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Classical and semiclassical dynamics in statistical environments with a mixed dynamical and statistical representation.

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Abstract

We present a basic theory to study real-time dynamics embedded in a large environment that is treated with statistical method. In light of great progress in the molecular-level studies on time-resolved spectroscopies, chemical reaction dynamics, and so on, not only in gas phase but in condensed phases like liquid solvents and even in crowded environments in living cells, we need to bridge over a gap between statistical mechanics and microscopic real-time dynamics. For instance, an analogy to gas-phase dynamics in which molecules are driven by the gradient of the potential energy hyper-surfaces (PES) suggests that particles in condensed phases should run on the free energy surface instead. Question is whether this anticipation is correct. To answer it, we here propose a mixed dynamics and statistical representation to treat chemical dynamics embedded in statistical ensemble. We first define entropy functional, which is a function of the phase-space position of the dynamical subsystem, being dressed with statistical weights from the statistical counterpart. We then consider the functionals of temperature, free energy, and chemical potential as their extensions in statistical mechanics, through which one can clarify the relationship between real-time microscopic dynamics and statistical quantities. As an illustrative example we show that molecules in the dynamical subsystem should run on the free-energy functional surface, if and only if the spatial gradients of temperature functional are all zero. Otherwise, additional forces emerge from the gradient of the temperature functional. Numerical demonstrations are presented in the very basic level of this theory of molecular dissociation in atomic cluster solvent.

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I. INTRODUCTION

Statistical mechanics, either equilibrium or nonequilibrium, is generally concerned with emergence and evolution of orders in macroscopic ensemble and their reduced dynamics.[1] On the other hand, progress in chemical reaction dynamics in gas phase such as ab initio molecular dynamics tempts us to see them in condensed phases. Also, chemical dynamics on a solid state surface has long been one of the most interesting subjects in catalytic chemistry. As one of the possible methodologies to study *chemical reaction dynamics* in condensed phases, we here propose a very basic theory for classical (and semiclassical) dynamics embedded in a statistically treated environment. In particular, we scrutinize the theoretical structure of mixed dynamical and statistical representation, rather than develop a cutting-edge technology for efficient method of molecular simulation. Through this representation, we attempt to clarify the relationship between classical dynamics and statistical mechanics by shedding a light to thermodynamical quantities like entropy, temperature, free energy, and chemical potential through an entropy functional we will define.

In gas phase dynamics, molecules are driven by potential functions, while in statistical mechanics the motion of the entire ensemble of particles along representative coordinates such as the so-called reaction coordinate is controlled by free energy but not by bare potential functions, a typical example of which is seen in the Marcus theory for electron transfer reaction in solvents.[2] In this respect, the methods of Nagaoka and his colleagues[3–5] and Yang's group[6–8] are quite stimulating in that they have explicitly formulated a method for molecules to be quenched down to the bottom on an *effective* "free-energy surface" in a solvent system. More explicitly, they first prepare a quasi-Boltzmann-distribution with a potential energy alone as a function of the molecular coordinates Q_1 and solvent coordinates Q_2 and integrate only over the Q_2 as

$$Z(Q_1) = \int \exp\left(-\beta V(Q_1, Q_2)\right) dQ_2, \tag{1}$$

where $\beta = 1/k_B T$ with T and k_B being canonical temperature and the Boltzmann constant, respectively. (Note that $\exp\left(-\beta V(Q_1, Q_2)\right)$ in Eq. (1) is not literally a Boltzmann distribution function by definition.) Then $Z(Q_1)$ is transformed to an effective "free energy" such that

$$A(Q_1) = -\frac{1}{\beta} \log Z(Q_1), \tag{2}$$

with which one can track a down-hill path using the gradient

$$-\frac{\partial A(Q_1)}{\partial Q_1} = \frac{1}{Z(Q_1)} \int \left[-\frac{\partial V(Q_1, Q_2)}{\partial Q_1} \right] \exp\left(-\beta V(Q_1, Q_2)\right) dQ_2 = \left\langle -\frac{\partial V(Q_1, Q_2)}{\partial Q_1} \right\rangle_{Q_2}, \tag{3}$$

which is an average force from the solvents acting on the molecule. This method actually materializes an idea about the role of the free energy surface rather than the quantum-chemical potential energy surfaces (PES). They have shown that the method indeed works well to determine the stable structures of product molecules under the influence of solvent configurations.

This theory looking neat and having been appropriately applied, a natural question inspired is whether and how the notion of "real-time dynamics on free energy surface" is valid in general? This classic yet unresolved problem becomes more and more important in the modern study of *chemical reaction dynamics* in liquid phase, since we ask far beyond the search of equilibrium molecular geometry and/or electronic structure in solvents. For instance, no kinematic (momentum) effect is explicitly taken into account in the above formalism, and therefore it is quite unlikely for this method to be able to treat more general reactions to surmount potential barriers and rate processes arising thereof. Besides, the temperature ($T = 1/k_B\beta$) is introduced as a parameter irrespective of the amount of heat formation by chemical reactions involved. Therefore we ask ourselves how we can treat chemical reaction dynamics in a field having temperature gradient, which may be spontaneously created by exo- or endo-thermicity of the involved reactions themselves.

To answer those questions, we propose a theory based on mixed dynamical and statistical representation. As usual dynamically treated subsystems in phase space, referred to as dynamical subsystem, are embedded in a large statistical system. Our formalism starts with an entropy functional, on which a consistent framework is constructed along with the natural definition of temperature functional as a direct consequence of energy gradient of the entropy functional. It is shown that mechanical (Newtonian) forces working in the dynamical subsystem are represented in terms of the functionals of entropy and temperature. Also it is suggested that an asymptotic connection to the solvent system consisting of molecules of the Avogadro number is possible with use of chemical potential functional defined in the same framework.

The goal of the present mixed dynamical and statistical representation is to study chemical reaction dynamics in condensed phases with our developed many-body quantum dynamics based on classical-path formalism (theory of action decomposed function)[9, 10] and nonadiabatic electron wavepacket dynamics propagated along branching paths (theory of path-branching representation as a mixed quantum and classical representation) scheme.[11–18] However, the present paper is mainly devoted to a possible link between statistical mechanics and classical dynamics embedded therein.

This paper is organized as follows: We first present in Sec. II a set of formal definitions of the central quantities such as the entropy functional. The basic properties and physical meanings of these quantities are discussed. Then equations of motion for the dynamical subsystem is formulated. In Sec. III, we pay particular attention to equilibration and fluctuation from it. Section IV demonstrates a numerical example of the theory applied to dissociation dynamics of Cl_3 solvated by around 1000 argon atoms to show the characteristics of the present dynamics. The paper concludes in Sec. V with some remarks.

II. ENTROPY FUNCTIONAL AND RELATED QUANTITIES

A. System composition to be studied and coordinates

We consider a large system of finite number of particles, a *microcanonical* ensemble, which has a well-defined mechanical energy. No external perturbation is to be considered throughout, and equilibrium is not assumed either unless otherwise specified. In this system, we pay a special attention to small subsystems, which we call dynamical subsystems in this paper. These serve as small windows through which to monitor the dynamics inside. Although one can assume many dynamical subsystems here and there in the whole system simultaneously, we consider only one as such for the sake of simplicity in formulation. Generalization is rather straightforward.

The total systems is composed of two interacting parts; one as a dynamical subsystem composed of N_1 particles and the rest consisting of N_2 particles. As usual we refer to the latter as reservoir. The spatial coordinates in their configuration space are accordingly described as

$$Q = (Q^{(1)}, Q^{(2)}), \tag{4}$$

where both $Q^{(1)}$ and $Q^{(2)}$ are also vectors defined as $Q^{(1)} = \left(Q_1^{(1)}, \cdots, Q_i^{(1)}, \cdots Q_{3N_1}^{(1)}\right)$ and $Q^{(2)} = \left(Q_1^{(2)}, \cdots, Q_j^{(2)}, \cdots Q_{3N_2}^{(2)}\right)$. Likewise their conjugate momenta are denoted as $P = (P^{(1)}, P^{(2)})$. In the present mixed dynamical and statistical representation, phase space $(Q^{(1)}, P^{(1)})$ is treated *dynamically* (either classically or semiclassically), while the subsystem represented in $(Q^{(2)}, P^{(2)})$ is to be expressed *statistically*. The dynamical subsystem may include some of the solvent molecules as its members, if they should be treated dynamically on equal footing with solute molecules, as in cases where some of solvent molecules are directly involved in chemical reactions with solute molecules. On the other hand, the composition of molecular species in the dynamical system may be or may not be the same as that of the reservoir. For a simple liquid, the present representation simply gives a conditional dynamics of $Q^{(1)}$ embedded in the $Q^{(2)}$ subsystem.

With use of the mass-scaled coordinates, the Hamiltonian of the entire system is formally written as

$$H(Q,P) = \left(\frac{P^{(1)2}}{2} + \frac{P^{(2)2}}{2}\right) + V(Q^{(1)}, Q^{(2)}), \tag{5}$$

where

$$P^{(1)2} = \sum_i P_i^{(1)2} \tag{6}$$

and the potential function being assumed to have the following form

$$V(Q^{(1)}, Q^{(2)}) = V^{(1)}(Q^{(1)}) + V^{(2)}(Q^{(2)}) + V^{(12)}(Q^{(1)}, Q^{(2)}), \tag{7}$$

where $V^{(1)}$, $V^{(2)}$, $V^{(12)}$ are, respectively, the potentials acting on the dynamical subsystem, the reservoir, and the coupling potential between the subsystem and the reservoir.

B. Entropy functional and dynamics

We next define the very basic quantities in a rather axiomatic way parallel to the standard statistical mechanics.[1]

1. *Entropy functional*

Just as a straightforward extension of statistical mechanics, we consider the so-called number of states integrated over the reservoir $\left(Q^{(2)}, P^{(2)}\right)$ consisting of N_2 particles, which is defined as

$$\Gamma(E, Q^{(1)}, P^{(1)}) = h^{-3N_2} \int \theta\left(E - H(Q,P)\right) dQ^{(2)} dP^{(2)} \tag{8}$$

at an arbitrary instant, where θ is the step function specifying that the energy of the entire phase-space points $(Q,P) = \left(Q^{(1)}, Q^{(2)}, P^{(1)}, P^{(2)}\right)$ should be below the total energy of the entire system E, and h is the Planck constant. We regard the entire system as a huge conservative system in total. Since there is physically no way to either determine or identify the initial conditions of solvent states $\left(Q^{(2)}, P^{(2)}\right)$, we regard all the statistically possible states equal in its phase space and perform the relevant integration over all the possible states with no bias. Therefore no matter how slowly the real dynamics in $\left(Q^{(2)}, P^{(2)}\right)$-space would respond to the dynamics in $\left(Q^{(1)}, P^{(1)}\right)$, all the necessary configurations to describe the surrounding system are included in the $\left(Q^{(2)}, P^{(2)}\right)$ integrations. Likewise the corresponding density of states is given in a straightforward manner as

$$\Omega(E, Q^{(1)}, P^{(1)}) = h^{-3N_2} \int \delta\left(E - H(Q,P)\right) dQ^{(2)} dP^{(2)}, \tag{9}$$

where $\delta\left(E - H(Q,P)\right)$ is the Dirac delta function resulting from $d\theta\left(E - H(Q,P)\right)/dE$. In what follows, we often use a shorthand notation for the variables as

$$\Xi = (E, Q^{(1)}, P^{(1)}), \tag{10}$$

recalling that both Γ and Ω are the distribution functions (not constant values) of these intrinsic variables.

It is natural to define entropy functional in terms of $\Gamma(E, Q^{(1)}, P^{(1)})$ (not with $\Omega(E, Q^{(1)}, P^{(1)})$) such that

$$\mathbb{S}(\Xi) \equiv k_B \log \Gamma(E, Q^{(1)}, P^{(1)}). \tag{11}$$

$\mathbb{S}(\Xi)$ is an attribute of the point Ξ yet reflects the "capacity" of $\left(Q^{(2)}, P^{(2)}\right)$-space. Then a temperature functional is naturally derived through

$$\frac{\partial}{\partial E}\mathbb{S}(\Xi) = k_B \frac{\Omega(\Xi)}{\Gamma(\Xi)} = \frac{1}{\mathbb{T}(\Xi)}, \tag{12}$$

and $\mathbb{T}(\Xi)$ is defined, as in standard statistical mechanics, as

$$\mathbb{T}(\Xi) = \frac{1}{k_B}\frac{\Gamma(\Xi)}{\Omega(\Xi)}. \tag{13}$$

Again $\mathbb{T}(\Xi)$ is an attribute of the point Ξ but it comes from the property of the phase space $\left(Q^{(2)}, P^{(2)}\right)$, that is, the ratio of the volume of the $\left(Q^{(2)}, P^{(2)}\right)$ to the surface of it. Obviously $\mathbb{T}(\Xi)$ is not a constant but can fluctuate in space-time, which reflects the finite rate of energy exchange between $Q^{(1)}$ and $Q^{(2)}$ subsystems and depends on the energy production in $(Q^{(1)}, P^{(1)})$-space due to chemical reactions and so on.

2. *Auxiliary for the proposed quantities*

To assure that our defined quantities are simple extension of the corresponding quantities by confirming the limit of them as

$$\lim_{N_1/N_2 \to 0} \Gamma(E, Q^{(1)}, P^{(1)}) = \Gamma, \qquad \lim_{N_1/N_2 \to 0} \Omega(E, Q^{(1)}, P^{(1)}) = \Omega, \tag{14}$$

Γ and Ω in the right hand sides are the value of the number of states and density of states of the entire system, respectively. Therefore, by definition we have the similar limits for the functionals of entropy and temperature according to

$$\lim_{N_1/N_2 \to 0} \mathbb{S}(E, Q^{(1)}, P^{(1)}) = S, \qquad \lim_{N_1/N_2 \to 0} \mathbb{T}(E, Q^{(1)}, P^{(1)}) = T, \tag{15}$$

where S and T are entropy and temperature of the entire system, respectively, which are defined according to pure statistical mechanics. These relations imply that if the reservoir is by far larger than the dynamical subsystem, the values of $\mathbb{S}(E, Q^{(1)}, P^{(1)})$ and $\mathbb{T}(E, Q^{(1)}, P^{(1)})$ are essentially the same as those of the reservoir. Therefore an increment of "entropy" in any dynamical subsystem can be regarded as virtually infinitesimal. Nevertheless the dynamics there can proceed significantly. This is because the gradient of $\mathbb{S}$ with respect to $Q^{(1)}$, which is much sensitive quantity than $\mathbb{S}$ itself, can drive the system. This is the main aspect we are going to investigate deep in this paper.

On the other hand, we can extend $\Gamma(E, Q^{(1)}, P^{(1)})$ and $\Omega(E, Q^{(1)}, P^{(1)})$ by introducing an *arbitrary* phase-space distribution function $f\left(Q^{(2)}, P^{(2)}\right)$ to choose a particular domain in $(Q^{(2)}, P^{(2)})$ in such a way that

$$\Gamma(E, Q^{(1)}, P^{(1)}) = h^{-3N_2} \int f\left(Q^{(2)}, P^{(2)}\right) \theta\left(E - H(Q, P)\right) dQ^{(2)} dP^{(2)} \tag{16}$$

and

$$\Omega(E, Q^{(1)}, P^{(1)}) = h^{-3N_2} \int f\left(Q^{(2)}, P^{(2)}\right) \delta\left(E - H(Q, P)\right) dQ^{(2)} dP^{(2)}. \tag{17}$$

As an special example, $f\left(Q^{(2)}, P^{(2)}\right)$ of the form

$$f\left(Q^{(2)}, P^{(2)}\right) = \delta\left(Q^{(2)} - Q^{(2)}(t)\right)\delta\left(P^{(2)} - P^{(2)}(t)\right), \tag{18}$$

where $\left(Q^{(2)}(t), P^{(2)}(t)\right)$ is supposed to run on classical trajectories, reduces to the standard Molecular Dynamics (MD) scheme. This simple example illustrates that $\left(Q^{(2)}, P^{(2)}\right)$-space over which to carry out the integration of Eqs. (8) and (9) contains everything we need to represent any situation, both equilibrium and nonequilibrium, subject to the condition of energy conservation. At the same time, it also demonstrates that the present theoretical framework lies in between statistical mechanics and pure dynamics. With a good choice of the weighting function $f\left(Q^{(2)}, P^{(2)}\right)$, one may be able to extended the formalism we are discussing here. However, since the main purpose of this paper is to link classical (semiclassical) dynamics with statistical mechanics, we henceforth set

$$f\left(Q^{(2)}, P^{(2)}\right) = 1. \tag{19}$$

3. *Force working on the dynamical subsystem*

With these thermodynamic functionals, one can build a formal theory similar to classical statistical mechanics. We start from the entropy functional as

$$\frac{\partial}{\partial Q_i^{(1)}}\mathbb{S}(\Xi) = k_B \frac{1}{\Gamma(\Xi)}\frac{\partial \Gamma(\Xi)}{\partial Q_i^{(1)}}, \tag{20}$$

where $Q_i^{(1)}$ denotes the ith component of the $Q^{(1)}$ vector. $\partial\Gamma(\Xi)/\partial Q_i^{(1)}$ can be readily rewritten as

$$\begin{aligned}
\frac{\partial \Gamma(\Xi)}{\partial Q_i^{(1)}} &= -h^{-3N_2}\int dQ^{(2)}dP^{(2)}\delta(E-H) \times \frac{\partial\left[\left(V^{(1)}(Q^{(1)}) + V^{(12)}(Q^{(1)}, Q^{(2)})\right)\right]}{\partial Q_i^{(1)}} \\
&= \Omega(\Xi)\left[-\frac{\partial V^{(1)}}{\partial Q_i^{(1)}} - \frac{\hbar^{-3N_2}}{\Omega(\Xi)}\int dQ^{(2)}dP^{(2)}\delta(E-H)\frac{\partial V^{(12)}(Q^{(1)}, Q^{(2)})}{\partial Q_i^{(1)}}\right] \\
&\equiv \Omega(\Xi)\left(-\frac{\partial V^{(1)}}{\partial Q_i^{(1)}} - \left\langle \frac{\partial V^{(12)}}{\partial Q_i^{(1)}} \right\rangle\right).
\end{aligned} \tag{21}$$

Thus we have obtained a basic relation

$$\frac{\partial}{\partial Q_i^{(1)}}\mathbb{S}(\Xi) = -\frac{1}{\mathbb{T}(\Xi)}\left(-\frac{\partial V^{(1)}}{\partial Q_i^{(1)}} - \left\langle \frac{\partial V^{(12)}}{\partial Q_i^{(1)}} \right\rangle\right) \tag{22}$$

with the help of Eq. (13), and

$$R_i^{(1)} \equiv -\left\langle \frac{\partial V^{(12)}}{\partial Q_i^{(1)}} \right\rangle = -\frac{\int dQ^{(2)} dP^{(2)} \delta(E-H) \frac{\partial V^{(12)}(Q^{(1)},Q^{(2)})}{\partial Q_i^{(1)}}}{\int dQ^{(2)} dP^{(2)} \delta(E-H)}, \tag{23}$$

represents the average of the forces between a point $Q^{(1)}$ in the dynamical subsystem and the points $Q^{(2)}s$ (with possible momenta $P^{(2)}s$) of the reservoir system, with all of these points lying on the energy shell of E. Since mechanical force working on $Q_i^{(1)}$ is

$$F_i^{(1)} = -\frac{\partial V^{(1)}}{\partial Q_i^{(1)}} - \left\langle \frac{\partial V^{(12)}}{\partial Q_i^{(1)}} \right\rangle, \tag{24}$$

it thus turns out that the force in the form of Eqs. (22) and (24) can be rewritten thermodynamically as

$$F_i^{(1)} = \mathbb{T}(\Xi) \frac{\partial}{\partial Q_i^{(1)}} \mathbb{S}(\Xi). \tag{25}$$

This identity contains no more than does Eq. (24), but one may be able to find novel approximations in this expression. As a first example, simply setting $\mathbb{T}(\Xi)$ to a constant as the externally given temperature should result in a simplified yet nontrivial approximation to $F_i^{(1)}$.

4. Averaged dynamics

So far $Q^{(1)}$ and $P^{(1)}$ have been both independent variables. To consider classical dynamics in $\left(Q^{(1)}, P^{(1)}\right)$-space, we need to borrow classical mechanics to define the evolution of the momenta $P^{(1)}$ as (in the form of Euler's approximation to integrate differential equations)

$$\frac{\Delta P_i^{(1)}}{\Delta t} \simeq F_i^{(1)} = \mathbb{T}(\Xi) \frac{\partial \mathbb{S}(\Xi)}{\partial Q_i^{(1)}} \tag{26}$$

and similarly we have

$$\frac{\Delta Q_i^{(1)}}{\Delta t} \simeq P_i^{(1)}, \tag{27}$$

where $P_i^{(1)}$ denotes the ith component of $P^{(1)}$ vector, and $\Delta Q_i^{(1)}$ and $\Delta P_i^{(1)}$ indicate their infinitesimal increments. Note that these canonical equations of motion cannot be solved unless the integrals over $(Q^{(2)}, P^{(2)})$ are performed, which in turn are dependent on $\left(Q^{(1)}, P^{(1)}\right)$. This makes a difference from the standard MD. In this way we explicitly bring the classical dynamics, denoted as $\left(Q^{(1)}(t), P^{(1)}(t)\right)$, into the dynamical subsystem, and thereby $\mathbb{S}(\Xi) = \mathbb{S}\left(E, Q^{(1)}(t), P^{(1)}(t)\right)$, for instance, turns to be a functional.

One particular point to note in this dynamics is that paths in the dynamical subsystems are supposed to feel an averaged force provided by the reservoir in addition to its own $V^{(1)}(Q^{(1)})$, as seen in Eq. (24). Theoretical frameworks in which averaged force (or potential) is adopted are widely found in the literature. In addition to Eq. (3), those include the classic theory of the integral equations[19, 20] to RISM-SCF method[21–23], and a generalization of QM/MM method such as the method of Averaged Solvent Electrostatic Potential/Molecular Dynamics (ASEP/MD) developed by Aguilar's group[24, 25] and a method based on the mean-field embedding approximation by Yamamoto et al.[26–28]. Most of these averaged potentials and forces are utilized to approximately evaluate the free energy (see also ref. [29–35] for progress in the methodology to evaluate free energy).

The present average, Eq. (23), is to be taken over all the possible points of $\left(Q^{(2)}, P^{(2)}\right)$-space in a given shell of the total energy E, sampling from which should be scanned equally with no bias. The physical meaning of the resultant paths $\left(Q^{(1)}(t), P^{(1)}(t)\right)$ in the dynamical subsystem is as follows: Suppose we have a $\left(Q^{(1)}(t), P^{(1)}(t)\right)$ in the dynamical subsystem. If there is no reservoir, the modified canonical equations of motion, Eqs. (26) and (27) give a simple classical path reaching $\left(Q^{(1)}_{pure}(t+\Delta t), P^{(1)}_{pure}(t+\Delta t)\right)$ in a deterministic manner. For a system in which the reservoir contains a lot of particles (so many that one cannot control the initial conditions of them at all), the dynamics under the averaged force is supposed to give a path, say $\left(Q^{(1)}_{av}(t+\Delta t), P^{(1)}_{av}(t+\Delta t)\right)$, which should be located nearby $\left(Q^{(1)}_{pure}(t+\Delta t), P^{(1)}_{pure}(t+\Delta t)\right)$. On the other hand, for a given $\left(Q^{(1)}(t), P^{(1)}(t)\right)$, there are infinitely many points $\left(Q^{(2)}, P^{(2)}\right)$ subject to the total energy E. Let us denote each of them as $\left(Q^{(2k)}, P^{(2k)}\right)$ $(k = 1, 2, \cdots, N_{path})$. (Note that the number of the paths N_{path} is actually uncountable infinity.) In the pure classical dynamics, each $\left(Q^{(2k)}, P^{(2k)}\right)$ shifts $\left(Q^{(1)}(t), P^{(1)}(t)\right)$ to $\left(Q^{(1k)}_{pure}(t+\Delta t), P^{(1k)}_{pure}(t+\Delta t)\right)$ with their own force

$$F_i^{(1k)} = -\frac{\partial V^{(1)}}{\partial Q_i^{(1)}} - \frac{\partial V^{(12)}(Q^{(1)}(t), Q^{(2k)})}{\partial Q_i^{(1)}}. \tag{28}$$

Then an intuitive application of the law of large number suggests that the average over $\left(Q^{(1k)}_{pure}(t+\Delta t), P^{(1k)}_{pure}(t+\Delta t)\right)$ with respect to the superscript k should be equivalent to a path that is driven by a force average over $F_i^{(1k)}$ with respect to the superscript k. This may be regarded as a reflection of the ergodic property of classical phase space. For a short time propagation the above equivalence holds as

$$\left(Q_{av}^{(1)}(t+\Delta t), P_{av}^{(1)}(t+\Delta t)\right) = \lim_{N_{path}\to\infty} \frac{1}{N_{path}} \sum_{k=1}^{N_{path}} \left(Q_{pure}^{(1k)}(t+\Delta t), P_{pure}^{(1k)}(t+\Delta t)\right), \tag{29}$$

since, for instance, the averaged force in a short time gives rise to the average increase of the momentum in such a way that

$$\begin{aligned} \lim_{N_{path}\to\infty} \frac{1}{N_{path}} \sum_{k=1}^{NN_{path}} P_{pure,i}^{(1k)}(t+\Delta t) &= P_i^{(1)}(t) + \Delta t \lim_{N_{path}\to\infty} \frac{1}{N_{path}} \sum_{k=1}^{N_{path}} F_i^{(1k)} \\ &\equiv P_{av,i}^{(1)}(t+\Delta t), \end{aligned} \tag{30}$$

where we have examined for the ith coordinate. The similar expression can be readily derived for $Q_{av}^{(1)}(t+\Delta t)$. For a long time dynamics, we may be able to apply mathematical induction of the above short time propagation, but more careful argument seems to be required, since the phase-space for $\left(Q^{(2)}, P^{(2)}\right)$ changes from time to time as $\left(Q^{(1)}(t), P^{(1)}(t)\right)$ is evolved.

In summary, an averaged path generated in the present theory does not represent any real Newtonian trajectory. However, if we could run an infinite number of trajectories for a given $\left(Q^{(1)}(t), P^{(1)}(t)\right)$ with randomly selected $\left(Q^{(2k)}, P^{(2k)}\right)$, their average should be reduced to a single path that is generated by the averaged force. To attain the expectation values of physical quantities in the dynamical subsystem, one should further take averages of them over $\left(Q^{(1)}(0), P^{(1)}(0)\right)$-space with respect to initial conditions under study.

As a theoretical consequence of the fact that the averaged force is taken over the density of states without use of any dynamical distribution function, we can readily see that the "classical paths" generated in terms of Eqs. (26) and (27) should theoretically satisfy time-reversal symmetry, as long as the reservoir is not connected to other dissipative systems.

C. Implications of the quantities defined

Before proceeding, we touch upon simple consequences from the identity of Eq. (25) regarding the relationship between dynamics and statistical mechanics.

1. *Dynamics on the free-energy functional surface*

Let us define free energy functional $\mathbb{A}(\Xi)$ such that

$$\mathbb{A}(\Xi) = E - \mathbb{T}(\Xi)\mathbb{S}(\Xi). \tag{31}$$

which is again a natural generalization of the standard Helmholtz A-function (free energy) $A = E - TS$ in the sense

$$\lim_{N_1/N_2 \to 0} \mathbb{A}(\Xi) = A. \tag{32}$$

Therefore, just as $\mathbb{S}(\Xi)$, the value of $\mathbb{A}(\Xi)$ is overwhelmingly dominated by the value coming from the reservoir. Consequently, lowering of the value of $\mathbb{A}(\Xi)$ tends to work to raise the energy of the dynamical subsystem, though this may sound counter-intuitive.

Recall that E is the total energy and therefore constant, and note moreover that $\mathbb{A}$ is a different quantity from the A function in Eq. (2). Then, in case where the spatial gradient of the temperature functional is small, that is

$$\frac{\partial}{\partial Q_i^{(1)}} \mathbb{T}(\Xi) \simeq 0, \tag{33}$$

we have

$$F_i^{(1)} \simeq -\frac{\partial}{\partial Q_i^{(1)}} \mathbb{A}(\Xi), \tag{34}$$

which gives a theoretical foundation that the free energy can be approximately regarded as a potential function of the $Q^{(1)}$ system, and consequently the force works as though it leads the system to the lower places in the basin of $\mathbb{A}(\Xi)$. On the other hand, if the constant temperature condition is violated, a correction term to Eq. (34) arises such that

$$F_i^{(1)} = -\frac{\partial}{\partial Q_i^{(1)}} \mathbb{A}(\Xi) - \mathbb{S}(\Xi) \frac{\partial}{\partial Q_i^{(1)}} \mathbb{T}(\Xi). \tag{35}$$

The residual force (the second term of the right hand side) works to the direction in which temperature functional becomes lower, which reminds of the Fourier law in heat conduction. This force should grow significant when both $\mathbb{S}(\Xi)$ and the gradient of $\mathbb{T}(\Xi)$ are large. The places of low temperature functional usually lie in regions of high potential energy such as the top of potential barriers, where the corresponding kinetic energy of the reservoir is relatively low (see Eq. (66)). The points of the low free-energy functional (the first term of Eq. (35)), to the contrary, tends to be located close to the region of low potential energy of the reservoir. Therefore the two terms in Eq. (35) can conflict with each other in effect, and $\mathbb{A}(\Xi)$ alone does not dominate the force in nonequilibrium stage of large gradient of $\mathbb{T}(\Xi)$, yet the entropy functional $\mathbb{S}(\Xi)$ does. Therefore we concentrate on the gradient of $\mathbb{S}(\Xi)$ but not that of $\mathbb{A}(\Xi)$ in what follows.

On the other hand, the systems satisfying Eq. (33) are in fact in equilibrium. This aspect will be discussed in the next section and Appendix. Dynamical calculations with application of Eq. (33) may asymptotically lead to correct equilibrium states, if any, but the resultant path ways to the final products are unlikely to represent reality.

2. On the increase of entropy functional

In statistical mechanics, one anticipates that the state of a statistical ensemble (microcanonical ensemble in particular) tends to proceed to a direction of increasing entropy. This is quite a reasonable *inference*. On the other hand, Eq. (25) states that the force working in the dynamical subsystem is directed towards larger entropy functional. This is a deterministic statement of *mechanics* but not inference, and therefore these two are fundamentally different. (Recall that our treated total system is governed by $H(Q,P)$ having the total energy E and is microcanonical ensemble as a whole.) However, we also note that Eq. (25) does never claim that entropy functional increases monotonically. Due to the inertia, the particles inside the dynamical subsystem can run to a direction in which the entropy functional decreases. This situation is similar to the ordinary Newton mechanics, which claims that the Newtonian force works to the direction of the lower potential energy but the moment of inertia can lead the system the other way around. Nonetheless Eq. (25) would provide a basic step from which to explore the statistical law of increase in entropy.

3. Entropy functional and energy production

For systems that are not in equilibrium, let us integrate Eq. (25) to evaluate energy production, say $\Delta E_i^{(1)}$, *released* from the dynamical subsystem due to a small displacement of $Q_i^{(1)}$, denoted as $\Delta Q_i^{(1)}$, along the direction of the applied force, that is

$$\Delta E_i^{(1)} = \int F_i^{(1)} \Delta Q_i^{(1)} = \int \mathbb{T}(\Xi) \frac{\partial \mathbb{S}(\Xi)}{\partial Q_i^{(1)}} \Delta Q_i^{(1)} \tag{36}$$

$$\simeq \mathbb{T}(\Xi) \Delta \mathbb{S}_i^{(1)}, \tag{37}$$

where $\Delta \mathbb{S}_i^{(1)}$ is the production of the enetropy functional in this process, in which $\mathbb{T}(\Xi)$ is assumed not to change much during the small shift. Then this leads to

$$\frac{\Delta E_i^{(1)}}{\mathbb{T}(\Xi)} \simeq \Delta \mathbb{S}_i^{(1)}(\Xi), \tag{38}$$

which is parallel to the well-known identity

$$\Delta S = \frac{\Delta Q}{T}. \tag{39}$$

Equation (38) tells that for a given energy production from $\left(Q^{(1)}, P^{(1)}\right)$-space a smaller increase of the entropy functional results with a larger temperature functional (recall that both $\mathbb{S}(\Xi)$ and $\mathbb{T}(\Xi)$ are actually the properties of $\left(Q^{(2)}, P^{(2)}\right)$-space).

Further, by dividing the both sides of Eq. (38) with a short time Δt, we obtain

$$\frac{\Delta \mathbb{S}_i^{(1)}}{\Delta t} \simeq \frac{1}{\mathbb{T}(\Xi)} \frac{\Delta E_i^{(1)}}{\Delta t}. \tag{40}$$

This approximate relation implies that the larger speed of energy production in the dynamical subsystem leads to the higher rate in the production of the entropy functional. However, the higher temperature functional tends to suppress the rate of production of entropy functional.

D. Thermodynamic limit through the chemical potential functionals

It is interesting and conceptually important to see how mixed dynamical and statistical systems can be smoothly connected to the stage of thermodynamics for the Avogadro number system. Although it seems that there is not practical significance in numerical realization, connecting microscopic and macroscopic physical worlds is yet an important but not easy problem. We herein consider a limiting procedure to enable the reservoir to approach the macroscopic limit. To do so, we consider a natural extension of chemical potential to the similar functional form. To this aim we denote the entropy functional as an explicit function of the particle number in the $Q^{(2)}$-space as $\mathbb{S}_{N_2}(E, Q^{(1)}, P^{(1)})$. Since temperature is more frequently used than the total energy E, we rewrite it in terms of a given temperature functional as $\mathbb{S}_{N_2}(\mathbb{T}, Q^{(1)}, P^{(1)})$, provided that the relation between E and $\mathbb{T}$ is estimated beforehand. Following the standard statistical mechanics, we simply generalize chemical potential by making use of the entropy functional as

$$\mathbb{S}_{N_2+\Delta N}(\mathbb{T}, Q^{(1)}, P^{(1)}) - \mathbb{S}_{N_2}(\mathbb{T}, Q^{(1)}, P^{(1)}) \simeq -\frac{\mu\left(\mathbb{T}, Q^{(1)}, P^{(1)}; N_2\right)}{\mathbb{T}}\Delta N, \tag{41}$$

where ΔN indicates an increment of the particles in the reservoir. Then the dynamics follows automatically as

$$\begin{aligned}&\frac{\partial}{\partial Q_i^{(1)}}\mathbb{S}_{N_2+\Delta N}(\mathbb{T}, Q^{(1)}, P^{(1)}) - \frac{\partial}{\partial Q_i^{(1)}}\mathbb{S}_{N_2}(\mathbb{T}, Q^{(1)}, P^{(1)})\\ &= -\Delta N\frac{\partial}{\partial Q_i^{(1)}}\left(\frac{\mu(\mathbb{T}, Q^{(1)}, P^{(1)}; N_2)}{\mathbb{T}}\right).\end{aligned}$$

With the help of Eq. (25) under the constant temperature functional approximation, the above expression is rewritten as

$$F_i^{(1)}\left(N_2 + \Delta N\right) - F_i^{(1)}\left(N_2\right) \simeq -\Delta N\frac{\partial}{\partial Q_i^{(1)}}\mu\left(\mathbb{T}, Q^{(1)}, P^{(1)}; N_2\right), \tag{42}$$

where $F_i^{(1)}\left(N_2\right)$ is the force acting on the dynamical subsystem in $Q_i^{(1)}$-direction from the reservoir composed of N_2 particles. Or, more symmetrically emerges an identity

$$\frac{\partial}{\partial N_2}F_i^{(1)}\left(N_2\right) \simeq -\frac{\partial}{\partial Q_i^{(1)}}\mu\left(\mathbb{T}, Q^{(1)}, P^{(1)}; N_2\right). \tag{43}$$

A plot of the quantity $\partial\mu\left(T, Q^{(1)}, P^{(1)}; N_2\right)/\partial Q_i^{(1)}$ against the particle number N_2 should give a converged value, actually approaching the Avogadro number N_A^0, as

$$\lim_{N_2\to N_A^0}\frac{\partial}{\partial Q_i^{(1)}}\mu\left(\mathbb{T}, Q^{(1)}, P^{(1)}; N_2\right) = 0, \tag{44}$$

which in turn can be made use of to evaluate the force $F_i^{(1)}\left(N_2\right)$ in such a limit. Incidentally, since the molar chemical potential μ is equivalent to the Gibbs free energy G, the force turns out to be related to G in this way.

III. EQUILIBRATION IN THE RESERVOIR

The present formalism for mixed dynamical and statistical representation allows nonequilibrium situation not only for the dynamical subsystem but even in the reservoir. However, since any statistical theory is required to describe equilibrium appropriately, we here in this section focus on equilibrium states, which should be dominated by the most probable "events" in the reservoir. Through the analysis a scope beyond equilibrium is also to be attained.

A. Entropy functional in $Q^{(2)}$-space alone

1. *Analytic integration over the $P^{(2)}$-space*

Adopting the standard method, we can perform an analytic integration of the number of states $\Gamma(\Xi)$ over $P^{(2)}$-space to a simpler form such that

$$
\begin{aligned}
\Gamma(\Xi) &= h^{-3N_2} \int dQ^{(2)} dP^{(2)} \theta \left(E - V(Q) - \frac{P^{(1)2}}{2} \right) \\
&= \frac{\pi^{3N_2/2} h^{-3N_2}}{\gamma(3N_2/2+1)} \int dQ^{(2)} \left(E - V(Q) - \frac{P^{(1)2}}{2} \right)^{\frac{3N_2}{2}} ,
\end{aligned}
\tag{45}
$$

where $\gamma(x)$ is the gamma function. Likewise, the density of states $\Omega(\Xi)$ as well is reduced to

$$
\Omega(\Xi) = \frac{\pi^{3N_2/2} h^{-3N_2}}{\gamma(3N_2/2+1)} \frac{3N_2}{2} \int dQ^{(2)} \left(E - V(Q) - \frac{P^{(1)2}}{2} \right)^{\frac{3N_2-2}{2}} .
\tag{46}
$$

Consequently $\mathbb{S}(\Xi)$ can also be written down explicitly as

$$
\begin{aligned}
\mathbb{S}(\Xi) &= k_B \log \Gamma(\Xi) \\
&= k_B \log \int dQ^{(2)} \left(E - V(Q) - \frac{P^{(1)2}}{2} \right)^{3N_2/2} + k_B \log \frac{\pi^{3N_2/2} h^{-3N_2}}{\gamma(3N_2/2+1)}
\end{aligned}
\tag{47}
$$

Now that both $\Gamma(\Xi)$ and $\Omega(\Xi)$ are formally at hand, the corresponding temperature functional $\mathbb{T}(\Xi)$ is also formally available through Eq. (13).

2. *The force expressions rewritten*

With the above reduction, we find a way of approximation to be applied to the forces working on the subsystem of $\left(Q^{(1)}, P^{(1)}\right)$. The combination of Eq. (25) and Eq. (47) leads

$F_i^{(1)}$ to

$$F_i^{(1)} = -\frac{3}{2} N_2 k_B \mathbb{T}(\Xi) \frac{\int dQ^{(2)} \frac{\partial V(Q_i^{(1)},Q^{(2)})}{\partial Q_i^{(1)}} \left[E - V(Q_i^{(1)},Q^{(2)}) - \frac{P^{(1)2}}{2}\right]^{3N_2/2-1}}{\int dQ^{(2)} \left[E - V(Q_i^{(1)},Q^{(2)}) - \frac{P^{(1)2}}{2}\right]^{3N_2/2}}. \tag{48}$$

Or, it may be approximated in terms of a finite difference such that

$$F_i^{(1)} \simeq \frac{k_B \mathbb{T}(\Xi)}{\Delta Q_i^{(1)}} \log \frac{\int dQ^{(2)} \left[E - V(Q_i^{(1)} + \Delta Q_i^{(1)},Q^{(2)}) - \frac{P^{(1)2}}{2}\right]^{3N_2/2}}{\int dQ^{(2)} \left[E - V(Q_i^{(1)},Q^{(2)}) - \frac{P^{(1)2}}{2}\right]^{3N_2/2}}. \tag{49}$$

The latter expression suggests that the denominator of the fraction in the logarithmic function may be reused recursively as the numerator at the next time step. $R_i^{(1)}$ of Eq. (23) is also approximated as

$$R_i^{(1)} = -\frac{\int dQ^{(2)} \frac{\partial V^{(12)}(Q^{(1)},Q^{(2)})}{\partial Q_i^{(1)}} \left[E - V(Q_i^{(1)},Q^{(2)}) - \frac{P^{(1)2}}{2}\right]^{3N_2/2-1}}{\int dQ^{(2)} \left[E - V(Q_i^{(1)},Q^{(2)}) - \frac{P^{(1)2}}{2}\right]^{3N_2/2-1}}. \tag{50}$$

B. The most probable configurations in $Q^{(2)}$-space

As seen above, one of the key integrals in the force expressions, to which other integrals can be numerically correlated, is

$$D \equiv \int dQ^{(2)} \left[E - V(Q^{(1)},Q^{(2)}) - \frac{P^{(1)2}}{2}\right]^{3N_2/2-1}, \tag{51}$$

which appears in the expression of the entropy functional of Eq. (47) and those of the force Eqs. (48) and (49). We hence investigate the property of this integral. To do so we first define an auxiliary function $\omega(\varepsilon; Q^{(1)})$, which is a volume in configuration space $Q^{(2)}$ that belongs to the total potential energy ε for a given point $Q^{(1)}$ as

$$\omega(\varepsilon; Q^{(1)}) \equiv \int dQ^{(2)} \delta\left(\varepsilon - V(Q^{(1)},Q^{(2)})\right), \tag{52}$$

the potential energy of which is to be included in the interval

$$\varepsilon \le V(Q^{(1)},Q^{(2)}) \le \varepsilon + \Delta\varepsilon \tag{53}$$

with a limit $\Delta\varepsilon \to 0$. At a given point $\left(Q^{(1)},P^{(1)}\right)$, making use of the property of the delta function, we insert $\omega(\varepsilon; Q^{(1)})$ into Eq. (51) to rewrite it to

$$D = \int d\varepsilon \; \omega(\varepsilon; Q^{(1)}) \left[E - \frac{P^{(1)2}}{2} - \varepsilon\right]^{3N_2/2-1}. \tag{54}$$

Bringing this function back into Eq. (50) we also rewrite it as

$$R_i^{(1)} = -\frac{\int d\varepsilon \, \frac{\partial V^{(12)}(Q^{(1)},Q^{(2)})}{\partial Q_i^{(1)}} \omega(\varepsilon;Q^{(1)}) \left[E - \frac{P^{(1)2}}{2} - \varepsilon\right]^{3N_2/2-1}}{\int d\varepsilon \omega(\varepsilon;Q^{(1)}) \left[E - \frac{P^{(1)2}}{2} - \varepsilon\right]^{3N_2/2-1}}. \tag{55}$$

In the function D of the form of Eq. (54), the integrand in the right hand side should have peaks, since $\omega(\varepsilon;Q^{(1)})$ is generally increasing as ε, while the term $\left[E - \frac{P^{(1)2}}{2} - \varepsilon\right]^{3N_2/2-1}$ becomes smaller with the larger ε (see Fig. 1). Our task is then to find ε^* that maximizes the integrand of Eq. (54), or equivalently to find the stationary points of

$$\log \omega(\varepsilon;Q^{(1)}) \left[E - \frac{P^{(1)2}}{2} - \varepsilon\right]^{3N_2/2-1}, \tag{56}$$

satisfying

$$\frac{d}{d\varepsilon}\left[\log \omega(\varepsilon;Q^{(1)}) + (3N_2/2-1)\log\left(E - \frac{P^{(1)2}}{2} - \varepsilon\right)\right] = 0. \tag{57}$$

Hence ε^* is the total potential energy at which the solvent configurations $Q^{(2)}$ can appear to be most probable, subject to a given set of $\Xi = \left(Q^{(1)}, P^{(1)}, E\right)$. (The process to find ε^* is exactly the same as that to define the microcanonical temperature.[36]) Remember that ε^* is a function of $\Xi = (E, Q^{(1)}, P^{(1)})$. There can exist plural solutions of ε^* for the equation (57) at a given Ξ, since there can exist plural total potential energies that realize "equilibrium" surrounding the dynamical subsystem of Ξ. Therefore, the system can have multi-stability $\varepsilon^*\left(E, Q^{(1)}, P^{(1)}\right)$ among them, and "hysteresis" phenomenon can be observed by scanning Ξ**,** depending on the viscosity and other properties of reservoir.

Incidentally, this situation is somewhat similar to the quantum and classical mixed representation (the Born-Oppenheimer approximation) if $\left(Q^{(1)}, P^{(1)}\right)$-system and $\left(Q^{(2)}, P^{(2)}\right)$-system are corresponded, respectively, to slow (nuclear) and fast (electron) subsystems.[18] An analogy then suggests that there can exist phenomena similar to the quantum mechanical nonadiabatic transitions at a place satisfying

$$\varepsilon_i^*\left(E, Q^{(1)}, P^{(1)}\right) = \varepsilon_j^*\left(E, Q^{(1)}, P^{(1)}\right), \tag{58}$$

where the left and right terms are, respectively, the ith and jth solutions of Eq. (57). In what follows, however, we proceed with an assumption that only a single solution for the maximum exists.

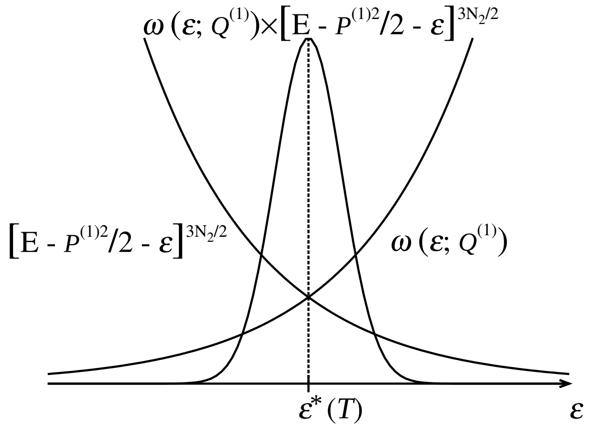

FIG. 1: Finding the maximum in the product of $\omega(\varepsilon; Q^{(1)})$ and $\left[E - \frac{P^{(1)2}}{2} - \varepsilon\right]^{3N_2/2-1}$ for a given set of $(E, Q^{(1)}, \frac{P^{(1)2}}{2})$.

C. Fluctuation around the equilibrium

Having sought the potential energy that maximizes the function as above in Eq. (56), we further consider the second derivative of it. Suppose that

$$\frac{d^2}{d\varepsilon^2}\left[\log\omega(\varepsilon; Q^{(1)}) + (3N_2/2-1)\log\left(E - \frac{P^{(1)2}}{2} - \varepsilon\right)\right]\Bigg|_{\varepsilon=\varepsilon^*} = -2\alpha, \tag{59}$$

α of which is anticipated to be large. This expression together with Eq. (57) leads to

$$\omega(\varepsilon; Q^{(1)})\left[E - \frac{P^{(1)2}}{2} - \varepsilon\right]^{3N_2/2-1} = \omega(\varepsilon^*; Q^{(1)})\left[E - \frac{P^{(1)2}}{2} - \varepsilon^*\right]^{3N_2/2-1} \exp\left[-\alpha(\varepsilon-\varepsilon^*)^2\right]. \tag{60}$$

Bringing this result back into Eq. (55), we have

$$R_i^{(1)} \simeq -\frac{\int d\varepsilon \int dQ^{(2)} \frac{\partial V^{(12)}(Q_i^{(1)}, Q^{(2)})}{\partial Q_i^{(1)}} \delta\left(\varepsilon^* - V(Q^{(1)}, Q^{(2)})\right) \exp\left[-\alpha(\varepsilon-\varepsilon^*)^2\right]}{\int d\varepsilon \int dQ^{(2)} \delta\left(\varepsilon^* - V(Q^{(1)}, Q^{(2)})\right) \exp\left[-\alpha(\varepsilon-\varepsilon^*)^2\right]}, \tag{61}$$

where the factor $\left[E - \frac{P^{(1)2}}{2} - \varepsilon^*\right]^{3N_2/2-1}$ of Eq. (60) has been cancelled out in the fraction. Equation (61) formally indicates that at the total potential energy satisfying $\varepsilon = \varepsilon^*$, the reservoir is equilibrated for a given $\Xi = (E, Q^{(1)}, P^{(1)})$, and the contributions from ε around ε^* manifest the effects of fluctuation around the equilibrium. (We will show in Appendix another force expression to take account of the fluctuation around equilibrium.)

Furthermore, the contribution in this $R_i^{(1)}$ arising from the equilibrating ε $(= \varepsilon^*)$ alone can be attained by taking a limit of large α, which is equivalent to ignoring the fluctuation around $\varepsilon = \varepsilon^*$, such that

$$R_i^{(1)*} \simeq -\frac{\int dQ^{(2)} \frac{\partial V^{(12)}(Q_i^{(1)},Q^{(2)})}{\partial Q_i^{(1)}} \delta\left(\varepsilon^* - V(Q^{(1)},Q^{(2)})\right)}{\int dQ^{(2)} \delta\left(\varepsilon^* - V(Q^{(1)},Q^{(2)})\right)}. \tag{62}$$

Therefore $R_i^{(1)*}$, the force from the equilibrated reservoir, requires only to integrate over all molecular configurations in $Q^{(2)}$-space that belong to the total potential energy ε^* alone.

D. Temperature functional at equilibrium

We next consider the notion of temperature within the present framework.

1. *Local temperatures*

The similar maximizing procedure can be applied to $F_i^{(1)}$ of Eq. (48). This time the maximization is introduced not to Eq. (54) but formally to

$$\int d\varepsilon\ \omega(\varepsilon; Q^{(1)}) \left[E - \frac{P^{(1)2}}{2} - \varepsilon\right]^{3N_2/2}, \tag{63}$$

since it does not make any significant difference when N_2 is large. After the similar manipulation, it appears that

$$F_i^{(1)} \simeq -\frac{\frac{3}{2}N_2 k_B T(\Xi)}{\left(E - \frac{P^{(1)2}}{2} - \varepsilon^*\right)} \frac{\int dQ^{(2)} \frac{\partial V(Q_i^{(1)},Q^{(2)})}{\partial Q_i^{(1)}} \delta\left(\varepsilon^* - V(Q^{(1)},Q^{(2)})\right)}{\int dQ^{(2)} \delta\left(\varepsilon^* - V(Q^{(1)},Q^{(2)})\right)}. \tag{64}$$

On the other hand, the result of Eq. (62) brings about $F_i^{(1)}$ in the form

$$F_i^{(1)} \simeq -\frac{\partial V_1(Q_i^{(1)})}{\partial Q_i^{(1)}} - \frac{\int dQ^{(2)} \frac{\partial V^{(12)}(Q_i^{(1)},Q^{(2)})}{\partial Q_i^{(1)}} \delta\left(\varepsilon^* - V(Q^{(1)},Q^{(2)})\right)}{\int dQ^{(2)} \delta\left(\varepsilon^* - V(Q^{(1)},Q^{(2)})\right)}. \tag{65}$$

For these two expressions to be consistent with each other, it should hold that

$$k_B \mathbb{T}(\Xi) = \frac{2}{3N_2}\left(E - \frac{P^{(1)2}}{2} - \varepsilon^*\right). \tag{66}$$

This expression indicates that $3k_B\mathbb{T}/2$ is the average kinetic energy of each particle in reservoir, just as in the standard equilibrium statistical mechanics.[37]

2. Temperature at global equilibrium

The major difference between the canonical temperature T and $\mathbb{T}(\Xi)$ is again that the latter is the function of $Q^{(1)}$, $P^{(1)}$, and the total energy E. Then, let us exchange the role of the dynamical subsystem and the reservoir simply by exchanging their names. To recall explicitly that the system 1 is a dynamical subsystem and the system 2 is the reservoir, we rewrite Eq. (66) as

$$k_B \mathbb{T}_2(\Xi_1) = \frac{2}{3N_2}\left(E - \frac{P^{(1)2}}{2} - \varepsilon^*\right). \tag{67}$$

Similarly, if the system 1 is the reservoir and the system 2 is a dynamical subsystem, we have

$$k_B \mathbb{T}_1(\Xi_2) = \frac{2}{3N_1}\left(E - \frac{P^{(2)2}}{2} - \varepsilon^*\right). \tag{68}$$

Then, at globally equilibrium situation, the values of these two local temperature functionals are supposed to be the same value, say T_{total}, as

$$\mathbb{T}_2(\Xi_1) = \mathbb{T}_1(\Xi_2) = T_{total}. \tag{69}$$

Now let us represent the system total energy E in terms of these kinetic energies as

$$\begin{aligned} E &= (\text{kinetic energy of subsystem 1}) + (\text{kinetic energy of subsystem 2}) + \text{potential energy} \\ &= \left(E - \frac{P^{(2)2}}{2} - \varepsilon^*\right) + \left(E - \frac{P^{(1)2}}{2} - \varepsilon^*\right) + \varepsilon^* \\ &= \frac{3N_2}{2} k_B \mathbb{T}_2(\Xi_1) + \frac{3N_1}{2} k_B \mathbb{T}_1(\Xi_2) + \varepsilon^* \\ &= \frac{3}{2} k_B \left(N_2 + N_1\right) T_{total} + \varepsilon^*, \end{aligned} \tag{70}$$

which leads to

$$k_B T_{total} = \frac{2}{3N_{total}}\left(E - \varepsilon^*\right), \tag{71}$$

where $N_{total} = N_1 + N_2$. Thus the well-known result in equilibrium statistical mechanism is reproduced.[37, 38]

Note that the above discussion does not depend on the way of partitioning the space. Therefore, at equilibrium, the total temperature, which is the same as that of any local area, should be given as above. Thus the temperature functional at equilibrium exactly coincides with the global statistical temperature. Note however that T_{total} should lose its primary sense if the system deviates from equilibrium, whereas the temperature functional $\mathbb{T}(\Xi)$ retains its physical significance.

E. On the dynamics at equilibrium

Dynamics relevant to the notion of equilibrium is revisited here.

1. *Revisiting the Nagaoka and Yang ansatz of Eq. (3)*

For a locally equilibrium state, we have obtained the expression for the force from the reservoir through Eq. (62) or Eq. (**??**) with fluctuation. Yet there is another standard way to approximate $R_i^{(1)}$ of Eq. (55) at an equilibrium state, by reducing $\left[E - \frac{P^{(1)2}}{2} - \varepsilon^*\right]^{3N_2/2-1}$ in Eq. (55) to a Boltzmann-like distribution function. The result is summarized as

$$R_i^{(1)*} = -\frac{\int dQ^{(2)} \frac{\partial V^{(12)}(Q_i^{(1)},Q^{(2)})}{\partial Q_i^{(1)}} \exp\left[-\frac{1}{k_B \mathbb{T}(\Xi)} V(Q^{(1)},Q^{(2)})\right]}{\int dQ^{(2)} \exp\left[-\frac{1}{k_B \mathbb{T}(\Xi)} V(Q^{(1)},Q^{(2)})\right]}. \tag{72}$$

The proof is given in Appendix A, together with its extension so as to include fluctuation around the equilibrium. This expression is readily reduced to Eq. (3) by replacing $\mathbb{T}(\Xi)$ with T_{total}. Therefore the Nagaoka-Yang ansatz turns out to be valid in the situation where the global equilibrium is retained.

2. *Retardation of response from the reservoir*

Equation (57) suggests that the most probable state for the solvent system to stay in can be specified by an optimal potential energy ε^*, and those configurations of statistical solvent $Q^{(2)}$ belonging to ε^* are likely to make the largest contribution to reproduce $R_i^{(1)}(t)$. Recall however that the above optimization procedure has been performed purely in statistical context and no dynamical causality has been brought in among the solvent molecules. Obviously this procedure assumes an instantaneously fast response that is mathematically idealized, but *in reality* they should take some time to relax themselves to each given internal state $\Xi = \left(Q^{(1)}, P^{(1)}, E\right)$. This is the physical origin of the time-delay of action from the solvents onto solute system. Therefore we need to introduce a method to estimate such relaxing time and the relevant responses. This suggests an insufficient aspect of the pure statistical treatment of the reservoir.

IV. NUMERICAL EXAMPLE

This section is devoted to demonstration of an application of the present formalism to dissociation dynamics of a small molecular system in an atomic solvent. Neither equilibrium state nor variational distribution of the reservoir as in Eq. (62) is assumed here. A selected dynamics is down-hill classical motion of Cl_3, which is by far more difficult problem than those to search the bottom of an effective free-energy basin like Eq. (2). To examine how the present averaged dynamics looks like, we compare it with the results of MD using the same systems.

A. Details of the calculations

1. System considered

The composite system we adopt here is rather hypothetical and borrowed from a paper by Bergsma et al.[40] It is a dissociation starting from a transition state

$$\mathrm{Cl}_3 \rightarrow \mathrm{Cl} + \mathrm{Cl}_2 \tag{73}$$

in 997 Ar atoms, 97 argon atoms out of which are treated as dynamical solvent in $Q^{(1)}$ along with three Cl's, while the remaining 900 Ar atoms are represented in $Q^{(2)}$ constituting the reservoir, which we refer to as statistical solvent. Since we intend to illustrate what are the pure outcomes from the theory presented, we do not install additional equipment like a thermostat. For the same reason, we do not adopt the so-called periodic boundary condition. Thus, all the particles are confined in a cubic box of hard walls having perfect elasticity, and the so-called reflective boundary condition is applied.

The chlorine atoms are driven by the LEPS potential among themselves, while all the other interaction potentials are represented in the Lennard-Jones potentials (the potential cut-off at 2.5σ is applied). The relevant parameters are those given in ref. [40]. We start the calculations from the transition state of Cl_3 with C_{2v} symmetry. The individual chlorine atoms are numbered as in Fig. 2, with the central one being #1 at the initial geometry.

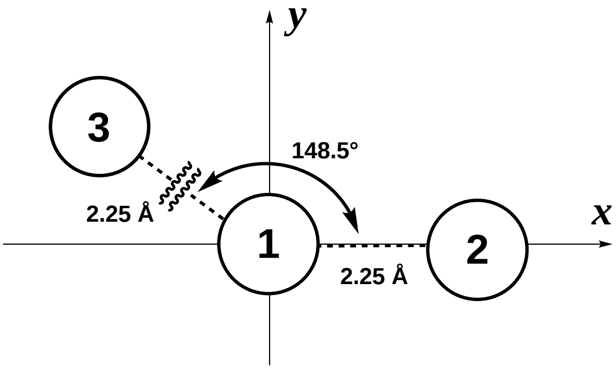

FIG. 2: The initial geometry of Cl_3 before starting dynamics.

The temperature of the solvent is assumed to be globally constant at 298 K in the initial stage, and the particle density is set to 1400 kg m^{-3}. This system models a reaction of Cl_3-like molecule in high-temperature and high-pressure liquid Ar.[40]

2. Total energy and initial temperature before dynamics

In the studies of macroscopic systems, temperature rather than energy is often used to specify the state. This requires a calibration curve between T and E. We here assign the initial temperature to the system with the relation Eq. (66), assuming that the reservoir is in equilibrium at first. The value of this obtained temperature functional is identified as the global temperature. To determine the relevant kinetic energy, we have conducted MD calculations with Cl atoms fixed at the initial position. With these kinetic energies sampled, the relation between the total energy and the temperature was estimated using the least square fit as shown in Fig. 3. Conversely, the total energy required to specify a temperature can be determined in terms of this graph. For instance, the initial state temperature 298 K in this system happens to correspond to the total energy 695.5 kJ/mol.

3. Calculation of the mean forces working on the $Q^{(1)}$ subsystem

To calculate the mean force of Eq. (24), we need to perform the integral over the phase space of the statistical solvent $(Q^{(2)}, P^{(2)})$ at each given state of the dynamical subsystem $(Q^{(1)}, P^{(1)})$. The integral over $P^{(2)}$ can be performed analytically, and the relevant integrals have been reduced to the integral of Eq. (52). We start the present numerical test

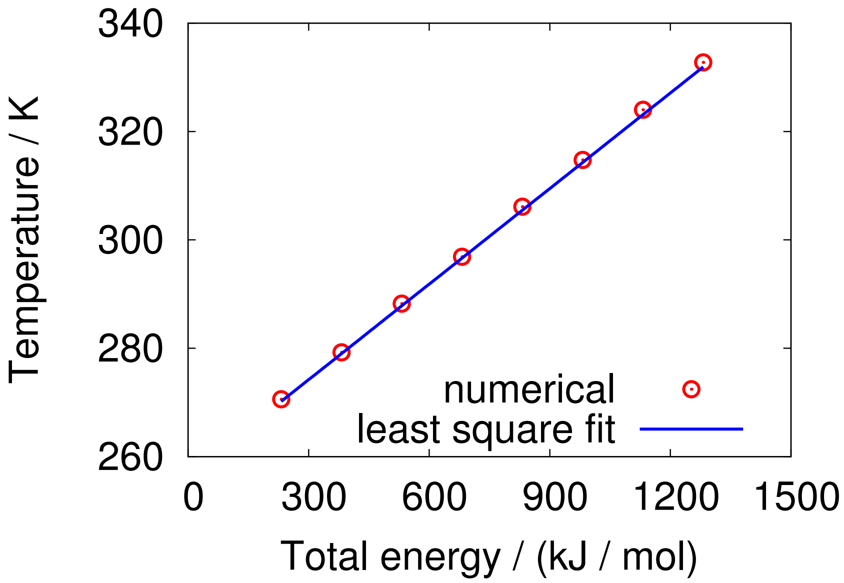

FIG. 3: Relationship between the total energy of the system and the initial temperature of the statistical solvent (reservoir).

deliberately using unbiased sampling techniques. Among several such methods we actually tried, we here show the results given by the so-called multi-histogram method[41] with multi-canonical sampling method (MCS)[42]. The other methods tested turned out to give essentially the same results.

We first carry out the MC calculations by the Metropolis method with different temperatures T', with $(Q^{(1)}, P^{(1)})$ fixed, where the temperatures T' are scanned beyond the targeted temperature T. We thus obtain the histograms along the coordinate of ε (corresponding to the potential energy) in Eq. (52). Then with the multi-histogram method the density of configurations $\omega\left(\varepsilon; Q^{(1)}\right)$ has been computed. With these densities of states in turn, the distribution in the ε-coordinate, which is the integrand of Eq. (54), can be obtained such that

$$p(\varepsilon;\Xi) = const. \times \omega\left(\epsilon; Q^{(1)}\right)\left[E - \frac{P^{(1)2}}{2} - \varepsilon\right]^{3N_2/2-1}, \qquad (74)$$

which is normalized. We then sample the configurations in the coordinates $Q^{(2)}$ by MCS method so as to reproduce this distribution function. Those configurations are sampled every 10 MC steps.

Furthermore, the integration over $(Q^{(2)}, P^{(2)})$ has been carried out only once for every 20 fs, while the force in the $(Q^{(1)}, P^{(1)})$ has been updated at every 0.2 fs. In other words, the effects from the statistical solvent have been renewed only once for every 100 time-steps of the calculations of $F_i^{(1)}$. This artificial yet time-saving procedure can generally result in retardation of the responses of $(Q^{(2)}, P^{(2)})$-subsystems to the dynamics in $(Q^{(1)}, P^{(1)})$. In this particular case, however, we have numerically confirmed in advance that this retardation effect was not significant as far as the above timing is concerned.

Further technical details including those to accelerate computational efficiency will be reported elsewhere along with applications to barrier crossing dynamics of chemical interest.[39]

4. Three ways of dynamics

To see the characteristics of the mean-force as evaluated above, we have performed two other dynamics for comparison: One is the usual MD for a system without the statistical solvent. That is the system composed of three chlorine atoms and 97 argon atoms. We call this MD calculation the vacuum MD. These hundred particles form a cluster in total floating in a box of the same size. The other one is another usual MD for the whole thousand particles. In this system there is no statistical solvent and every particle is regarded as a member of the $(Q^{(1)}, P^{(1)})$ system. Again, these particles are confined in the same box under the same physical conditions such as temperature and pressure under the reflective boundary condition. We denote this calculation as the whole system MD.

In the whole system MD, we ran 100 trajectories with 100 initial conditions varying the initial phase-space positions of only 900 argon atoms with fixing the 100 inner particles (3 Cl and 97 Ar). The initial conditions of these inner particles are commonly chosen to those of the mean-force dynamics and vacuum MD. In both MD's, the velocity Verlet algorithm is used with setting the time step to 0.2 fs.

B. Results and discussion

We track the interatomic distances between the chlorine atoms #1 and #3, r_{13}, and #2 and #3, r_{23} to illustrate how the mean-force dynamics looks like.

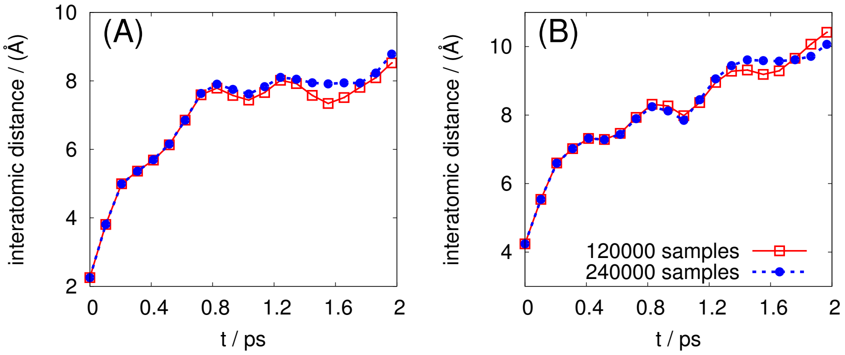

FIG. 4: Convergence of the mean-forces with respect to the number of sampling points for the integration in $Q^{(2)}$ space. Panel (A) for r_{13} and (B) for r_{23}. Data marked with the square and filled circles represent those of 120,000 and 240,000 sampling points, respectively, for 2700-dimensional intgrations.

1. Convergence of the mean-force

To examine whether the above integrations over the $Q^{(2)}$-coordinates actually give convergent results with respect to the number of the sampling points, we first demonstrate Fig. 4, in which the time evolutions of r_{13} (panel A) and r_{23} (panel B) taken from a randomly selected initial condition are depicted. Two cases are compared in each panel between the choice of 120,000 and 240,000 as the number of the sampling points. As seen in the figure and also supported by other calculations (not shown), the convergence with respect to the sampling points is securely realized. In what follows, we hence choose 120,000 as the number of sampling points. The convergence also suggests that the present calculations basically work well.

2. Characteristics of the dynamics

We compare the results of the mean-force dynamics, vacuum MD and whole system MD, under the initial conditions stated above. To capture their similarities and differences, we display their resultant dynamics of r_{13} and r_{23} in Fig. 5. The r_{13} and r_{23} of the whole system MD arising from the 100 different initial conditions for the reservoir particles have been averaged over at each time, although 100 trajectories are very few compared to possible choices. The averaged values and the upper and lower standard deviations for this statistical ensemble are shown as well in each panel of the figure.

An inspection over the vacuum MD in Fig. 5 quickly shows that the interatomic distances of chlorine atoms increase almost linearly with time, suggesting that the solute atoms move more freely than in the other dynamics, which simply reflects the dissociation reaction and possible drift in the argon cluster. This system of 100 particles in total is essentially floating in the vacuum and can expand making use of the energy released from the dissociation reaction. It is obvious that friction from the argon atoms on chlorine atoms is not as strong as in the other two systems composed of thousand particles.

On the other hand, the mean-force dynamics and the average of the whole system dynamics turn out to exhibit somewhat similar behaviors: the inter-chlorine distances increase promptly right after the dissociation begins up to about 0.4 ps and then slow down by friction and/or recoil of the statistical solvent in the mean-force dynamics. The figure suggests that the mean-force dynamics may underestimate the effects from the statistical solvents compared to the whole MD. A possible factor to account for this suggestion is that we did not take account of the nonlinear time-delay responses at all from the statistical solvent to the dynamical motions in the $(Q^{(1)}, P^{(1)})$ subsystem. To the dynamical subsystem, molecules in the statistical solvent seem to respond almost instantaneously within the tolerance of energy conservation. Indeed, our preliminary calculations that take account of such time-delay responses show that the rate of the expansion of the Cl system (not shown) tends to be suppressed by this effect.

However, the situation behind the average of the whole system MD dynamics is by far more complicated as suggested in Fig. 5. To show it, we superimpose 18 of randomly selected unaveraged MD results with the averaged one in Fig. 6. It turns out that the individual MD trajectories with different initial conditions (yet with the same total energy (temperature) and density) behave in a quite violent manner, and each is largely different from the average. The physical origin of the hard dependence on the initial conditions (of the reservoir molecules but not those of chlorine atoms) is ascribed to classical chaos in the present system. Indeed, we have computed the so-called Liapunov exponents for this large system and found the maximum value to be largely positive.[39] For these large chaotic systems, in which one can neither specify the initial conditions nor track the individual dynamics, only the average values are physically meaningful as possible observables. However it is obviously hard to judge whether a data set attained with MD calculations gives sufficiently convergent

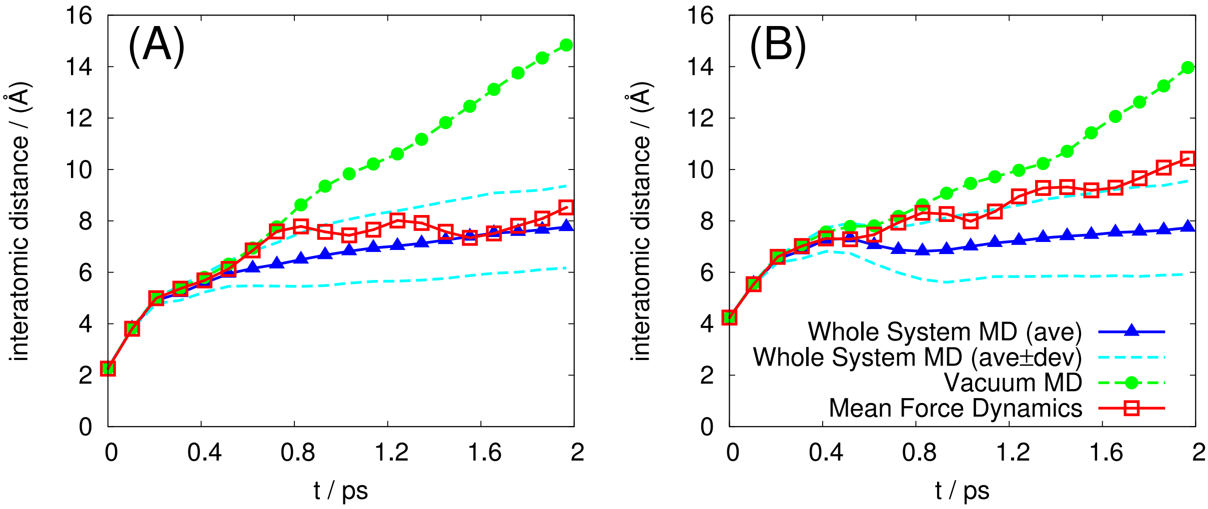

FIG. 5: Dynamics of the bond lengths. Panel (A) for r_{13} and (B) for r_{23}. Data points marked with square, filled triangle, and filled circle represent those given by the mean-force, the whole system MD (averaged), and the vacuum MD, respectively. The broken lines above and below the whole system MD curve indicate, respectively, the upper and lower standard deviation of the whole system MD data set.

result. Therefore one needs a careful thought in interpreting MD results for those systems that are chaotic and too large to run sufficiently enough trajectories.

On the other hand, the averaging in the mean-force dynamics is taken over the possible configurations of the surrounding statistical solvent. As stated before, the resultant paths of the mean-force do not represent any single classical-mechanical path, but each should manifest a representative dynamics reflecting the possible solvent configurations. The force averaging is thus rather similar to the way of natural averaging in the semiclassical Ehrenfest theory in mixed quantum and classical representation for nonadiabatic dynamics.[18]

It is obvious that a single trajectory calculation in the whole MD is much faster than the present method in terms of mixed dynamical and statistical representation. On the other hand, since the distribution functions with respect to the solvent configurations are available in this scheme, so do any statistical averages and moments. Even a thermodynamical limit may be accessible as discussed above. Efficiency in the computational aspect should be measured in terms of what one really aims at.[39]

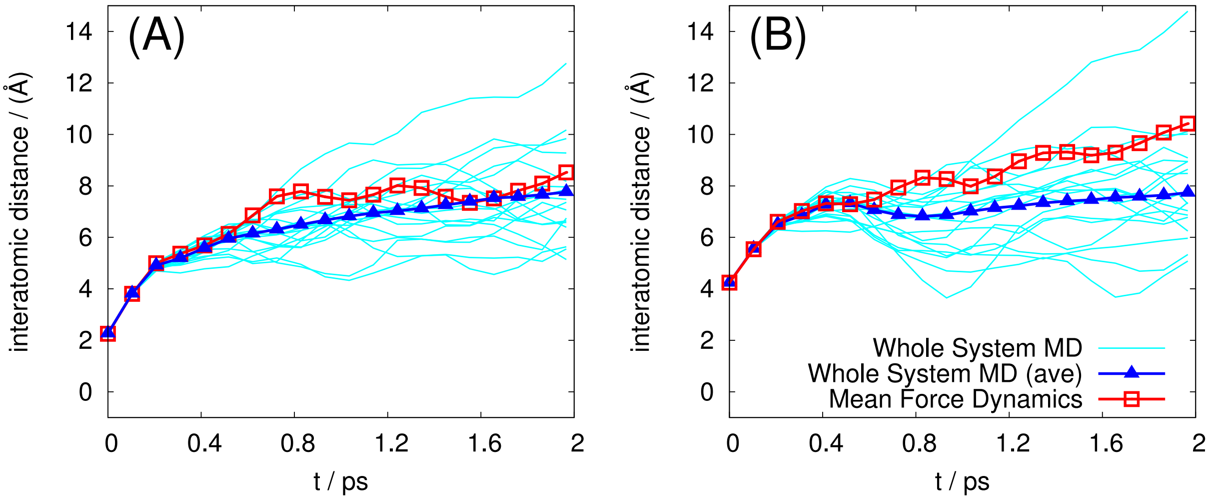

FIG. 6: Dynamics of the bond lengths. Panel (A) for r_{13} and (B) for r_{23}. Data points in the marks of square and filled circle represent those given by the mean-force and the whole system MD (averaged), respectively. The other thin curves represent the data of randomly selected 18 trajectories out of 100 ones for the whole system MD. The deviation of each trajectory data from the averaged one is seen to be quite large.

V. CONCLUDING REMARKS

We have proposed a theoretical framework that facilitates an attempt to bridge a gap between real-time dynamics and statistical mechanics based on a mixed dynamical and statistical representation. The dynamical subsystem, which is treated in classical and/or semiclassical, is embedded in a reservoir that is treated with statistical methods. The two subsystems are designed to exchange energy from time to time. Starting from a slight extension of the definitions of number of states and density of states in a well-defined energy conserving system (microcanonical ensemble), we have defined entropy functional, which is the function of the phase-space points for the dynamical subsystem. This functional is dressed with statistical weights from its corresponding reservoir. We further consider temperature functional, free energy functional, and chemical potential functional as the extensions of their corresponding quantities in statistical and thermodynamical quantities. The heart of this formalism to connect dynamics and statistical mechanics is an identity Eq. (25). The dynamical role of the Helmholtz free energy is clarified in Eq. (35). It turns out that particles in the dynamical subsystems are supposed to run on the free-energy functional surface if and only if the gradients of temperature functional are all zero. Also, we have suggested that the chemical potential functional defined here may provide a possible way to asymptotically connect a statistical reservoir composed of finite particles to that of the Avogadro (infinite) number.

Basically any theory for chemical reaction dynamics can be incorporated in the present mixed dynamical and statistical representation, provided that it is formulated along "classical" paths. For instance, quantization of the paths of the dynamical subsystem can be formally performed with, for instance, the methods of semiclassical approximation such as the WKB theory[43, 44] and a higher approximation we have recently proposed.[9, 10] Phase-space quantum mechanics like the Wigner phase-space distribution function[45–47] and the Dynamical Characteristic Function[48] will be also useful for this purpose. Incidentally, the delta-function in Eq. (9) has come from the Thomas-Fermi density of states, and hence it suggests a *formal* way to retrieve the quantum effects in the reservoir $\left(Q^{(2)}, P^{(2)}\right)$, if the higher order Moyal expansion of the quantum density of states is available. However, we have currently no idea on how such generalization can be realized in a practical level. Also, nonadiabatic electron dynamics associated with electron transfer and electronically excited state dynamics can be well treated by means of the path-branching representation,[11–18] which generates non-Born-Oppenheimer paths with the so-called force matrix, a generalization of Newtonian force. A very practical method used in electron dynamics is the semiclassical Ehrenfest theory, which generates purely classical paths on an average potential surface.[18] These are all within the scope of the works in our laboratory.

The present paper has been devoted mainly to presentation of the theoretical framework. However, we admit that there remain many methodological issues to overcome for this theory to be practical enough. Among others we are particularly interested in how to incorporate the nonlinear retarded responses between dynamical subsystem and reservoir.[39] Also, efficient and accurate numerical integrations over the $Q^{(2)}$ space is among the most important technical matters.

Appendix A: On the formula of Nagaoka and Yang

Return to Eq. (54), and herein define the density of states in $P^{(2)}$-space as

$$\Omega_P(\varepsilon) = \left[E - \frac{P^{(1)2}}{2} - \varepsilon\right]^{3N_2/2-1}. \tag{A1}$$

Then, back in Eq. (57), we find

$$\begin{aligned}\left.\frac{\partial}{\partial\varepsilon}\log\Omega_P\right|_{\varepsilon=\varepsilon^*} &= -\left(3N_2/2-1\right)\left[E - \frac{P^{(1)2}}{2} - \varepsilon^*\right]^{-1} \\ &= -\left(3N_2/2-1\right)\frac{\frac{2}{3N_2}}{k_B\mathbb{T}(\boldsymbol{\Xi})} \simeq -\frac{1}{k_B\mathbb{T}(\boldsymbol{\Xi})},\end{aligned} \tag{A2}$$

where the relation Eq. (66) has been used. The second derivative of $\log\Omega_P$ at the equilibrium potential energy is

$$\begin{aligned}\left.\frac{\partial^2}{\partial\varepsilon^2}\log\Omega_P\right|_{\varepsilon=\varepsilon^*} &= -\left(3N_2/2-1\right)\left[E - \frac{P^{(1)2}}{2} - \varepsilon^*\right]^{-2} \\ &= -\left(3N_2/2-1\right)\left(\frac{\frac{2}{3N_2}}{k_B\mathbb{T}(\boldsymbol{\Xi})}\right)^2 \\ &\simeq -\frac{2}{3N_2}\left(\frac{1}{k_B\mathbb{T}(\boldsymbol{\Xi})}\right)^2,\end{aligned} \tag{A3}$$

and therefore $\Omega_P(\varepsilon)$ is approximated after all as

$$\Omega_P(\varepsilon) \simeq \Omega_P(\varepsilon^*)\exp\left[-\frac{1}{k_B\mathbb{T}(\boldsymbol{\Xi})}\left(\varepsilon-\varepsilon^*\right) - \frac{1}{3N_2}\left(\frac{1}{k_B\mathbb{T}(\boldsymbol{\Xi})}\right)^2\left(\varepsilon-\varepsilon^*\right)^2\right]. \tag{A4}$$

(To give an idea about the ratio of the magnitudes between the first and second terms in the exponential function more intuitively, let us alternatively write Eq. (A4) as follows. Define the kinetic energy of the reservoir as K^* at the equilibrium, which is $K^* = E - \frac{P^{(1)2}}{2} - \varepsilon^*$. Then it is rewritten as

$$\Omega_P(\varepsilon) \simeq \Omega_P(\varepsilon^*)\exp\left[-\frac{3}{2}N_2\frac{(\varepsilon-\varepsilon^*)}{K^*} - \frac{3}{2}N_2\left(\frac{\varepsilon-\varepsilon^*}{K^*}\right)^2\right]. \tag{A5}$$

This form may seem more comfortable than Eq. (A4).)

Inserting Eq. (A4) to Eq. (55), and integrating the Dirac delta function $\delta\left(\varepsilon - V(Q^{(1)},Q^{(2)})\right)$ over the ε-coordinate, we find $R_i^{(1)}$ to be approximated as

$$R_i^{(1)} = -\frac{\int dQ^{(2)}\frac{\partial V^{(12)}(Q_i^{(1)},Q^{(2)})}{\partial Q_i^{(1)}}\exp\left[-\frac{1}{k_B\mathbb{T}(\boldsymbol{\Xi})}V(Q^{(1)},Q^{(2)}) - \frac{1}{3N_2}\left(\frac{1}{k_B\mathbb{T}(\boldsymbol{\Xi})}\right)^2\left(V(Q^{(1)},Q^{(2)})-\varepsilon^*\right)^2\right]}{\int dQ^{(2)}\exp\left[-\frac{1}{k_B\mathbb{T}(\boldsymbol{\Xi})}V(Q^{(1)},Q^{(2)}) - \frac{1}{3N_2}\left(\frac{1}{k_B\mathbb{T}(\boldsymbol{\Xi})}\right)^2\left(V(Q^{(1)},Q^{(2)})-\varepsilon^*\right)^2\right]}. \tag{A6}$$

Further, neglecting the contribution from the fluctuation, we can reduce the approximation to the first order as

$$R_i^{(1)} = -\frac{\int dQ^{(2)} \frac{\partial V^{(12)}(Q_i^{(1)}, Q^{(2)})}{\partial Q_i^{(1)}} \exp\left[-\frac{1}{k_B \mathbb{T}(\Xi)} V(Q^{(1)}, Q^{(2)})\right]}{\int dQ^{(2)} \exp\left[-\frac{1}{k_B \mathbb{T}(\Xi)} V(Q^{(1)}, Q^{(2)})\right]}. \tag{A7}$$

This looks akin to the Nagaoka and Yang formula of Eq. (3). Indeed, it is reproduced simply replacing $\mathbb{T}(\Xi)$ with T, where T is the canonical temperature. Therefore, it is justified to apply Eq. (3) in order to seek a state that will become equilibrium eventually, while the resultant pathways to the equilibrium point can be unrealistic or unphysical. (Incidentally, it should be remarked that the exponential function involved in Eq. (A7) arose from the density of state in momentum space Eq. (A1) but not from the original Boltzmann distribution.)

Acknowledgments

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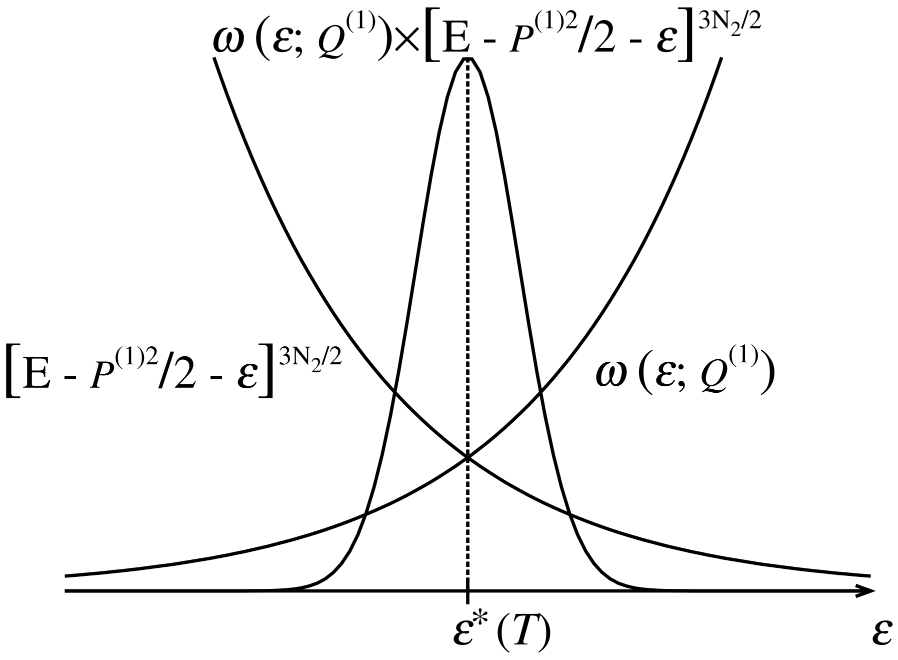
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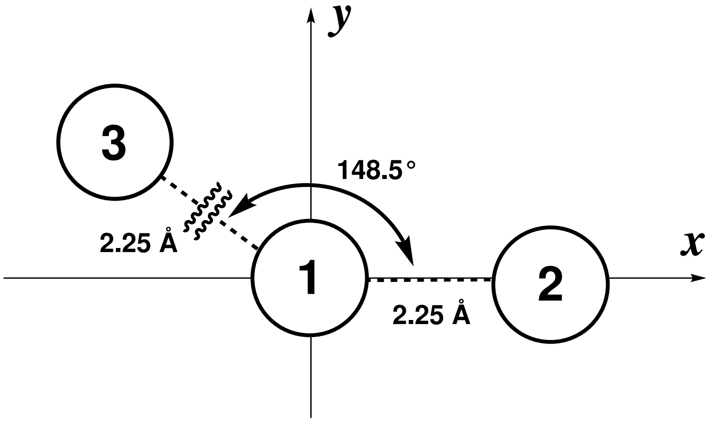
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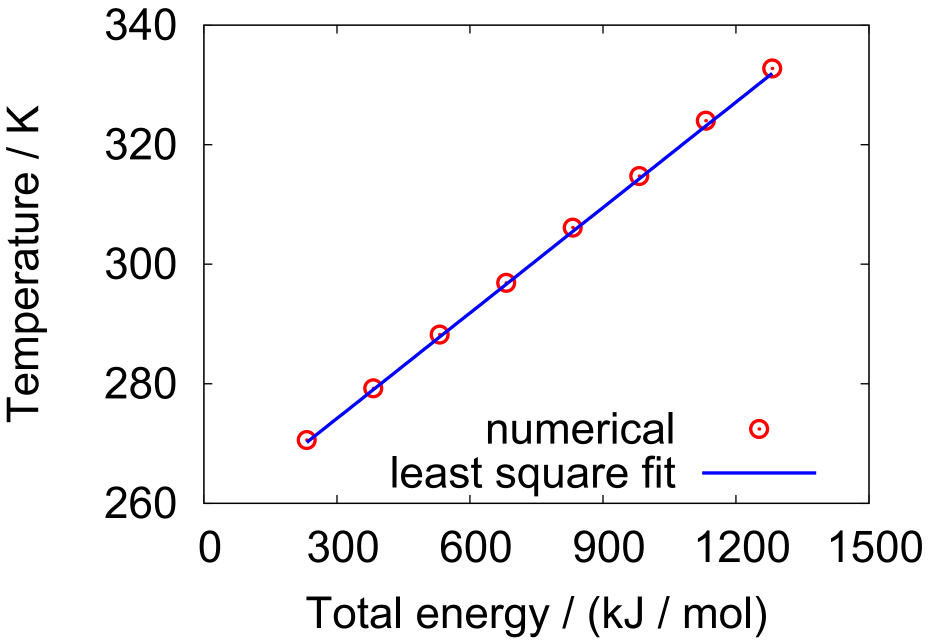
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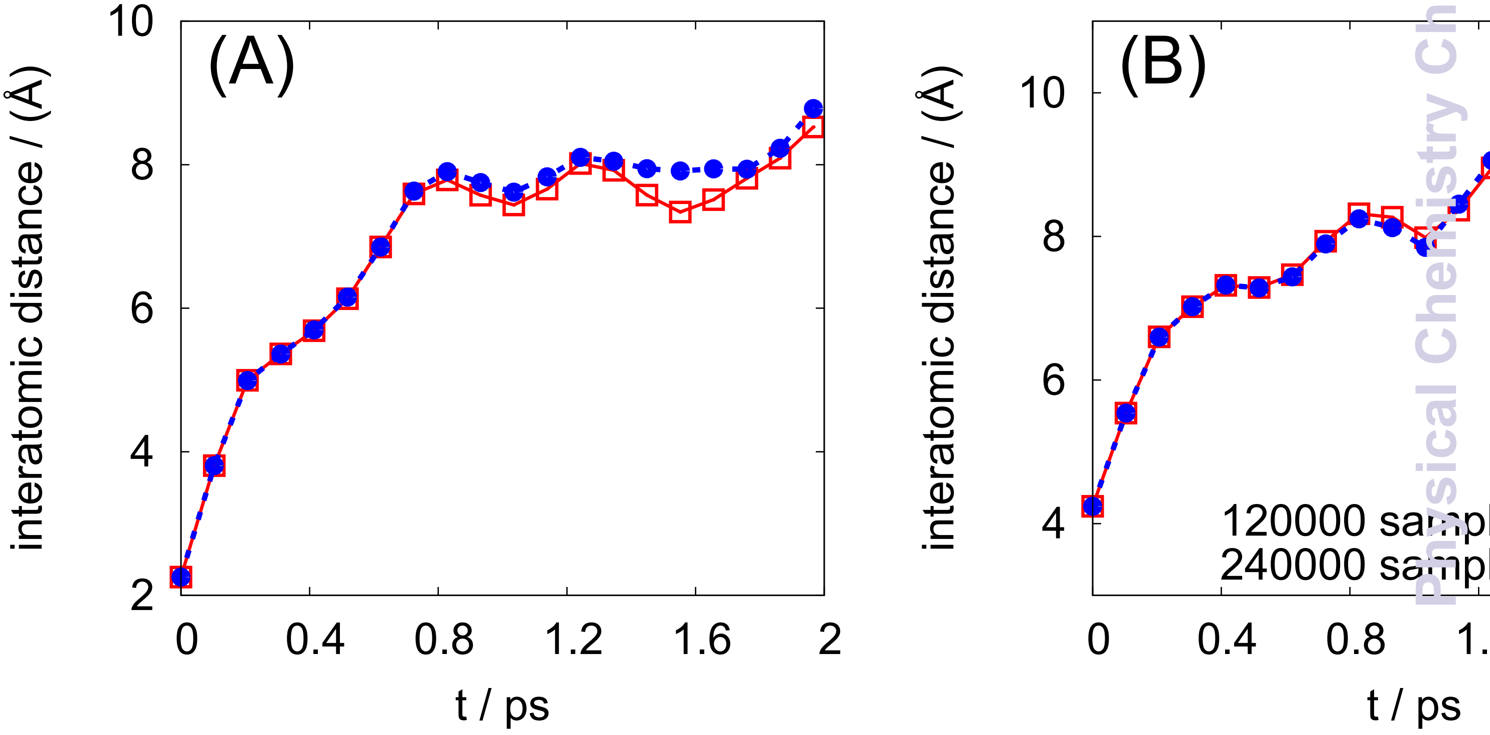
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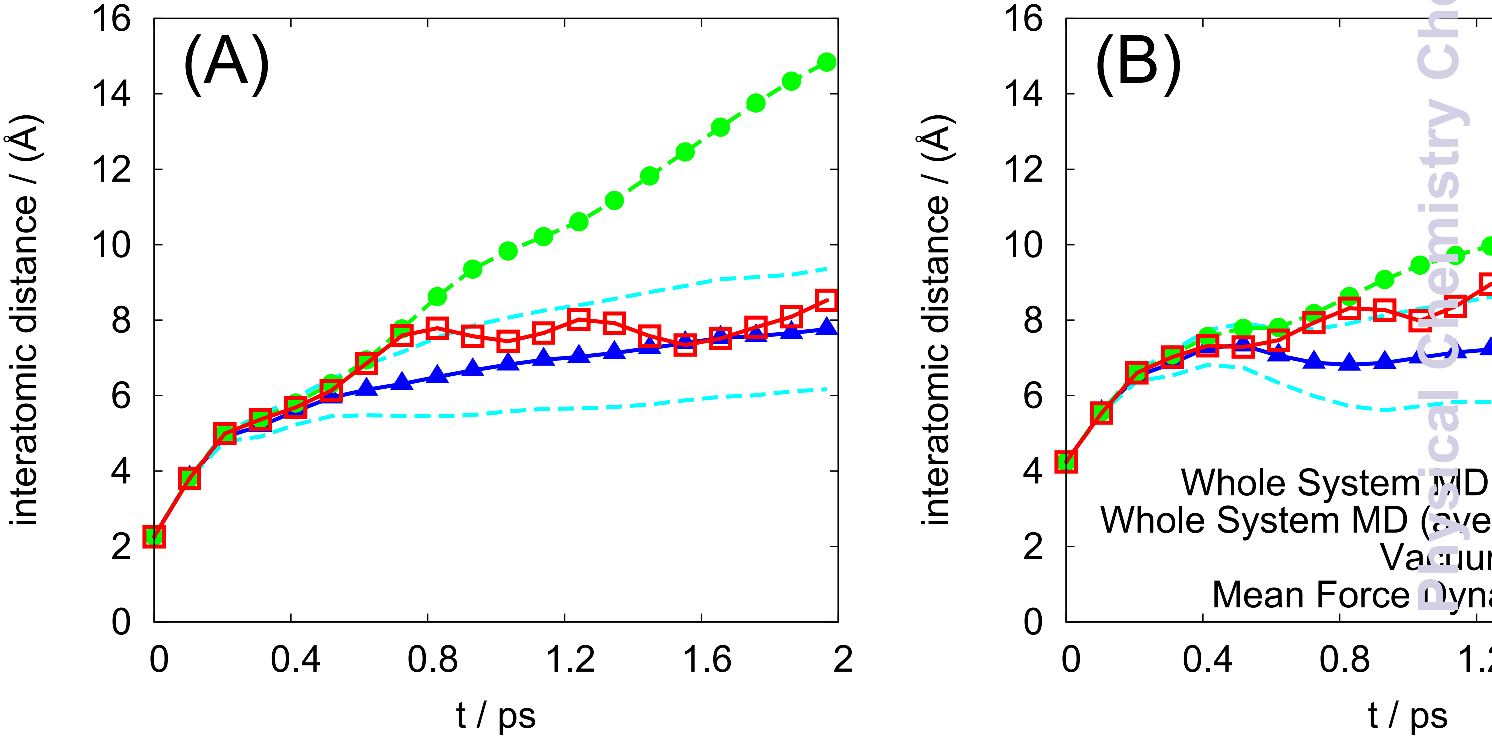
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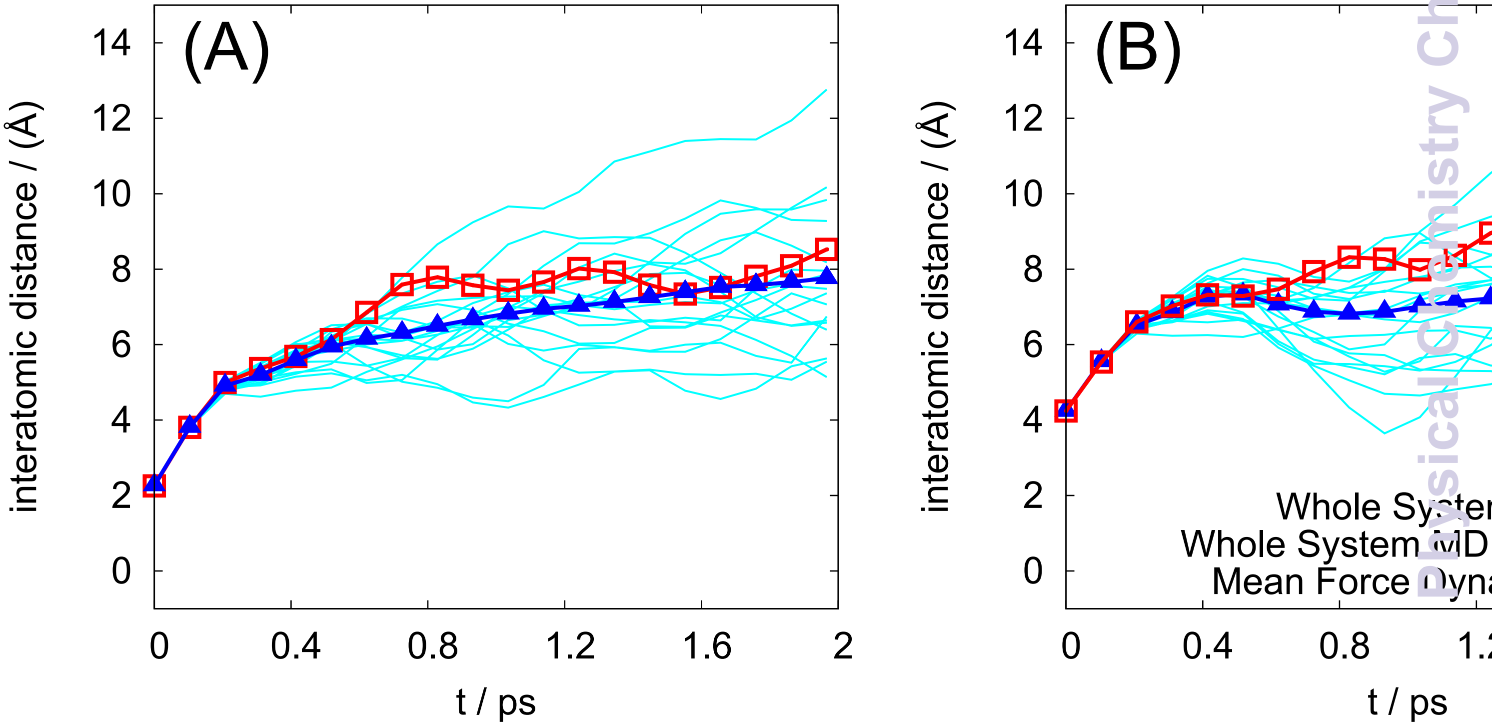
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