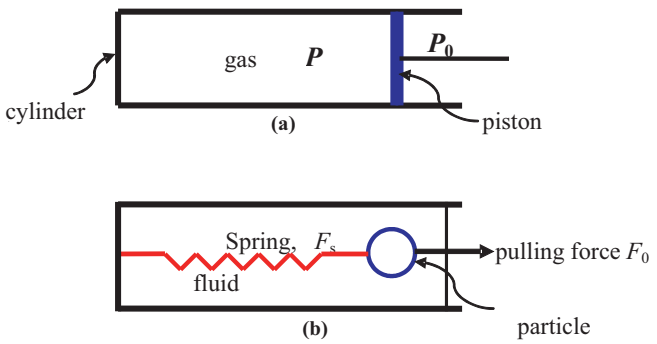

FIG. 2. We schematically show a system of (a) gas in a cylinder with a movable piston (at a distance l from the left wall) under an external pressure P_0 controlling the volume V of the gas and the piston, and (b) a particle attached to an end of a spring in a fluid and being pulled by an external force F_0, which causes the spring to stretch or compress depending on its direction. The other end of the spring is fixed to the left wall and l denotes the spring length. The volume of Σ in (b) is kept fixed. In an irreversible process, the internal pressure P or the spring force F_s is different in magnitude from the external pressure P_0 or the external force F_0, respectively. Their difference is the force imbalance that causes the irreversible macrowork. The temperature of the system is T; T_0, P_0 or F_0 are the macrofields of the medium $\widetilde{\Sigma}$.

we deal with relative motion between Σ (the BP) and $\widetilde{\Sigma}$; the existence of this motion is central for viscous dissipation as we will see in Sec. II C.

B. Ensemble stochasticity and the second law

We consider a system Σ, see Fig. 1, that contains a single BP that is shown explicitly in Fig. 2 as part of Σ. The single BP is our focus in this work. We follow the standard formulation for a statistical system Σ [1], which interacts weakly with a much larger medium $\widetilde{\Sigma}$ so this interaction $U_{\rm int}$ is normally ignored. This is possible as we do not allow any relative motion between Σ and $\widetilde{\Sigma}$ as noted above; see also Sec. II C. However, $U_{\rm int}$ must not be zero identically otherwise there cannot be any energy (heat and work) exchange between Σ and $\widetilde{\Sigma}$. Together, they form an isolated system $\Sigma_0 \doteq \Sigma \cup \widetilde{\Sigma}$. The system may be far away from equilibrium so the new theory is more general than the EQ treatments by Einstein and Langevin.

As said above, treating NEQ states normally requires some (extensive) internal variables that are generated due to *internal processes* [3–8]. Their conjugate fields, called *affinity*, vanish only in equilibrium. The system is specified by a Hamiltonian $\mathcal{H}(\mathbf{z}|\mathbf{Z})$ in which $\mathbf{z}$ denotes a phase point in its phase space and $\mathbf{Z} \doteq \{Z\}$ denotes the set of parameters such as the volume V, the number of particles N which we do not show, etc. and internal variables.

The time dependence in some or all components in $\mathbf{Z}$ gives rise to time dependence in the Hamiltonian $\mathcal{H}(\mathbf{z}|\mathbf{Z})$; the dynamical variable $\mathbf{z}$ plays no role as we show in Eqs. (6a) and (6b). From $\mathcal{H}(\mathbf{z}|\mathbf{Z})$, we identify microstates $\mathfrak{m}_k(\mathbf{Z})$ and their microenergies $E_k(\mathbf{Z})$; we will usually suppress the $\mathbf{Z}$-dependence unless necessary for clarity. The microstate $\mathfrak{m}_k$ appears with probability p_k in the statistical ensemble. The set $\{p_k\}$ determines the stochasticity in the ensemble. Accordingly, it determines the nature of the macrostate (EQ vs NEQ) but the sets $\{E_k\}$ and $\{\mathfrak{m}_k\}$ are independent of $\{p_k\}$ so they are deterministic.

In the μNEQT, the two aspects can be separated out in an unambiguous fashion so we can uniquely determine the deterministic quantities such as $\{F_{k,\rm BP}\}$. Accordingly, we do not need to partition microforces into "slow" and "fast" components. There is no random force in our approach so we avoid the complications of the conventional Wiener process in the Langevin approach. Clearly, the deterministic microforces are oblivious to the stochastic nature of the thermodynamic system. The second law emerges automatically after averaging, but not without it. Thus, the μNEQT as an extension of the MNEQT will be based solely on the sets $\{E_k\}$ and $\{p_k\}$ so it provides a *first-principles* deterministic theory from which the MNEQT is trivially reconstructed.

To investigate the ensemble, it is useful to treat a microquantity that takes values $\{q_k\}$ over $\{\mathfrak{m}_k\}$ at each instant as a *random variable* q defined over $\{\mathfrak{m}_k\}$. Thus, $\{E_k\}$ and $\{F_{k,\rm BP}\}$ refer to the outcomes of the random variables E and $\mathsf{F}_{\rm BP}$, respectively. In this study, we use sans serif typeface to denote random variables to distinguish them from their outcomes. For a given $\{p_k\}$, q is characterized by its ensemble average $\langle\mathsf{q}\rangle$ and various moments such as the variance $\langle(\Delta\mathsf{q})^2\rangle$ in terms of the fluctuation $\Delta\mathsf{q} \doteq \mathsf{q} - \langle\mathsf{q}\rangle$. As p_k's continue to change in a NEQ state, $\langle\mathsf{q}\rangle$ and $\langle(\Delta\mathsf{q})^2\rangle$ also change. In the μNEQT, the macroforce $\mathbf{F}_{\rm BP} \doteq \langle\mathsf{F}_{\rm BP}\rangle$ corresponding to $\{\mathbf{F}_{k,\rm BP}\}$ must oppose the motion in accordance with the second law as does $\mathbf{F}_{k,\rm f}(t)$ but not individual $\mathbf{F}_{k,\rm BP}$'s. The nonvanishing fluctuations, see Eqs. (34) and (35), in $\mathbf{F}_{k,\rm BP}$ even in equilibrium (where $\mathbf{F}_{\rm BP} = 0$) demonstrates that $\mathbf{F}_{k,\rm BP}$'s do not always oppose the motion of $\mathfrak{m}_k$ in the μNEQT. This effectively means that if we consider $\mathsf{F}_{\rm BP}$ to be of the form $(-\gamma\mathsf{v})$, v, γ having the outcomes $\{v_k\}$, $\{\gamma_k\}$, respectively, then γ_k is of either sign.

For thermodynamic considerations, instead of considering $\mathsf{F}_{\rm BP}$, we will find it convenient to consider the *internal microwork* $d_i\mathsf{W}_{\rm BP}$ done by it with outcomes $\{d_iW_{k,\rm BP}\}$, see Eq. (30). Being specific to $\mathfrak{m}_k$, the internal microwork $d_iW_{k,\rm BP}$ also has a unique value but no specific sign; only the ensemble average $d_iW_{\rm BP} \doteq \langle d_i\mathsf{W}_{\rm BP}\rangle \geqslant 0$ in accordance with the second law as we will see. That $d_iW_{k,\rm BP}$ and γ_k have no sign restriction and $\mathbf{F}_{k,\rm BP}$ does not always oppose motion is the *unique* feature of our approach.

We consider the two systems (a) and (b) shown in Fig. 2 as our system Σ. In Fig. 2(a), P, V represent some generic work field and variable, which we label pressure and volume for convenience. We treat the piston or the particle as a BP. As the BP forms a subsystem, we denote it by $\Sigma_{\rm BP}$ and the remainder of Σ by $\Sigma_{\rm R}$. We assume that the piston in Fig. 2(a) may be either mesoscopic or macroscopic, while the particle in Fig. 2(b) will be assumed to denote a mesoscopic particle. Thus, our approach will unify the two different scales. We will establish that both experience fluctuating Brownian motion v over $\{\mathfrak{m}_k\}$, except that for the macroscopic size piston, it is not noticeable because of its macroscopic mass.

We follow Einstein and focus on the BP's center-of-mass. Let V denote the volume of Σ and $\mathbf{P}_{\rm BP}$ and $\mathbf{P}_{\rm R}$ the linear

momenta of $\Sigma_{\rm BP}$ and $\Sigma_{\rm R}$, respectively. Let $\mathbf{R}_{\rm BP}$ and $\mathbf{R}_{\rm R}$ denote the displacement of the CM of $\Sigma_{\rm BP}$ and $\Sigma_{\rm R}$, respectively. This makes Σ nonuniform and out of EQ [2]. We assume Σ stationary in the laboratory-frame (compare with Ref. [8]), so that

$$\mathbf{P}_{\rm BP} + \mathbf{P}_{\rm R} = 0; \tag{5}$$

we also take $\widetilde{\Sigma}$ and, hence, Σ_0 to be stationary so that Σ has no relative motion with respect to $\widetilde{\Sigma}$ and Σ_0 as noted above.

We will establish here that $\mathbf{P}_{\rm BP}$ and $\mathbf{P}_{\rm R}$ must be treated as parameters, which is in the spirit of the original assumption of Einstein about the CM-motion. As $\mathbf{P}_{\rm BP}$ and $\mathbf{P}_{\rm R}$ denote the total momenta that we will associate with respective CMs of $\Sigma_{\rm BP}$ and $\Sigma_{\rm R}$, they can only be changed by "external" forces to the two bodies, *i.e.*, only the force exerted by $\Sigma_{\rm R}$ on $\Sigma_{\rm BP}$ can change $\mathbf{P}_{\rm BP}$, and the force exerted by $\Sigma_{\rm BP}$ on $\Sigma_{\rm R}$ can change $\mathbf{P}_{\rm R}$. These forces are equal and opposite as they are internal forces for Σ, and cancel out in Σ; recall that it is stationary. Thus, we need to determine one of these forces in the following. This cancellation also applies to each microstate of Σ. However, these "external" forces are due to some mutual interactions between the two bodies as we discuss at length in Sec. IV. In the absence of this interaction, $\mathbf{P}_{\rm BP}$ and $\mathbf{P}_{\rm R}$ cannot change so it is required for the viscous drag and it cannot be neglected as we have observed above.

We can treat $\Sigma_{\rm R}$ as our medium $\widetilde{\Sigma}$ and treat $\Sigma_{\rm BP}$ as our system Σ with $\mathbf{P}_{\rm R}$ replaced by the linear momentum $\widetilde{\mathbf{P}}$ of $\widetilde{\Sigma}$ if we want the BP to interact directly with $\widetilde{\Sigma}$, a case that is a trivial modification but which is usually studied [[33], for example]. We will discuss this situation in Sec. IV.

C. Deriving microstate thermodynamics

1. Thermodynamic parameters

This section is important to demonstrate the importance of relative internal motion between two parts of a system for viscous dissipation. We will first treat the piston problem as it is commonly discussed in introductory physics. The Hamiltonian of the system is written as $\mathcal{H}(\mathbf{z}|V, \mathbf{P}_{\rm BP}, \mathbf{P}_{\rm R})$ in which V, $\mathbf{P}_{\rm BP}$ and $\mathbf{P}_{\rm R}$ form $\mathbf{Z}$; here $\mathbf{P}_{\rm BP}$ and $\mathbf{P}_{\rm R}$ are two internal variables. In the following, we treat $\mathbf{z}$ as discrete and use k as a label. Let us consider the change

$$d\mathcal{H} = \frac{\partial \mathcal{H}}{\partial \mathbf{z}} \cdot d\mathbf{z} + \frac{\partial E_k}{\partial V} dV + \frac{\partial \mathcal{H}}{\partial \mathbf{P}_{\rm BP}} \cdot d\mathbf{P}_{\rm BP} + \frac{\partial \mathcal{H}}{\partial \mathbf{P}_{\rm R}} \cdot d\mathbf{P}_{\rm R}. \tag{6a}$$

The first term on the right vanishes identically due to Hamilton's equations of motion, so it is the variations due to $d\mathbf{Z}$ (dV, $d\mathbf{P}_{\rm BP}$ and $d\mathbf{P}_{\rm R}$) that generate any change in $\mathcal{H}$:

$$d\mathcal{H} = \frac{\partial E_k}{\partial V} dV + \frac{\partial \mathcal{H}}{\partial \mathbf{P}_{\rm BP}} \cdot d\mathbf{P}_{\rm BP} + \frac{\partial \mathcal{H}}{\partial \mathbf{P}_{\rm R}} \cdot d\mathbf{P}_{\rm R}. \tag{6b}$$

We identify this as the *generalized* work dW_k done by the system [31,32,38,39]. We introduce "generalized mechanical forces" in terms of E_k (we suppress $\mathbf{Z}$ and use E_k for $\mathcal{H}(\mathbf{z}|\mathbf{Z})$ unless clarity is needed) using the standard definition

$$P_k \doteq -\frac{\partial E_k}{\partial V}, \quad -\mathbf{V}_{k,\rm BP} \doteq -\frac{\partial E_k}{\partial \mathbf{P}_{\rm BP}}, \quad -\mathbf{V}_{k,\rm R} \doteq -\frac{\partial E_k}{\partial \mathbf{P}_{\rm R}}; \tag{7}$$

these are the conjugate microfields of V, $\mathbf{P}_{\rm BP}$ and $\mathbf{P}_{\rm R}$, respectively. As E_k is uniquely determined by its arguments, these microforces are *deterministic* functions of V, $\mathbf{P}_{\rm BP}$, and $\mathbf{P}_{\rm R}$ and are continuous in a proper thermodynamic theory; see below. The corresponding generalized microworks are $P_k dV$, etc., so the net microwork done by Σ is

$$dW_k = P_k dV - \mathbf{V}_{k,\rm BP} \cdot d\mathbf{P}_{\rm BP} - \mathbf{V}_{k,\rm R} \cdot d\mathbf{P}_{\rm R} = -dE_k. \tag{8}$$

The ensemble averages of the various microworks are given by PdV, etc., see Landau and Lifshitz [1,40] and elsewhere [8], where

$$P \doteq -\partial E/\partial V, \quad \mathbf{V}_{\rm BP} \doteq \partial E/\partial \mathbf{P}_{\rm BP}, \quad \mathbf{V}_{\rm R} \doteq \partial E/\partial \mathbf{P}_{\rm R} \tag{9}$$

denote macroforces in the MNEQT; here E is the macroenergy $E = \langle \mathcal{H}(\mathbf{z}|V, \mathbf{P}_{\rm BP}, \mathbf{P}_{\rm R}) \rangle$ in the laboratory frame; the conjugate macrofields are the average pressure P and the average velocities (or affinities) $\mathbf{V}_{\rm BP}, \mathbf{V}_{\rm R}$ of the BP and $\Sigma_{\rm R}$, respectively, with $E, V, \mathbf{P}_{\rm BP}, \mathbf{P}_{\rm R}$ forming $\mathfrak{S}$, where the entropy S is defined as a state function.

We assume that Σ is in IEQ [7,8]. Thus, S is a state function $S(E, V, \mathbf{P}_{\rm BP}, \mathbf{P}_{\rm R})$ defined in $\mathfrak{S}$ because of which IEQ macrostates have close similarities with EQ macrostates so that the temperature T of the system is given by Eq. (3) and the generalized macroheat by $dQ = TdS$; see below. In addition, IEQ states have no memory of where they come from. Despite this, IEQ states have irreversible entropy generation. In EQ, $T = T_0$, $P = P_0$; see Fig. 1. In addition, $\mathbf{V}_{\rm BP}$ and $\mathbf{V}_{\rm R}$ *vanish* in EQ so they also represent the vanishing affinities of the medium. As they vanish, they contribute nothing to the *exchange* microwork $d_e W_k$ [3,4], which then becomes $d_e W_k = P_0 dV$.

From $E(S, V, \mathbf{P}_{\rm BP}, \mathbf{P}_{\rm R})$ we have $dE = TdS - PdV + \mathbf{V}_{\rm BP} \cdot d\mathbf{P}_{\rm BP} + \mathbf{V}_{\rm R} \cdot d\mathbf{P}_{\rm R}$, which we rewrite using Eq. (5) as

$$dE = TdS - PdV + \mathbf{V} \cdot d\mathbf{P}_{\rm BP}, \tag{10}$$

in terms of the *relative velocity* or the *drift velocity*,

$$\mathbf{V} \doteq \mathbf{V}_{\rm BP} - \mathbf{V}_{\rm R} = \mathbf{P}_{\rm BP}/m, \tag{11}$$

of the BP with respect to $\Sigma_{\rm R}$ in the MNEQT; here m is the reduced mass of $\Sigma_{\rm BP}$ and $\Sigma_{\rm R}$.

We remark that even though $\mathbf{P}_{\rm BP}$ as the total momentum of the BP is its intrinsic property, it is coupled to $\Sigma_{\rm R}$ in accordance with Eq. (5). Consequently,

$$E_{\rm CM} = \mathbf{P}_{\rm BP}^2/2m \tag{12}$$

is the sum of the kinetic energies of the CM's of $\Sigma_{\rm BP}$ and $\Sigma_{\rm R}$. This is not surprising as the CM-kinetic energies can be always separated out from the motion of the particles in Σ. As discussed in Sec. II A, it is possible to have a different temperature $T_{\rm CM}$ associated with the CM-motion, which can be very different from T. As this motion slows down, $T_{\rm CM}$ will continue to decrease; cf. Eq. (37c).

2. Einstein-Langevin duality of the relative motion

We can also rewrite the drift velocity term using the identity

$$\mathbf{V}\cdot d\mathbf{P}_{\rm BP}\equiv \mathbf{F}_{\rm BP}\cdot d\mathbf{R}=d\big(\mathbf{P}_{\rm BP}^2/2m\big), \tag{13}$$

where $\mathbf{F}_{\rm BP}\doteq d\mathbf{P}_{\rm BP}/dt$ is the "external" *macroforce* as discussed above, and $d\mathbf{R}=\mathbf{V}dt$ is the *relative displacement* of the BP in the MNEQT. Because of this identity, we can either use $\mathbf{P}_{\rm BP}$ or $\mathbf{R}$ as a parameter in $\mathbf{Z}$ so the macroenergy E can be expressed either as $E_{\mathbf{P}}\doteq E(S,V,\mathbf{P}_{\rm BP})$ or $E_{\mathbf{R}}\doteq E(S,V,\mathbf{R})$, a simplification due to the thermodynamic treatment, with

$$\mathbf{V}=\partial E(S,V,\mathbf{P}_{\rm BP})/\partial\mathbf{P}_{\rm BP},\quad \mathbf{F}_{\rm BP}=\partial E(S,V,\mathbf{R})/\partial\mathbf{R}. \tag{14}$$

We now deal with a reduced state space $\mathcal{S}'$ formed by $E,V,\mathbf{P}_{\rm BP}$ or $E,V,\mathbf{V}$. In a proper thermodynamic theory, E is at least twice differentiable (we do not consider any phase transition in this work) so the above derivatives exist and are continuous.

There is very interesting duality hidden in Eq. (13). The choice of using $\mathbf{R}$ as a parameter provides a justification for Einstein's approach involving the CM location of the BP and considering the "osmotic" force $\mathbf{F}_{\rm BP}$ acting on it; there was no need to consider its momentum at all. Thus, his choice in our approach corresponds to using E as $E(S,V,\mathbf{R})$. However, Langevin's interest was not in using $\mathbf{R}$ but its momentum $\mathbf{P}_{\rm BP}$ to write down the equation of motion; cf. Eq. (2). While he was not interested in thermodynamics, his choice in our approach will correspond to using E as $E(S,V,\mathbf{P}_{\rm BP})$. As a consequence, our thermodynamic approach is a hybrid approach capable of allowing both approaches in a unifying way. However, as the first equation in Eq. (14) merely gives back $\mathbf{P}_{\rm BP}=m\mathbf{V}$, it is not much of a use. Therefore, we will normally use $E(S,V,\mathbf{R})$ with $\mathbf{R}$ as a parameter, which will be extremely useful in our thermodynamic investigation.

3. Microwork and microheat

Using the generalized macrowork $dW=PdV-\mathbf{F}_{\rm BP}\cdot d\mathbf{R}$ and macroheat $dQ=TdS$, we have $dE=dQ-dW$, which expresses the first law in terms of the generalized quantities. This expresses an important fact: the two terms in it denote *independent* variations of the energy E: dQ denotes the change due to entropy variation and dW isentropic variation. This allows us to deal with dW as a purely mechanical ($dS=0$) quantity resulting in microstate energy changes. This is easily seen from the following argument. From $E\equiv\langle\mathsf{E}\rangle\doteq\sum_k E_k p_k$ in terms of $E_k=E_k(V,\mathbf{P}_{\rm BP})$ [or equivalently $E_k=E_k(V,\mathbf{R})$] and p_k, we have

$$dE=\sum_k E_k dp_k+\sum_k p_k dE_k,$$

where

$$dE_k=(\partial E_k/\partial V)dV+(\partial E_k/\partial\mathbf{P}_{\rm BP})\cdot d\mathbf{P}_{\rm BP}.$$

The first sum in dE involves dp_k at fixed E_k, and evidently corresponds to the entropy change dS. It denotes the generalized heat,

$$dQ=\langle d\mathsf{Q}\rangle=\sum_k p_k dQ_k\doteq\sum_k E_k dp_k.$$

Here, we have used $d\mathsf{Q}$ to denote a random variable with outcomes $\{dQ_k\}$. The second sum in dE involves dE_k at fixed p_k and evidently corresponds to $dS=0$. Its negative is the generalized work (we use $d\mathsf{W}$ to denote a random variable with outcomes $\{dW_k\}$),

$$dW=\langle d\mathsf{W}\rangle\doteq-\sum_k p_k dE_k,$$

and *uniquely* identifies microwork $dW_k=-dE_k$ from which we can uniquely identify mechanical microforces $P_k=-(\partial E_k/\partial V)$ and $(-\mathbf{V}_k)=-\partial E_k/\partial\mathbf{P}_{\rm BP}$ that appear in the μNEQT; these quantities refer to the system alone. This can be done because dW_k is a mechanical quantity and is oblivious to p_k.

We use this uniqueness of identifying system-specific microforces to construct the μNEQT in $\mathcal{S}'$. We have

$$dW_k=P_k dV-\mathbf{V}_k\cdot d\mathbf{P}_{\rm BP}\equiv P_k dV-\mathbf{F}_{k,\rm BP}\cdot d\mathbf{R}, \tag{15a}$$

where

$$\mathbf{V}_k\doteq\partial E_k/\partial\mathbf{P}_{\rm BP},\mathbf{F}_{k,\rm BP}\doteq\partial E_k/\partial\mathbf{R}. \tag{15b}$$

Using $d_eW=P_0dV$, we identify the *irreversible* macrowork $d_iW\doteq dW-d_eW$,

$$d_iW=(P-P_0)dV-\mathbf{F}_{\rm BP}\cdot d\mathbf{R}\geqslant 0, \tag{16}$$

from the second law so that we must have

$$(P-P_0)dV\geqslant 0,\quad \mathbf{F}_{\rm BP}\cdot d\mathbf{R}\leqslant 0 \tag{17}$$

separately as each term refers to an *independent* internal process. For the example in Fig. 2(b), we must replace $(P-P_0)dV$ by $(F_{\rm s}-F_0)dl$, where dl is the spring compression. Similarly, the exchange heat with $\widetilde{\Sigma}$ is $d_eQ=T_0d_eS$ and the irreversible heat is

$$d_iQ=TdS-T_0d_eS=(T-T_0)d_eS+Td_iS\geqslant 0. \tag{18}$$

As $dE=d_eQ-d_eW$ also expresses the first law, we must have

$$d_iQ=d_iW\geqslant 0 \tag{19}$$

in the MNEQT. Therefore, determining d_iW allows us to indirectly determine d_iQ. In this study, we will not be directly studying generalized heat, which we will consider in a future publication.

We thus see that the μNEQT is obtained directly and uniquely from the MNEQT. However, the most important and distinguishing feature of our approach as noted above is that the microwork dW_k is deterministic (independent of the probability p_k) so it represents a truly microscopic mechanical work from which we can directly identify various microscopic forces. Thus, even though we have started with the MNEQT, the microscopic work dW_k in Eq. (15a) directly and uniquely identifies microscopic forces P_k and $\mathbf{V}_k$ in terms of purely mechanical quantities of the system alone. As we will see, the μNEQT provides additional details than are not available from using the MNEQT alone.

4. IEQ microstate probabilities

In an IEQ state [41], we have two possible forms of p_k based on the choice of the parameters $\mathbf{R}$ or $\mathbf{F}_{\rm BP}$:

$$p_k = \exp[\Phi - (E_k + P_k V - \mathbf{F}_{k,\rm BP}\cdot\mathbf{R})]/T], \tag{20}$$

$$p_k = \exp[\Phi - (E_k + P_k V - \mathbf{F}_{\rm BP}\cdot\mathbf{R}_k)]/T], \tag{21}$$

with $\langle 1\rangle$, $\langle \mathsf{E}\rangle$, $\langle \mathsf{P}\rangle$, and $\langle \mathsf{F}_{\rm BP}\rangle$ in Eq. (20) or $\langle \mathsf{R}\rangle$ in Eq. (21), fixed so that $\beta = 1/T$, βV and $(-\beta\mathbf{R})$ or $(-\beta\mathbf{F}_{\rm BP})$ are Lagrange multipliers to maximize the entropy [39]. Here, the normalization function Φ ensures that p_k's add to unity. The form is what is expected in EQ except for the presence of the internal variable term and of the fields T and P of the IEQ state. Thus, most of the EQ results can be easily extended to an IEQ state.

We now prove a very useful and general theorem for systems in IEQ that allows us to identify the change in the IEQ temperature as its parameters change.

Theorem 1. As the parameters in $\mathbf{Z}$ change and change the microstate probabilities, the change in the temperature is given by

$$dT = T\frac{\langle d\Psi\rangle}{\langle\Psi\rangle}, \tag{22}$$

where we have introduced

$$\Psi_k = \Phi - (E_k + P_k V - \mathbf{F}_{k,\rm BP}\cdot\mathbf{R}). \tag{23a}$$

proof. Using

$$p_k = \exp(\Psi_k/T), \tag{24a}$$

we find that

$$dp_k = p_k\left[\frac{d\Psi_k}{T} - \frac{\Psi_k dT}{T^2}\right]. \tag{24b}$$

The average $\langle\Psi\rangle$ is given by

$$\langle\Psi\rangle = \Phi - E - PV + \mathbf{F}_{\rm BP}\cdot\mathbf{R}, \tag{25a}$$

and $\langle d\Psi\rangle$ is given by

$$\langle d\Psi\rangle = d\Phi + dW - d(PV) + d(\mathbf{F}_{\rm BP}\cdot\mathbf{R}). \tag{25b}$$

Eq. (22) now follows from $\sum_k dp_k = 0$ as an identity for any IEQ macrostate. ■

To use Eq. (22), we must explicitly evaluate $\langle\Psi\rangle$ and $\langle d\Psi\rangle$ using Eqs. (25a) and (25b), respectively, in terms of quantities appearing on their right sides.

D. Viscous drag and the Langevin limit

We use the notation

$$d_i W_{\rm BP} \doteq -\mathbf{F}_{\rm BP}\cdot d\mathbf{R} \equiv -\mathbf{V}\cdot d\mathbf{P}_{\rm BP} \geqslant 0, \tag{26}$$

related to the second irreversible contribution in Eq. (17). It follows that for the inequality to be valid, we must have the following form for NEQ $\mathbf{F}_{\rm BP}$ in the MNEQT:

$$\mathbf{F}_{\rm BP} = -\mathbf{V} f(T,\mathbf{V},t),\ f(T,\mathbf{V},t) > 0, \tag{27}$$

in which $f(T,\mathbf{V},t)$ must be an even scalar function of $\mathbf{V} = \mathbf{P}_{\rm BP}/m$ at each instant so that $d_i W_{\rm BP} = f(T,\mathbf{V},t)\mathbf{V}^2 dt \geqslant 0$. As $\mathbf{F}_{\rm BP}$ opposes motion, it represents the viscous force we are interested in. Let us compare $\mathbf{F}_{\rm BP}$ above with its definition in Eq. (14), according to which it is a derivative of E with respect to $\mathbf{R}$. The only way this derivative can give a result along the direction of $\mathbf{V}$ is for the scalar function E to be a function of the combination

$$u \doteq \mathbf{V}\cdot\mathbf{R} \tag{28}$$

as a scalar. We thus conclude that

$$f(T,\mathbf{V},t) = -\partial E(S,V,u)/\partial u, \tag{29}$$

so $f(T,\mathbf{V},t)$ will also include a dependence on $\mathbf{R}$ in f through u so we must write it as $f(T,V,u)$. Hopefully, this will make Eq. (27) suitable for some active BPs [14–17]. In general, the dependence on $\mathbf{V}$ through u may be very complex as will become clear in Sec. IV.

As $\mathbf{F}_{\rm BP}$ is the macroforce corresponding to the viscous drag, the above discussion provides a *thermodynamic justification* of the viscous drag. To make connection with the Langevin equation, we will assume $f(u,t)$ to be a power series in u^2 with $f(0,t) = \gamma(t) \geqslant 0$ so that $d_i W_{\rm BP} \simeq \gamma(t)\mathbf{V}\cdot d\mathbf{R}$ is the *frictional work* in the small-speed approximation, which will be called the *Langevin limit* from now on. In this limit, $d_i W_{\rm BP} \simeq \gamma(t)\mathbf{V}^2(t)dt \geqslant 0$ at any instant t. Langevin takes $\gamma(t)$ to be a constant γ.

The above discussion also provides a thermodynamic justification of the viscous drag in the Langevin equation in the small-speed approximation. For arbitrary speeds, we can treat $f(T,u,t)$ as the analog of an *effective* $\gamma_{\rm eff}$ in Eq. (2), which is a complicated function of T, $\mathbf{V}$ and t, a situation commonly encountered in active BPs [14–17]. We will not pursue active BPs in this work except tangentially; they will be treated later.

As we will see below, we get more insight into the viscous force $\mathbf{F}_{\rm BP}(t)$ when we consider its microanalogs $\mathbf{F}_{k,\rm BP}(\mathbf{V},t)$ in the μNEQT.

III. FLUCTUATIONS AND A NEW EQUATION OF MOTION

The fluctuations in random variables are the hallmark of a statistical system and are always present whether we consider a reversible or an irreversible process. Let us consider the random variable P with outcomes $\{P_k\}$. The fluctuation $\Delta\mathsf{P}$ has outcomes $\{P_k - P\}$ with $P = \langle\mathsf{P}\rangle$, which determine the mean square fluctuation $\langle(\Delta\mathsf{P})^2\rangle \geqslant 0$. We know from EQ statistical mechanics ($P = P_0$, $T = T_0$) [1] that

$$\langle(\Delta\mathsf{P})^2\rangle_{\rm eq} = -T_0(\partial P/\partial V)_S$$

is not identically zero so P_k fluctuates over $\mathfrak{m}_k$ and takes values on both sides of P_0. Since P is not determined by any macrostate, $\{P_k\}$ remain the same whether we are dealing with an EQ or a NEQ macrostate. Moreover, $d_i W_{k,V} \doteq (P_k - P_0)dV$ does not have a particular sign in general, even though the macrowork $d_i W_V \doteq (P - P_0)dV \geqslant 0$ is never negative; see Eq. (17). Because of this conformity, it is customary to call the macrowork $d_i W_V$ the *irreversible* work. As the microwork $d_i W_{k,V}$ does not follow the sign requirement, it is better to call it internal microwork as noted above.

Similarly, there are fluctuations in the *random variables* $\mathsf{F}_{\rm BP}$ and V (with outcomes $\{\mathbf{F}_{k,\rm BP}\}$ and $\{\mathbf{V}_k\}$, respectively) around the average $\mathbf{F}_{\rm BP} \equiv \langle\mathsf{F}_{\rm BP}\rangle$ and $\mathbf{V} \equiv \langle\mathsf{V}\rangle$, respectively, which are always present. This will be explicitly demonstrated

later; see Eqs. (34) and (35). As the EQ affinity $\mathbf{F}_{0\mathrm{BP}} = 0$ or $\mathbf{V}_0 = 0$ so that $d_eW_{k,\mathrm{BP}} \equiv 0$ [3–5], we conclude that $d_iW_{k,\mathrm{BP}} \equiv dW_{k,\mathrm{BP}}$ fluctuates over $\{\mathfrak{m}_k\}$ around the macroaverage $dW_{\mathrm{BP}} \equiv d_iW_{\mathrm{BP}}$. Thus, the internal microwork $d_iW_{k,\mathrm{BP}}$ does not have a particular sign, while d_iW_{BP} does as seen in Eq. (26).

It is important to make the following three remarks concerning $\mathbf{F}_{k,\mathrm{BP}}(t)$:

(a) It is not broken into a fast- and a slow-component for each k as is common in the Langevin approach.

(b) It represents the outcome of a random variable F_{BP} over the microstates.

(c) For a given k, F_{BP} possesses no randomness so $\mathbf{F}_{k,\mathrm{BP}}(t)$ has a unique value.

A. A new equation of motion

That the internal microwork $d_iW_{k,\mathrm{BP}}$ has no sign restriction is another point of departure from Langevin's approach and is discussed next. We focus on the form

$$d_iW_{k,\mathrm{BP}} \doteq -\mathbf{F}_{k,\mathrm{BP}} \cdot d\mathbf{R}_k \tag{30}$$

for $\mathfrak{m}_k$ and determine Newton's equation for the BP at a relative location $\mathbf{R}_k(t)$; k on $\mathbf{R}_k(t)$ is added for clarity. The *deterministic* equation

$$md^2\mathbf{R}_k(t)/dt^2 = md\mathbf{V}_k(t)/dt = \mathbf{F}_{k,\mathrm{BP}}(t) \tag{31}$$

describes the trajectory of the BP in the μNEQT. The trajectory $\mathbf{R}_k(t)$ is obtained by integrating twice Eq. (31) using basic calculus, and is also deterministic and at least twice differentiable. Introducing the deviation $\Delta\mathbf{F}_{k,\mathrm{BP}}(t) \doteq \mathbf{F}_{k,\mathrm{BP}}(t) - \mathbf{F}_{\mathrm{BP}}(t)$, we can express $\mathbf{F}_{k,\mathrm{BP}}(t)$ in terms of $\mathbf{F}_{\mathrm{BP}}(t)$ as

$$\mathbf{F}_{k,\mathrm{BP}}(t) \doteq \mathbf{F}_{\mathrm{BP}}(t) + \Delta\mathbf{F}_{k,\mathrm{BP}}(t), \tag{32}$$

which may suggest that $\Delta\mathbf{F}_{k,\mathrm{BP}}(t)$ is Langevin's $\boldsymbol{\xi}(t)$. This is where other important differences from the Langevin approach appear. The $\mathbf{F}_{\mathrm{BP}}(t)$ is a function of the average relative velocity $\mathbf{V}(t) \equiv \langle \mathsf{V}(t)\rangle$ so it does not represent the microforce $\mathbf{F}_{k,\mathrm{f}}(t)$ that appears in Eqs. (1) and (2). Furthermore, $\mathbf{F}_{k,\mathrm{BP}} \doteq \partial E_k/\partial\mathbf{R}$ is deterministic in the μNEQT as noted above. So is $\mathbf{F}_{\mathrm{BP}}(t)$. Thus, $\Delta\mathbf{F}_{k,\mathrm{BP}}(t)$ also takes a *single* value for each $\mathfrak{m}_k$, while $\boldsymbol{\xi}(t)$ is stochastic. The stochasticity in the μNEQT emerges as we average Eq. (31) over all microstates to yield

$$md^2\mathbf{R}(t)/dt^2 = \mathbf{F}_{\mathrm{BP}}(t) - 2m\langle \dot{p}\dot{\mathbf{R}}/p\rangle - m\langle \ddot{p}\mathbf{R}/p\rangle, \tag{33}$$

with $\mathbf{R}(t) \doteq \langle \mathbf{R}(t)\rangle$, $p_k > 0$, and a dot represents the total time derivative; the last two terms on the right side are due to temporal changes in $\{p_k\}$; they vanish in EQ so that we obtain a simple equation of motion for the average trajectory $\mathbf{R}(t)$ of $\mathbf{R}_k(t)$ that is normally discussed in the literature for the Langevin equation.

1. Solving Eq. (31)

We will consider the simpler case by keeping V constant so we do not have to worry about the PV-work. Let $\mathbf{R}_k(0)$ and $\mathbf{V}_k(0)$ be the initial values of $\mathbf{R}_k(t)$ and $\mathbf{V}_k(t)$, respectively; let $T(0)$ be the initial value of T. It is convenient to discretize the situation by dividing a predetermined time interval Δt, over which we are interested in finding the solution, into n nonoverlapping intervals $\delta t_{l-1} = t_l - t_{l-1}$, $l = 1, \ldots, n$, with $t_0 = 0$ and $t_n = \Delta t$. We determine the initial value $\mathbf{F}_{k,\mathrm{BP}}(0)$ of $\mathbf{F}_{k,\mathrm{BP}}(t)$ using Eq. (15b), and we use Eq. (20) to determine the initial probability $p_k(0)$; note that we must not consider the P_kV term for this case. We now solve Eq. (31) during δt_0 to determine the next values of $\mathbf{R}_k(t_1)$, which is then used to determine the next values of $\mathbf{F}_{k,\mathrm{BP}}(t_1)$ and $p_k(t_1)$. We repeat these steps n times to obtain the solution over the interval $(t_n, t_0) = \Delta t$.

2. Entropy and temperature changes

The instantaneous macroentropy is given by $S \doteq \sum_k p_k s_k$, $s_k \doteq -\ln p_k$. Using $dp_k(t_{l-1}) = p_k(t_l) - p_k(t_{l-1})$ obtained above, we determine $dS(t_{l-1}) \doteq \sum_k dp_k(t_{l-1})(s_k(t_{l-1}) - 1)$ and $dQ(t_{l-1}) = T(t_{l-1})dS(t_{l-1})$ in the MNEQT. Using $d_eQ(t_{l-1}) = \widetilde{C}(T_0 - T(t_{l-1}))$, where $\widetilde{C}$ is the heat capacity of $\widetilde{\Sigma}$, and equating it with $T_0d_eS(t_{l-1})$, we determine $d_eS(t_{l-1})$, which is then used to determine the irreversible macroentropy generation $d_iS(t_{l-1}) = dS(t_{l-1}) - d_eS(t_{l-1})$.

The temperature change during δt_{l-1} is given in Theorem 1. We thus have a complete MNEQT.

B. Fluctuations

Standard fluctuation theory [1,42,43] deals with EQ fluctuations where no internal variables are present. However, as we have shown elsewhere [39] and also discussed above, their presence in IEQ states causes no new complications and we can just follow the standard formulation to obtain *instantaneous* fluctuations in $\mathbf{F}_{\mathrm{BP}}, \mathbf{R}, \mathbf{V}$, and $\mathbf{P}_{\mathrm{BP}}$ when the system is in an IEQ state involving the internal variable $\mathbf{F}_{\mathrm{BP}}$ or $\mathbf{P}_{\mathrm{BP}}$.

We restrict ourselves to a one-dimensional (1D) case for simplicity (R replaced by X). The probability of fluctuations about the IEQ state [1] is given by $W_0 \exp(-\beta\rho/2)$, where

$$\rho = \Delta T\Delta S - \Delta P\Delta V + \Delta F_{\mathrm{BP}}\Delta X$$

in terms of various fluctuations from the IEQ state and W_0 is some unimportant constant. As ρ is a thermodynamic expression, we have the liberty to chose T, V, and F_{BP} as independent variables to express ρ in terms of ΔT, ΔV and ΔF_{BP} :$\rho = (\partial S/\partial T)(\Delta T)^2 - (\partial P/\partial V)(\Delta V)^2 + 2(\partial X/\partial T)\Delta T\,\Delta F_{\mathrm{BP}} + (\partial X/\partial F_{\mathrm{BP}})(\Delta F_{\mathrm{BP}})^2$ by exploiting some Maxwell relations [9]. The coefficients of fluctuations in the ΔT-ΔF_{BP} subspace define a 2×2 matrix $\mathbf{M}$ from which we can determine various mean square fluctuations [1,42,43]. For the interesting mean-square fluctuation $\langle(\Delta\mathsf{F}_{\mathrm{BP}})^2\rangle$, we obtain

$$\langle(\Delta\mathsf{F}_{\mathrm{BP}})^2\rangle = T(\partial S/\partial T)_{V,F_{\mathrm{BP}}}/M, \tag{34}$$

where $M \doteq (\partial S/\partial T)(\partial X/\partial F_{\mathrm{BP}}) - (\partial X/\partial T)^2 \geqslant 0$ is the determinant of $\mathbf{M}$. From these fluctuations, we can determine any other fluctuation such as $\langle(\Delta X)^2\rangle$. However, a simple method is to use T, V, and X as independent variables, which yields

$$\langle(\Delta\mathsf{X})^2\rangle = -T(\partial P/\partial V)_{T,X}/M',$$

where $M' \doteq -(\partial P/\partial V)(\partial F_{\mathrm{BP}}/\partial X) - (\partial F_{\mathrm{BP}}/\partial V)^2 \geqslant 0$.

C. Microwork fluctuations

The above NEQ fluctuation calculation is valid in general for small fluctuations about some IEQ state and are by very

nature Gaussian. To go beyond the Gaussian form, we must expand to higher order, which we will not do here as we are only interested in establishing the feasibility of the μNEQT and the reproducibility of known results. As $\mathbf{F}_{k,\mathrm{BP}}$ is specific to $\mathfrak{m}_k$, $d_iW_{k,\mathrm{BP}}$ is not affected by p_k; it is the same whether we consider an EQ or a NEQ state. In the present case, $d_iW_{k,\mathrm{BP}} \doteq -F_{k,\mathrm{BP}}dX$ fluctuates around its average $d_iW_{\mathrm{BP}} \doteq \langle d_i\mathsf{W}_{\mathrm{BP}}\rangle \geqslant 0$. As the average fluctuation $\langle(\Delta F_{\mathrm{BP}})^2\rangle(dX)^2$ does not necessarily vanish, $d_iW_{k,\mathrm{BP}}$ takes values on both sides of d_iW_{BP}. To understand its variation, we consider the EQ state for which $d_iW_{\mathrm{BP,eq}} \equiv 0$ so that $d_iW_{k,\mathrm{BP}}$ takes both positive and negative values around 0. This variation remains true even in a NEQ state; only p_k's change.

Thus, we have finally established that there is no sign restriction. Having no restriction on the sign of $d_iW_{k,\mathrm{BP}}$ means that $\mathbf{F}_{k,\mathrm{BP}}$ may or may not oppose the motion for $\mathfrak{m}_k$. This is different from the Langevin approach. In the latter, the deterministic force $\mathbf{F}_{k,\mathrm{f}}(t) \doteq -\gamma\mathbf{v}_k(t) \neq 0$ *always* opposes the motion for every microstate $\mathfrak{m}_k$; this is in accordance with the second law. Therefore, $d_iW_{k,\mathrm{f}} \doteq \mathbf{F}_{k,\mathrm{f}}(t)\cdot d\mathbf{R}$ must generate some irreversible entropy $d_iS > 0$; cf. Eqs. (16) and (18). In our theory, $\mathbf{F}_{k,\mathrm{BP}}$ is a mechanical force so it does not change p_k and, hence, the entropy. The other difference is the following. As $\mathbf{F}_{k,\mathrm{f}}(t)$ is obtained from $\mathbf{F}'_{k,\mathrm{BP}}$ by averaging over the fast Langevin force $\boldsymbol{\xi}$, it is analogous is some crude sense to our deterministic microforce $\mathbf{F}_{k,\mathrm{BP}}$ but the latter does not always oppose the motion. Recall that $\mathbf{F}_{k,\mathrm{f}}(t)$ represents the slow component of the microforce on BP, while $\mathbf{F}_{k,\mathrm{BP}}$ is the net microforce on BP. If we insist on using the Langevin interpretation for γ, then this is equivalent to allowing γ to have both signs as is considered to be the case for active BPs [14–17].

D. The Langevin limit

If $(\partial S/\partial F_{\mathrm{BP}})_{T,V} = (\partial X/\partial T)_{V,F_{\mathrm{BP}}}$ can be neglected, then the fluctuations in T, V, and F_{BP} become independent. In particular, $\langle(\Delta\mathsf{F}_{\mathrm{BP}})^2\rangle = T(\partial F_{\mathrm{BP}}/\partial X)_{T,V}$. It follows from Eq. (14) that $F_{\mathrm{BP}}(S,V,X)$ is a function of X, and using $F_{\mathrm{BP}} \simeq -\gamma\dot{X}$ in the Langevin limit, we find that $\partial F_{\mathrm{BP}}/\partial X \simeq -\gamma\ddot{X}/\dot{X} = \gamma^2/m$, so that

$$\langle(\Delta\mathsf{F}_{\mathrm{BP}})^2\rangle \simeq T_0\gamma^2/m > 0, \tag{35}$$

which is precisely what we expect in this approximation since $(\Delta F_{\mathrm{BP}})^2 = \gamma^2\dot{X}^2$ and $\langle\dot{X}^2\rangle = T_0/m$ in EQ; see below. We can similarly obtain $\langle(\Delta X)^2\rangle = T_0(\partial X/\partial F_{\mathrm{BP}})_{T,V} = mT_0/\gamma^2 > 0$ and $\langle\Delta X\,\Delta\mathsf{F}_{\mathrm{BP}}\rangle = T_0$. In a highly viscous environment, the mean square CM-fluctuation becomes very small as expected, and $\langle(\Delta F_{\mathrm{BP}})^2\rangle$ become large. All these results are valid for any BP of any reduced mass m ranging from mesoscales to macroscales in this limit.

E. Relative velocity fluctuations

Integrating Eq. (30) over an interval $(0,t)$, we have

$$\Delta_iW_{k,\mathrm{BP}} = -\int_0^t \mathbf{F}_{k,\mathrm{BP}}(t)\cdot\mathbf{V}_k(t)dt, \tag{36a}$$

where $\mathbf{V}_k(t)$ is the relative velocity. Note that we do not need p_k to calculate the microwork, which makes it trivial; see Sec. IV F. We thus have the general result

$$\Delta_iW_{k,\mathrm{BP}} = -(m/2)\big[\mathbf{V}_k^2(t) - \mathbf{V}_k^2(0)\big], \tag{36b}$$

which can have any sign. The above result is an identity so it is not restricted to small speeds only. As $\mathfrak{m}_k$ at 0 and t may have different probabilities, we take the ensemble average using joint probabilities to obtain

$$\Delta_iW_{\mathrm{BP}} = (m/2)(\langle\mathsf{V}^2(0)\rangle - \langle\mathsf{V}^2(t)\rangle) \geqslant 0. \tag{37a}$$

From the comments above about the close similarity between the IEQ and EQ states, we conclude that the velocity distribution is given by the Maxwell distribution at the instantaneous temperature $T_{\mathrm{CM}}(t)$ of the degrees of freedom associated with the CM-motion as described in Sec. II A. Thus, we have the conventional result

$$\langle\mathsf{V}^2(t)\rangle = 3T_{\mathrm{CM}}(t)/m \tag{37b}$$

for the BP in an IEQ state so that

$$\Delta_iW_{\mathrm{BP}} = (3/2)[T_{\mathrm{CM}}(0) - T_{\mathrm{CM}}(t)] \geqslant 0, \tag{37c}$$

showing that the slowing down of the CM-motion results in its temperature falling as time goes on. Eventually, $T_{\mathrm{CM}}(t) \to T_0$. In EQ, the Brownian motion does not undergo any temperature change ($\Delta_iW_{\mathrm{BP}} = 0$) as is the case for the Langevin equation, even though $\mathbf{V}_k$ varies over $\mathfrak{m}_k$.

In the Langevin limit, the equation of motion for $\mathfrak{m}_k$ with a time-dependent $\gamma_k(t)$ becomes [see Eq. (50) for justification]

$$d\mathbf{V}_k(t)/dt = -(\gamma_k(t)/m)\mathbf{V}_k(t), \tag{38a}$$

whose solution is

$$\mathbf{V}_k(t) = \mathbf{V}_k(0)\exp\bigg(-\int_0^t \gamma_k(u)du/m\bigg), \tag{38b}$$

which is independent of p_k. To be consistent with Eq. (37b), $\gamma_k(t)$ must not have a fixed sign over $\{\mathfrak{m}_k\}$. This is consistent with the observation that $\Delta_iW_{k,\mathrm{BP}}$ has no particular sign over $\{\mathfrak{m}_k\}$. This means that the components of the possible velocities can range from $-\infty$ to $+\infty$ to satisfy Eq. (37b). Consequently,

$$\langle\mathsf{V}^2(t)\rangle = \bigg\langle\mathsf{V}^2(0)\exp\bigg(-2\int_0^t\gamma(u)du/m\bigg)\bigg\rangle \leqslant \langle\mathsf{V}^2(0)\rangle, \tag{39}$$

where the last inequality follows from Eq. (37a) and where the random variable γ has outcomes $\{\gamma_k\}$. We thus see that our approach has allowed the equipartition theorem to remain valid at all times. From $\langle\mathsf{V}^2(t)\rangle \propto 1/m$, we conclude that larger the mass, smaller the mean square fluctuations such as for a macroscopic piston. However, for a mesoscopic Brownian particle, it can be appreciable and can be observed.

For the Langevin case $\gamma_k(u) \simeq \gamma > 0$ for all k so that $\langle\mathsf{V}^2(t)\rangle = e^{-2\gamma t/m}\langle\mathsf{V}^2(0)\rangle \leqslant \langle\mathsf{V}^2(0)\rangle$, which is consistent with the above inequality but shows that $\langle\mathsf{V}^2(t)\rangle \to 0$ as $t \to \infty$. This highlights another important difference from the Langevin approach: in the μNEQT, $\gamma_k(t)$ has *no* sign restriction. Because of this, it cannot be taken out of the averaging process. By taking it out in the Langevin case results in an incorrect answer. To see it clearly, we evaluate Δ_iW_{BP} in Eq. (37a) to obtain $\Delta_iW_{\mathrm{BP}} = (m/2)\langle\mathsf{V}^2(0)\rangle(1 - e^{-2\gamma t/m}) \geqslant 0$. As $t \to \infty$, $\Delta_iW_{\mathrm{BP}} = (m/2)\langle\mathsf{V}^2(0)\rangle > 0$, while it must vanish in EQ as noted above.

F. EQ diffusion

We now determine the average square displacement of the BP over a long time. For the sake of simplicity, we will only consider diffusion in an EQ state as considering IEQ states creates complications that we wish to avoid. We consider the relative displacement $\Delta\mathbf{R}_k(t,0) \doteq \mathbf{R}_k(t) - \mathbf{R}_k(0)$ over all $\{\mathfrak{m}_k\}$ at long time and follow Einstein again [10]. The distribution function of the relative displacement $\Delta\mathbf{R}_k = \Delta\mathbf{R}_k(t,0)$ over all $\{\mathfrak{m}_k\}$ is given by $p_k(\Delta\mathsf{R},t) = e^{-\Delta\mathsf{R}^2/4Dt}/(4\pi Dt)^{3/2}$, so that

$$\langle\Delta\mathsf{R}^2(t)\rangle = 6Dt \tag{40}$$

as a function of time; here, D is the diffusion constant, which is related to the viscosity of the fluid by $D = T/6\pi\eta a$. We can also compute $\langle\Delta\mathsf{R}^2(t)\rangle$ from Eq. (38a) in a standard way but we will not stop to do that.

IV. COMPUTATIONAL SCHEME

To establish the feasibility of our theory, we describe the computational methodology by considering a simpler version of the case studied in Sec. II: $\Sigma_{\rm BP}$ as the system Σ (previously denoted by $\Sigma_{\rm BP}$) in a medium $\widetilde{\Sigma}$, which with Σ forms the isolated system Σ_0 (as before). It is this version that is normally considered in the literature, and its computational scheme must be consistent with the μNEQT we have already developed in the previous sections, except that $\Sigma_{\rm R}$ is absent in the current consideration. The BP contains $N_{\rm BP}$ particles, each of mass $m_{\rm BP}$ so that $M = N_{\rm BP}m_{\rm BP}$, and $\widetilde{\Sigma}$ contains $\widetilde{N}$ particles, each of mass $\widetilde{m}$, so that its total mass is $\widetilde{M} = \widetilde{N}\widetilde{m}$. In addition, V and $\widetilde{V}$ are the volumes of the BP and the medium, respectively, which we keep fixed along with $N_{\rm BP}$ and $\widetilde{N}$. Accordingly, we do not exhibit them as parameters in the Hamiltonians. Our choice for the volumes means that there is no "pressure-volume" work, so the only microwork we need to consider is due to the microforce $\mathbf{F}_{k,\rm BP}$ resulting in $d_iW_{k,\rm BP}$; note that now k refers to the BP microstate $\mathfrak{m}_k$. Earlier, $\mathfrak{m}_k$ refereed to the joint macrostates of $\Sigma_{\rm BP}$ and $\Sigma_{\rm R}$. This simplifies the computational complexity considerably.

We will take $\widetilde{\Sigma}$ to be in equilibrium as before in a canonical ensemble with equilibrium temperature T_0,

$$\widetilde{p}_{\widetilde{k}} = \exp[\beta_0(\widetilde{F} - \widetilde{E}_{\widetilde{k}})], \tag{41a}$$

for its microstate $\widetilde{\mathfrak{m}}_{\widetilde{k}}$; here, $\widetilde{F}$ is the thermodynamic potential (the Helmholtz free energy). We take Σ, i.e., $\Sigma_{\rm BP}$ in an internal equilibrium with temperature T and microforce $\mathbf{F}_{k,\rm BP}$; its microstate probability is

$$p_k = \exp[\beta(\Phi - E_k + \mathbf{F}_{k,\rm BP}\cdot\mathbf{R})], \tag{41b}$$

cf. Eq. (20), where Φ is the thermodynamic potential, and $\mathbf{F}_{k,\rm BP}$ is given in Eq. (15b) and determined below for the current case. As noted earlier, β_0, β, and $\mathbf{R}$ are the Lagrange multipliers so they are not fluctuating over $\widetilde{\mathfrak{m}}_{\widetilde{k}}$ and $\mathfrak{m}_k$, as the case may be. In other words, they are parameters and must be held *fixed* as we use these probabilities to take averages. However, we can also treat $\mathbf{F}_{\rm BP}$ as the parameter so that $\mathbf{R}_k$ is fluctuating; cf. Eq. (21). However, we will not do so here.

A. Various frames

We consider three different frames K_0, $\widetilde{K}$, and K, in which Σ_0, $\widetilde{\Sigma}$, and Σ are at rest, respectively, with their CM's at the origins of the frames. These frames determine their thermodynamic, i.e., *internal* energies E_0, $\widetilde{E}$, and E, respectively. The Hamiltonian of Σ_0 is denoted by $\mathcal{H}_0(\mathbf{z}_0,\widetilde{\mathbf{z}}_0|\mathbf{R}_{\rm BP},\widetilde{\mathbf{R}})$ with $\mathbf{z}_0 = \{\mathbf{z}_{0i} = (\mathbf{x}_{0i},\mathbf{p}_{0i})\}_{i=1}^{N_{\rm BP}}$ and $\widetilde{\mathbf{z}}_0 = \{\widetilde{\mathbf{z}}_{0j} = (\widetilde{\mathbf{x}}_{0j},\widetilde{\mathbf{p}}_{0j})\}_{j=1}^{\widetilde{N}}$ referring to the particles composing the BP and $\widetilde{\Sigma}$, respectively, and $\mathbf{R}_{\rm BP}$ and $\widetilde{\mathbf{R}}$ denoting the CM-displacements of the BP and $\widetilde{\Sigma}$, respectively, with respect to K_0. In the following, we will exclusively use i for a BP-particle and j for a medium particle. The Hamiltonian of Σ with respect to K and of $\widetilde{\Sigma}$ with respect to $\widetilde{K}$ are denoted by $\mathcal{H}(\mathbf{z}|\mathbf{R}_{\rm BP})$ and $\widetilde{\mathcal{H}}(\widetilde{\mathbf{z}}|\widetilde{\mathbf{R}})$, respectively (see below); here, $\mathbf{z} = \{\mathbf{z}_i = (\mathbf{x}_i,\mathbf{p}_i)\}$ and $\widetilde{\mathbf{z}} = \{\widetilde{\mathbf{z}}_j = (\widetilde{\mathbf{x}}_j,\widetilde{\mathbf{p}}_j)\}$ refer to K and $\widetilde{K}$, respectively. By definition,

$$\begin{aligned}
&\sum_{i=1}^{N_{\rm BP}}\mathbf{z}_i = 0, \quad \sum_{j=1}^{\widetilde{N}}\widetilde{\mathbf{z}}_j = 0,\\
&m_{\rm BP}\sum_{i=1}^{N_{\rm BP}}\mathbf{x}_{0i} + \widetilde{m}\sum_{j=1}^{\widetilde{N}}\widetilde{\mathbf{x}}_{0j} = 0,\\
&\sum_{i=1}^{N_{\rm BP}}\mathbf{p}_{0i} + \sum_{j=1}^{\widetilde{N}}\widetilde{\mathbf{p}}_{0j} = 0.
\end{aligned} \tag{42}$$

The first sum in the last equation is $\mathbf{P}_{\rm BP}$ and the second sum is $\widetilde{\mathbf{P}} = -\mathbf{P}_{\rm BP}$.

B. Separating center of mass motion

Let $(\mathbf{R}_{\rm BP},\mathbf{V}_{\rm BP})$ and $(\widetilde{\mathbf{R}},\widetilde{\mathbf{V}})$ denote the (displacement, velocity) of the CM's of K and $\widetilde{K}$, respectively, with respect to K_0. We have $\mathbf{R} = \mathbf{R}_{\rm BP} - \widetilde{\mathbf{R}}$ as the relative displacement and $\mathbf{V} = \mathbf{V}_{\rm BP} - \widetilde{\mathbf{V}}$ as the relative velocity of the BP relative to $\widetilde{\Sigma}$. Then

$$\begin{aligned}
&\mathbf{x}_{0i} \doteq \mathbf{x}_i + \mathbf{R}_{\rm BP}, \quad \mathbf{p}_{0i} \doteq \mathbf{p}_i + m_{\rm BP}\mathbf{V}_{\rm BP},\\
&\widetilde{\mathbf{x}}_{0i} \doteq \widetilde{\mathbf{x}}_i + \widetilde{\mathbf{R}}, \quad \widetilde{\mathbf{p}}_{0i} \doteq \widetilde{\mathbf{p}}_i + \widetilde{m}\widetilde{\mathbf{V}}.
\end{aligned}$$

We can obtain E_0 in K_0 by adding to $\widetilde{E} + E$ the CM-kinetic energies $E_{\rm CM} \doteq \mathbf{P}_{\rm BP}^2/2M + \widetilde{\mathbf{P}}^2/2\widetilde{M} = \mathbf{P}_{\rm BP}^2/2m$ of the BP and $\widetilde{\Sigma}$, and their mutual interaction energy $\widehat{U}$:

$$E_0 = E_{\rm CM} + \widetilde{E} + \widehat{U} + E; \tag{43a}$$

cf. Eq. (4b). It should be noted that because of no pressure-volume work here, this interaction energy is responsible for the viscous drag. As Eq. (43a) is a purely mechanical relation, it also refers to a microstate $\mathfrak{m}_{0k_0}$ ($k_0 = \widetilde{k}\otimes k$) of Σ_0 in terms of the microstates $\widetilde{\mathfrak{m}}_{\widetilde{k}}$ and $\mathfrak{m}_k$ of the medium and the BP, respectively. Thus, E_0, $\widetilde{E}$, E, and $\widehat{U}$ can be replaced, respectively, by their microanalogs E_{0k_0}, $\widetilde{E}_{\widetilde{k}}$ and E_k, and $\widehat{U}_{k\widetilde{k}}$ or $\widehat{U}_{k_0}$, while we can replace $E_{\rm CM}$ by its microanalog $E_{{\rm CM},k}$ or $E_{{\rm CM},\widetilde{k}}$. Thus, we have the identity

$$E_{0k_0} = E_{{\rm CM},k} + E_k + \widehat{U}_{k\widetilde{k}} + \widetilde{E}_{\widetilde{k}}; \tag{43b}$$

cf. Eq. (4a). We obtain various macroenergies from them:

$$E_0 = \sum_{k_0} p_{k_0} E_{0k_0}, \quad \widehat{U} = \sum_{k_0} p_{k_0} \widehat{U}_{k\widetilde{k}},$$
$$\widetilde{E} = \sum_{\widetilde{k}} p_{\widetilde{k}} \widetilde{E}_{\widetilde{k}} = \sum_{k_0} p_{k_0} \widetilde{E}_{\widetilde{k}},$$
$$E = \sum_{k} p_k E_k = \sum_{k_0} p_{k_0} E_k. \tag{44a}$$

Let us introduce conditional probabilities $p(\widetilde{k} \mid k)$ of $\widetilde{k}$ given k so that $p_{k_0} = p_k p(\widetilde{k} \mid k)$. We use them to determine microenergies E_{0k} and $\widetilde{E}_k$ of Σ_0 and $\widetilde{\Sigma}$, respectively, that can be associated with $\mathfrak{m}_k$:

$$E_{0k} \doteq \sum_{\widetilde{k}} p(\widetilde{k} \mid k) E_{k_0},$$
$$\widetilde{E}_k \doteq \sum_{\widetilde{k}} p(\widetilde{k} \mid k) \widetilde{E}_{\widetilde{k}},$$
$$E_0 = \sum_{k} p_k E_{0k}, \quad \widetilde{E} = \sum_{k} p_k \widetilde{E}_k. \tag{44b}$$

If the medium and the BP are quasi-independent, then $p(\widetilde{k} \mid k) = p_{\widetilde{k}}$.

As $\widetilde{\Sigma}$ is in equilibrium, no irreversibility can be associated with it. Accordingly, we ascribe the irreversibility to the BP itself in the following. For this, we need to obtain the interaction energy associated with the BP alone so we must average $\widehat{U}_{k,\widetilde{k}}$ over the medium [see the second equation in Eq. (44b)] as follows:

$$\widehat{U}_k \doteq \sum_{\widetilde{k}} p(\widetilde{k} \mid k) \widehat{U}_{k,\widetilde{k}}; \tag{44c}$$

it is the interaction energy associated with $\mathfrak{m}_k$ for a given macrostate of the medium. We can now extract E_{0k} from Eq. (43b):

$$E_{0k} = E_{\mathrm{CM},k} + E_k + \widehat{U}_k + \widetilde{E}_k. \tag{45}$$

We did not explicitly consider $\widehat{U}$ in Secs. II C and II D as we were considering the microstates of Σ_{BP} and Σ_{R} together forming Σ. This tremendously simplified our discussion there as $\widehat{U}_k$ was already included in E_k. The situation is different here where we consider Σ_{BP} and $\widetilde{\Sigma}$ together but we wish to consider the microstate $\mathfrak{m}_k$ of the BP alone so we need to deal with $\widehat{U}_{k,\widetilde{k}}$ separately and determine $\widehat{U}_k$ in our discussion.

C. Hamiltonians

We first focus on the BP. In its rest frame K, its Hamiltonian is given by

$$\mathcal{H}_{\mathrm{BP}}(\mathbf{z}) = \sum_{i=1}^{N_{\mathrm{BP}}} \mathbf{p}_i^2/2m_{\mathrm{BP}} + {\sum_{i,i'=1}^{N_{\mathrm{BP}}}}' U(\mathbf{x}_i - \mathbf{x}_{i'}), \tag{46a}$$

where $U(\mathbf{x}_i - \mathbf{x}_{i'})$ is the potential energy between BP particles at $\mathbf{x}_i$ and $\mathbf{x}_{i'}$. The prime over the summation implies $i \neq i'$. The Hamiltonian when applied to $\mathfrak{m}_k$ determines E_k so that $E = \langle \mathcal{H}_{\mathrm{BP}} \rangle = \langle \mathsf{E} \rangle$ with microstate probabilities p_k given above.

The Hamiltonian of $\widetilde{\Sigma}$ in its rest frame $\widetilde{K}$ is given by

$$\widetilde{\mathcal{H}}(\widetilde{\mathbf{z}}) = \sum_{j=1}^{\widetilde{N}} \widetilde{\mathbf{p}}_j^2/2\widetilde{m} + {\sum_{j,j'=1}^{\widetilde{N}}}' \widetilde{U}(\widetilde{\mathbf{x}}_j - \widetilde{\mathbf{x}}_{j'}), \tag{46b}$$

where $\widetilde{U}(\widetilde{\mathbf{x}}_j - \widetilde{\mathbf{x}}_{j'})$ is the potential energy between the particles of $\widetilde{\Sigma}$ at $\widetilde{\mathbf{x}}_j$ and $\widetilde{\mathbf{x}}_{j'}$. It gives the microstate energy $\widetilde{E}_{\widetilde{k}}$ of $\widetilde{\mathfrak{m}}_{\widetilde{k}}$ so that $\widetilde{E} = \langle \widetilde{\mathcal{H}} \rangle_{\widetilde{\Sigma}} = \langle \widetilde{\mathsf{E}} \rangle_{\widetilde{\Sigma}}$ with microstate probabilities $\widetilde{p}_{\widetilde{k}}$ given above.

In terms of these Hamiltonians, $\mathcal{H}_0$ is given by

$$\mathcal{H}_0 = \mathcal{H}_{\mathrm{BP}}(\mathbf{z}_0 | \mathbf{R}_{\mathrm{BP}}) + \widetilde{\mathcal{H}}(\widetilde{\mathbf{z}}_0 | \widetilde{\mathbf{R}}) + \sum_{i=1}^{N_{\mathrm{BP}}} \sum_{j=1}^{\widetilde{N}} \widehat{U}(\mathbf{x}_{0i} - \widetilde{\mathbf{x}}_{0j}), \tag{46c}$$

in the K_0 frame. Here, $\widehat{U}(\mathbf{x}_{0i} - \widetilde{\mathbf{x}}_{0j})$ denotes the mutual potential energy between a BP particle at $\mathbf{x}_{0i}$ and a medium particle at $\widetilde{\mathbf{x}}_{0j}$. The mutual interaction between the BP and $\widetilde{\Sigma}$ is described by the last term above.

D. Frame change

We need to express the interaction energy explicitly in terms of $\mathbf{R}$; cf. Eqs. (14) and (15b). This will be needed below; see Eq. (50). Using the identity $\mathbf{x}_{0i} - \widetilde{\mathbf{x}}_{0j} = \mathbf{x}_i - \widetilde{\mathbf{x}}_j + \mathbf{R}$, we rewrite $\widehat{U}(\mathbf{x}_{0i} - \widetilde{\mathbf{x}}_{0j}) = \widehat{U}(\mathbf{x}_i - \widetilde{\mathbf{x}}_j + \mathbf{R})$; here, $\mathbf{x}_i$ is defined in the K frame and $\widetilde{\mathbf{x}}_j$ is defined in the $\widetilde{K}$ frame so that we can manipulate this energy conveniently as required below. The last sum in Eq. (46c) is the potential energy between the BP in a given microstate $\mathfrak{m}_k$ and the medium in a given microstate $\widetilde{\mathfrak{m}}_{\widetilde{k}}$, and defines $\widehat{U}_{k\widetilde{k}}$. To obtain $\widehat{U}_k$, we need to average it according to Eq. (44c) using $p(\widetilde{k}|k)$. While this can be done, for computational simplicity here, we will average using $\widetilde{p}_{\widetilde{k}}$, the canonical distribution of $\widetilde{\Sigma}$ in its rest frame, given above, which we denote by $\langle \rangle_{\widetilde{\Sigma}}$. It is a *restricted* average and gives us

$$\widehat{U}_k(T_0, \mathbf{R}) \doteq \sum_{i=1}^{N_{\mathrm{BP}}} \left\langle \sum_{j=1}^{\widetilde{N}} \widehat{U}(\mathbf{x}_i + \mathbf{R} - \widetilde{\mathbf{x}}_j) \right\rangle_{\widetilde{\Sigma}}, \tag{47}$$

for $\mathfrak{m}_k$ determined by $\{\mathbf{x}_i\}$; see the definition of $\widetilde{E}_k$ in Eq. (44b); the dependence on T_0 is due to the above averaging.

E. Determination of $\mathbf{F}_{\mathrm{BP}}$ and $\mathbf{F}_{k,\mathrm{BP}}$

The average of $\widehat{U}_k(T_0, \mathbf{R})$ over p_k determines the macroscopic potential

$$\widehat{U}(T, T_0, u) = \langle \widehat{\mathsf{U}}(T_0, \mathbf{R}) \rangle, \tag{48}$$

where $\widehat{\mathsf{U}}(T_0, \mathbf{R})$ is the random variable with outcomes $\{\widehat{U}_k(T_0, \mathbf{R})\}$, T appears due to the ensemble averaging, and u is defined in Eq. (28) as we now explain. This average is the $\widehat{U}$ in E_0 in Eq. (43a). Using E_0 for E in Eq. (14) and recognizing that only $\widehat{U}$ depends on $\mathbf{R}$, we realize that this dependence must be through u as explained in Sec. II D. We thus find that the macroforce $\mathbf{F}_{\mathrm{BP}}$ is given by

$$\mathbf{F}_{\mathrm{BP}}(t) = \mathbf{V} \frac{\partial \widehat{U}(T, T_0, u)}{\partial u}, \quad \frac{\partial \widehat{U}(T, T_0, u)}{\partial u} < 0, \tag{49}$$

in which $\partial\widehat{U}(T,T_0,u)/\partial u$ represent $(-f(T,\mathbf{V},t))$ in Eq. (27) for the current case; cf. Eq. (29).

We now use Eq. (15b) by replacing E_k there with E_{0k}. We obtain

$$\mathbf{F}_{k,\mathrm{BP}}(t)=\frac{\partial\widehat{U}_k(T_0,\mathbf{R})}{\partial\mathbf{R}}. \tag{50}$$

This determines the microforce thermodynamically.

As we have already discussed the CM-motion of the BP, we can go back to the K frame and consider $\mathcal{H}_{\mathrm{BP}}(\mathbf{z})$ to write down the equations of motions for $\mathbf{x}_i$ and $\mathbf{p}_i$ for $\mathfrak{m}_k$,

$$\frac{d\mathbf{p}_i}{dt}=-\sum_{i'}{}'\frac{\partial U(\mathbf{x}_i-\mathbf{x}_{i'})}{\partial\mathbf{x}_i},\quad m_{\mathrm{BP}}\frac{d\mathbf{x}_i}{dt}=\mathbf{p}_i, \tag{51}$$

dealing only with internal forces. These equations determine how $\mathfrak{m}_k$ evolves in time and determine the evolution of $\{\mathbf{z}_i\}$ in time in the K frame. From this, we extract $\{\mathbf{x}_i(t)\}$ to be used in Eq. (48) to determine $\widehat{U}_k(T_0,\mathbf{R})$. We then determine $\mathbf{F}_{k,\mathrm{BP}}(t)$ and follow the prescription of the solution of Eq. (31) over Δt.

Note that we do not need to solve the Hamilton's equations for the particles in $\widetilde{\Sigma}$, which provides a major simplification of our approach. The stochasticity, as we have mentioned several times, emerges and is completely captured when we average over $\mathfrak{m}_k$ using p_k from Eq. (41b).

The BP equation of motion in Eq. (31) differs from the original Langevin equation in Eq. (1) in that it is missing the partitioning shown in Eq. (2). Since the Hamiltonian in Eq. (46c) does not have any stochasticity, $\mathbf{F}_{k,\mathrm{BP}}(t)$ above cannot be compared with the $\mathbf{F}'_{k,\mathrm{BP}}(t)$ in Eq. (1). It follows from Eq. (31) that $\mathbf{V}=\mathbf{V}_k$ in a given BP-microstate $\mathfrak{m}_k$ is a slowy-varying function that is differentiable. The random fluctuations in it are described by considering it over microstates. Thus, the fast fluctuations similar but not identical to $\boldsymbol{\xi}$ are captured when we consider the ensemble $\{\mathbf{V}_k\}$ or $\{\mathbf{F}_{k,\mathrm{BP}}\}$ over $\{\mathfrak{m}_k\}$. The fluctuations in the medium are not relevant in our approach as we have performed an average over $\widetilde{\mathfrak{m}}_{\widetilde{k}}$ for reasons explained above.

We can use well-established solution and surface thermodynamic theories [44] to determine useful forms of $\widehat{U}$, which can be useful to validate any approximation, if any, is made in the evaluation of $\widehat{U}_k$. In most cases, the interaction potential can be approximated by considering $N_{\mathrm{BP}}^{(\mathrm{s})}$ and $\widetilde{N}^{(\mathrm{s})}$ particles in a thin interface surrounding the BP-surface and not all the particles. This will provide a further simplification in the calculation. The averaging in Eq. (48) is limited to only the thin interface and not the entire medium. Indeed, Einstein used this interface to determine the osmotic force in his analysis of the Brownian motion. Other sophisticated techniques may also be useful to deal with the computation [45–49].

F. A BP with $N_{\mathrm{BP}}=1$

Let us consider the simplest possible case $N_{\mathrm{BP}}=1$ that is commonly studied; see, for example, Ref. [33]. In this case, Eq. (51) is meaningless and $\widehat{U}_k$ depends only on a single phase point $\mathbf{z}=0$ of the BP, which also refers to its CM. The BP-microstate $\mathfrak{m}_k$ is now the small cell $\delta\mathbf{z}$ around $\mathbf{z}$ in a 6-dimensional phase space. With respect to the CM of $\widetilde{\Sigma}$, the BP has a relative displacement $\mathbf{R}$ and a relative velocity $\mathbf{V}_k$. We determine $\widehat{U}_k(T_0,\mathbf{R})$ for general $\mathbf{R}$. This has to be done once. We now determine $\mathbf{F}_{k,\mathrm{BP}}(t)$ using Eq. (50) and $\mathbf{F}_{\mathrm{BP}}(t)$ for all possible values of $\mathbf{R}$. We then integrate the equation of motion using basic calculus.

As an example, let us assume that $\widehat{U}_k(T_0,\mathbf{R})$ is given by

$$\widehat{U}_k(T_0,\mathbf{R})=-\gamma_k(T_0,t)\mathbf{R}(t)\cdot\mathbf{V}_k(t), \tag{52}$$

in terms of the scalar product; cf. Sec. II D. This results in

$$\mathbf{F}_{k,\mathrm{BP}}(t)=-\gamma_k\mathbf{V}_k(t),\quad d_iW_{k,\mathrm{BP}}(t)=\gamma_k\mathbf{V}_k^2(t)dt. \tag{53a}$$

Comparing with Eq. (38a), we see that $\mathbf{V}_k(t)$ after basic integration is given by Eq. (38b). Note again that we do not need to consider $\widetilde{\Sigma}$ in obtaining the solution, which demonstrate the usefulness of the new theory. The macroforce $\mathbf{F}_{\mathrm{BP}}(t)=\langle-\gamma_k(T_0,t)\mathbf{V}_k(t)\rangle$ must follow the form for viscous drag in Eq. (49) so we have

$$\mathbf{F}_{\mathrm{BP}}(t)=-\gamma_{\mathrm{eff}}\mathbf{V}(t),\quad d_iW_{\mathrm{BP}}(t)=\gamma_{\mathrm{eff}}\mathbf{V}^2(t)dt,\quad \gamma_{\mathrm{eff}}>0, \tag{53b}$$

where $d\mathbf{R}(t)/dt=\mathbf{V}(t)\doteq\langle\mathsf{V}\rangle$, and γ_{eff} is an effective parameter defined by $\gamma_{\mathrm{eff}}(T_0,t)\mathbf{V}^2(t)\doteq\langle\gamma(T_0,t)\mathsf{V}^2(t)\rangle$.

G. Returning to the BP in Σ

We now return to the earlier case of the BP as a part of Σ. In this case, $\widehat{U}_k(\mathbf{R})$ is the analog of $\widehat{U}_k(T_0,\mathbf{R})$ for the microstate $\mathfrak{m}_k$ of Σ. Its ensemble average $\widehat{U}(T,u)\doteq\langle\widehat{U}_k(\mathbf{R})\rangle$ over $\mathfrak{m}_k$ is subsumed into E in Eq. (14); the dependence on $\mathbf{R}$ appears through u as explained in Sec. II D. Because of this, there is no reason to extract it from E so we identify the viscous force $\mathbf{F}_{\mathrm{BP}}(t)$ by differentiating E with respect to u; see Eq. (29). This macroforce is for the entire system Σ and not for just Σ_{BP}. Thus, the microforce $\mathbf{F}_{k,\mathrm{BP}}(t)$ is for Σ's microstate $\mathfrak{m}_k$. While we did not do, it is possible to extract the microforce associated with a BP-microstate by the method presented in this section.

V. DISCUSSION AND CONCLUSIONS

The present work was motivated by a desire to obtain a deterministic equation of motion of a BP in microstate $\mathfrak{m}_k$ by considering a microstate thermodynamics (μNEQT) to provide an alternative to the stochastic Langevin approach that contains the original phenomenological Langevin equation of motion and the more advanced generalized Langevin equations such as due to Zwanzig and Mori [29,30]. The central concept in the latter approaches is the partition of the microforce acting on a BP into fast and slow components, which finds its formal justification in the Mori-Zwanzig approach [29,30]. The stochasticity due to the fast component is determined by the conditional probability of $\boldsymbol{\xi}$ and the stochasticity of the slow component is determined by the initial conditions.

In contrast, we have adopted a hybrid approach to derive the equation of motion of the BP, in the spirit of Langevin, by following not his mechanical approach but a thermodynamic approach based on the energy E, which generalizes the one adopted by Einstein [10]. Instead of focusing only on the BP and its diffusion in a medium (which we treat in Sec. IV), we take a comprehensive first-principle approach to consider

the BP as a part of a system Σ, embedded in a medium $\widetilde{\Sigma}$; see Fig. 1. All of them form the isolated system Σ_0. We consider the rest frame K_0 in which Σ_0, $\widetilde{\Sigma}$, and Σ are at rest (except in Sec. IV), but we allow the BP and Σ_R (replaced by $\widetilde{\Sigma}$ in Sec. IV) to have a relative motion specified by $\mathbf{R}$ and $\mathbf{V}$, necessary to describe the process of viscous drag as we find that the *relative* motion between Σ_{BP} and Σ_R (or $\widetilde{\Sigma}$) is the source of viscous dissipation. We treat $\mathbf{R}$ as a parameter and consider the energy $E(S, V, \mathbf{R})$, from which we determine the viscous force $\mathbf{F}_{BP}$ as it opposes motion in accordance with the second law. After identifying this macroforce in our thermodynamic approach, we go a step further and obtain a deterministic equation of motion of the microstate $\mathfrak{m}_k$ of Σ, which was not the focus of Einstein. Later in Sec. IV, we return to the simple system of a BP in a medium, and obtain the deterministic equation of motion of the BP-microstate $\mathfrak{m}_k$ (not to be confused with $\mathfrak{m}_k$ of Σ discussed above). There we establish that the mutual interaction energy $\widehat{U}$ between them is the source of viscous dissipation.

We accomplish our goal by developing a μNEQT that deals with each microstate individually. At this level, the microworks are done at fixed microstate probabilities p_k so evaluating them is simplified. The inherent determinism comes from the fact that the Hamiltonians and the Hamiltonian equations have no randomness and apply directly to the microstates individually. At this level, the potential energies in the Hamiltonian determine various microforces including the one ($\mathbf{F}_{k,BP}$), see Eq. (50), responsible for viscous dissipation in terms of the macroforce $\mathbf{F}_{BP}$. We do not partition $\mathbf{F}_{k,BP}$ into slow and fast components as required in the Langevin approach. This is one of the distinctions between the two approaches.

The stochasticity and the second law emerges automatically in our approach when the ensemble average over microstates is taken as is standard in statistical thermodynamics. To obtain the μNEQT, we need to uniquely extract from the MNEQT a description suitable at the microstate level. We have introduced the μNEQT a while back [8,39,50,51]. It is a first-principles theory and its main purpose here is to study BP in NEQ situations, where the Langevin equation in Eqs. (1) and (2) are inapplicable. To have a well-defined NEQ temperature T of the system, we need to assume the system to be in an IEQ state requiring internal variables; cf. Sec. II A. For simplicity, we have considered a single internal variable $\mathbf{P}_{BP}$ or $\mathbf{R}$ in this study, which along with V are independent state variables in the state space $\mathfrak{S}'$.

The deterministic equation of motion in Eq. (31) for the microforce is easy to solve as described in Sec. III A 1. We do not need the sophisticated concepts like the Wiener process, Itô and Stratonovich integrals, etc. This is a benefit of adopting the μNEQT. The method of solution does not require knowing any interaction with $\widetilde{\Sigma}$; it only requires interactions between Σ_{BP} and Σ_R. This becomes very important in Sec. IV that we will discuss below. As the second law is inoperative at the microstate level, the microforce $\mathbf{F}_{k,BP}$ does not always oppose motion in our approach; that holds only for the macroforce $\mathbf{F}_{BP}$. The uniquely defined microforces $\{\mathbf{F}_{k,BP}\}$ and microworks $\{d_iW_{k,BP} = -\mathbf{F}_{k,BP} \cdot d\mathbf{R}\}$ done by them become, as expected, fluctuating quantities over $\{\mathfrak{m}_k\}$. We make no assumptions about the nature of these fluctuations as is needed for the stochastic forces in the Langevin approach. The internal microwork $d_iW_{k,BP}$ also has no fixed sign. However, $d_iW_{k,BP}$ and the change in the kinetic energy $E_{k,CM} = m\mathbf{V}_k^2/2$ satisfy

$$d_iW_{k,BP} + dE_{k,CM} = 0,$$

as seen from Eq. (13); see also Eq. (36b). This is expected at the microstate level where classical mechanics operates. Some microforces increase $E_{k,CM}$; some decrease it. Things change at the macroscopic level after ensemble averaging as seen from Eq. (37a). Now, $d_iW_{BP} \geqslant 0$ is constrained by the second law so the macroforce always opposes motion.

Within the MNEQT, we determine fluctuations in various thermodynamically relevant random variables. We limit ourselves to only second order in expansion so we have only Gaussian fluctuations to reproduce all known EQ results such as the Einstein relation in Eq. (40). We need to go to higher order in expansion to obtain non-Gaussian fluctuations, but the machinery is there. We show that the equipartition theorem is satisfied at all times as the system is in IEQ, except that the degrees of freedom associated with the CM-motion have their own temperature T_{CM}, which may be different from T or T_0; see the discussion in Sec. II A. This temperature always decreases as the CM-motion ceases as the system (or the BP) comes to equilibrium; cf. Eq. (37c). Therefore, it cannot be T, which can either go up, down or remain unchanged depending on how it relates to T_0. Even if $T = T_0$, T_{CM} will continue to decrease if $\mathbf{P}_{BP} \neq 0$. We also obtain other results such as a complex velocity-dependent microscopic friction coefficient γ_k or the internal microwork $\Delta_iW_{k,BP}$, both of which can be of either sign.

An important aspect of the μNEQT approach should be mentioned. As $\mathbf{F}_{k,BP}$ is oblivious to p_k, it does not change whether we are dealing with an EQ case or a NEQ case; the latter are specified only by p_k's. Thus, we can determine $\mathbf{F}_{k,BP}$ in an EQ situation, but use it in a NEQ situation by merely using the NEQ p_k's. In EQ, $\mathbf{F}_{BP} = 0$, while in a NEQ case, $\mathbf{F}_{BP} \neq 0$. But the fluctuations in $\{\mathbf{F}_{k,BP}\}$ are present in both cases. The same discussion also applies to $\{d_iW_{k,BP}\}$.

We have taken V to be some generic work parameter and that the irreversible macroworks $d_iW_V = (P - P_0)dV$ and d_iW_{BP} were treated as independent, which allowed us to get the two inequalities in Eq. (17). For a genuine piston problem in which the volume V changes due to piston displacement dX_{BP}, they are not independent. Indeed, the force imbalance $P - P_0$ causes the friction force, which eventually ensures $P = P_0$ in EQ as is well known; see, for example, Refs. [7,8]. Recognizing that $dV = AdX_{BP} = AmdX/M_{BP}$, where A is the area of the piston, we must have $F_{BP} = -(P - P_0)Am/M_{BP}$ in the 1D case. We thus see that the standard piston behaves as a BP undergoing Brownian motion. A similar discussion can be carried out for the particle in Fig. 2(b), which also undergoes Brownian motion.

The choice of using only IEQ states should not be taken as a limitation of the μNEQT. As the system gets farther and farther away from the EQ state, we need more and more of the independent internal variables, which requires a larger and larger state space $\mathfrak{S}$ in which the IEQ states are defined [8,37]. This requires a trivial extension of the

present approach. We may also need to treat the system as inhomogeneous (see Ref. [8] for details). Thus, the μNEQT is capable of describing any complex NEQ state. The challenge is to identify additional internal variables.

We have discussed the feasibility of the new theory in Sec. IV by considering a simple version of the problem often studied in the literature: a single BP consisting of $N_{\rm BP}$ particles in a medium consisting of $\widetilde{N}$ particles. We treat a NEQ macrostate of the BP by having a temperature difference between the BP and the medium and a relative motion between them. Here, we relate the microforce $\mathbf{F}_{k,\rm BP}$ to the mutual interaction $\widehat{U}_k$ associated with the BP-microstate $\mathfrak{m}_k$. The discussion is very general and $\widehat{U}_k$ includes the mutual interaction between all pairs of medium and BP particles, except that we average it over all microstates of the medium; see Eq. (48). Thus, $\widehat{U}_k$ depends only on $N_{\rm BP}$ as it only depends on the microstate $\mathfrak{m}_k$ of the BP alone. Once this "average" potential is obtained as a function of $\mathbf{R}$, we do not need to worry about the particles of $\widetilde{\Sigma}$. We can use $\widehat{U}_k$ for $\mathfrak{m}_k$, regardless of whether the BP is in EQ or not with respect to the medium; the latter is controlled by p_k. This is the same conclusions we had arrived at for $\{\mathbf{F}_{k,\rm BP}\}$ and $\{d_iW_{k,\rm BP}\}$ above.

A good approximation for $\widehat{U}_k$ will be obtained by limiting the mutual interactions between particles in a thin interface between the BP and the medium. This is the approximation used by Einstein who used the osmotic pressure across it to develop his theory. In Sec. IV F, we consider the case of a BP made up of a single particle ($N_{\rm BP} = 1$) in a medium so $\mathfrak{m}_k$ refers to a single particle in a six-dimensional phase space. Here, the simplicity of our approach becomes obvious. Once $\widehat{U}_k$ has been obtained, the solution of the equation of motion requires only following the single particle. A simple model given in Eq. (52) clarifies this point.

At a fundamental level, there are subtle but profound differences in the μNEQT approach and the Langevin approach. It is important to draw attention to them before closing, which we list below.

(1) $\mathbf{F}_{k,\rm BP}$ and $d_iW_{k,\rm BP}$ are uniquely determined by $\mathfrak{m}_k$, deterministic, and independent of p_k. Because of the presence of $\boldsymbol{\xi}$ in the Langevin approach, $\mathbf{F}'_{k,\rm BP}$ in Eq. (1) and the microwork done by it are random quantities.

(2) The trajectory from Eq. (31), being deterministic, requires integration using basic calculus. The trajectory from the Langevin equation, being stochastic, requires technical concepts of the Wiener processes (the Itô and Stratonovich integrals), which are not as easy as the basic calculus.

(3) As the sign of γ_k is not fixed, it cannot be taken out of averaging in Eq. (39) in the μNEQT. Doing so in the Langevin limit gives an unphysical result showing that the fluctuating sign is crucial for correct physics.

(4) The MNEQT approach provides a thermodynamic justification for the frictional drag for small relative velocities. In the Langevin approach, it appears phenomenologically. The μNEQT further unravels the mystery behind the microforce as noted above.

Thus, we hope that the μNEQT presented here will prove useful to study both passive and active BPs, and NEQ BP in general.

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