Technical note:
Estimating relative entropies of path ensembles

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We consider the problem of estimating the relative Kolmogorov-Sinai entropies of path (trajectory) ensembles aided by transition path sampling biased by trajectory activity. We loosely follow the development and terminology in [1].

PRELIMINARIES

Consider a system of N particles, with a point in phase space for this system denoted by x. Let X denote a trajectory of the system observed at discrete intervals for a fixed total observation time t_{obs}. For convenience, we write $X \equiv \{x_0, x_1, \ldots, x_T\}$, where the subscripted x_t denote these discrete observation times indexed by $t = 0, 1, \ldots, T$.

The equilibrium dynamics of this system is given by the probability functional (sometimes termed a "path ensemble")

$$P_0[A] = Z_0^{-1}\, q_0[X] \tag{1}$$

$$Z_0 = \int dX\, q_0[X] \tag{2}$$

where Z_0 is a normalizing constant, or partition function over trajectories, the integral is taken over the entire phase space, dX is an appropriate path differential or measure, and $q_0[X] \geq 0$ is an unnormalized probability density.

For simplicity, we suppose here that the system evolves under Hamiltonian dynamics with initial phase space points x_0 canonical distributed accordng to an equilibrium NVT ensemble:

$$q_0[X] = e^{-\beta H(x_0)} \tag{3}$$

where β denotes the inverse temperature $1/k_B T$ and $H(x)$ the Hamiltonian for the system. This assumption is not essential to the subsequent analysis and suggested sampling scheme; other dynamical models (e.g. Langevin, Brownian) or ensembles (e.g. NPT) can be treated by substituting alternative definitions of $q_0[X]$ that will be related to the exponentiated path action.

Define an order parameter related to the dynamical *activity* of the sytem

$$K[X] \equiv \sum_{t=1}^{T} ||x_t - x_{t-1}||^2 \tag{4}$$

We consider modified path ensembles $P_s[X]$ parameterized by the conjugate field variable s:

$$P_s[X] = Z_s^{-1}\, q_s[X] \tag{5}$$

$$Z_s = \int dX\, q_s[X] \tag{6}$$

$$q_s[X] = q_0[X]\, e^{-s\, K[X]} \tag{7}$$

When $s < 0$, trajectories with large activity $K[X]$ will be more frequently sampled than in the equilibrium ensemble $P_0[X]$. Similarly, when $s > 0$, these trajectories will be suppressed. Choosing $s = 0$ recovers equilibrium dynamics.

KOLMOGOROV-SINAI TRAJECTORY ENTROPY

Suppose we are interested in the Kolmogorov-Sinai entropy of trajectories for some arbitrary path ensemble $P[X] = Z^{-1} q[X]$:

$$S\{P[X]\} \equiv -\int dX\, P[X]\, \ln P[X] \tag{8}$$

$$= -\langle \ln P[X] \rangle \tag{9}$$

$$= -\langle \ln q[X] \rangle + \ln Z \tag{10}$$

While it is difficult to compute the *absolute* entropy for a given path ensemble due to the difficulty of determining the absolute normalization constant Z, we are often only interested in the *relative entropy* of two path ensembles. The relative entropy of the path ensembles $P_s[X]$ at different values of s, for example, is:

$$\begin{aligned}\Delta S(s_1, s_2) &\equiv S\{P_2[X]\} - S\{P_1[X]\} \\ &= -\langle \ln P_{s_2}[X] \rangle_{s_2} + \langle \ln P_{s_1}[X] \rangle_{s_1} \\ &= -\langle \ln q_{s_2}[X] \rangle_{s_2} + \langle \ln q_{s_1}[X] \rangle_{s_1} + \ln(Z_{s_2}/Z_{s_1})\end{aligned} \tag{11}$$

This quantity involves only expectations of known functions $q_s[X]$ and *ratios* of normalization constants Z_{s_2}/Z_{s_1}, which are readily computed by standard simulation approaches.

For convenience, we define the functional

$$U_s[X] \equiv -\ln q_s[X] = -\ln q_0[X] + s\, K[X] \tag{12}$$

which, for the case of Hamiltonian dynamics, reduces to

$$U_s[X] = \beta H(x_0) + s\,K[X] \tag{13}$$

This functional is analogous to an *internal energy* with contribution from an external field parameterized by s.

Similarly, we define a quantity F_s that is analogous to a free energy:

$$F_s \equiv -\ln Z_s \tag{14}$$

With these definitions, the relative entropy can be written a form reminiscent of a restatement of the Helmholtz free energy:

$$\Delta S(s_1, s_2) = [\langle U_{s_2}\rangle_{s_2} - \langle U_{s_1}\rangle_{s_1}] - [F_{s_2} - F_{s_1}] \tag{15}$$

Alternatively, consider the computation of the relative entropy of the subset of trajectories in the unbiased path ensemble $P_0[X]$ for which $K[X] > K_*$. We define a modified path ensemble $P_*[X]$ such that

$$\begin{aligned} P_*[X] &= Z_*^{-1} q_*[X] \\ Z_*[X] &= \int dX\, q_*[X] \\ q_*[X] &= \chi_*[X]\, q_0[X] \end{aligned} \tag{16}$$

where $\chi_*[X]$ is an indicator function such that

$$\chi_*[X] = \begin{cases} 1 & \text{if } K[X] > K_* \\ 0 & \text{otherwise} \end{cases} \tag{17}$$

This gives the relative entropy

$$\begin{aligned} \Delta S_* &= S\{P_*[X]\} - S\{P_0[X]\} \\ &= -\langle \ln q_*[X]\rangle_* + \langle \ln q_0[X]\rangle_0 + \ln(Z_*/Z_0) \\ &= [\langle U_0\rangle_* - \langle U_0\rangle_0] - [F_* - F_0] \end{aligned} \tag{18}$$

The next section shows how to efficiently estimate these quantities from simulations such as those conducted in [1].

EFFICIENT ESTIMATION FROM SIMULATION

Suppose we have selected K values of the field s, denoted $\{s_1, \ldots, s_K\}$, from which we have sampled N_k i.i.d. trajectories from each of the corresponding path ensembles $P_{s_k}[X]$:

$$X_{kn} \sim P_{s_k}[X] \;,\; n = 1, \ldots, N_k \tag{19}$$

These samples can be generated efficiently from transition path sampling [2] simulations, potentially employing a replica-exchange scheme [3] among field values to ensure ergodic sampling from all selected values s_k. We will additionally use an indexing scheme where all $N = \sum_{k=1}^K N_k$ samples are denoted by X_n indexed by a single $n = 1, \ldots, N$, where the order in which samples coming from different $P_{s_k}[X]$ are arranged is irrelevant.

We can optimally estimate path averages of the form

$$\langle \mathcal{F}\rangle \equiv \int dX\, P[X]\, \mathcal{F}[X] \tag{20}$$

and ratios of normalization constants Z_i/Z_j from trajectories sampled from multiple path ensembles (in the sense that the estimator is *asymptotically efficient*) using a recently-developed formalism [4] based on the optimal *extended bridge sampling* estimators developed in statistics [5–8] and recently applied to statistical mechanics [9].

To compute the optimal estimator, we first solve a set of K nonlinear equations self-consistently for the estimates $\hat{Z}_{s_1}, \ldots, \hat{Z}_{s_K}$ of the normalizing constants $Z_{s_1}, \ldots, Z_{s_K}$:

$$\begin{aligned} \hat{Z}_{s_i} &= \sum_{n=1}^N \frac{q_{s_i}[X_n]}{\sum_{k=1}^K N_k\, \hat{Z}_{s_k}^{-1}\, q_{s_k}[X_n]} \\ &= \sum_{n=1}^N \frac{q_0[X_n]\, e^{-s_i K[X_n]}}{\sum_{k=1}^K N_k\, \hat{Z}_{s_k}^{-1}\, q_0[X_n]\, e^{-s_k K[X_n]}} \\ &= \sum_{n=1}^N \left[\sum_{k=1}^K N_k\, \hat{Z}_{s_k}^{-1}\, e^{-(s_k - s_i)K[X_n]}\right]^{-1} \end{aligned} \tag{21}$$

Though any scheme to solve the K coupled nonlinear equations indexed by $i = 1, \ldots, K$ can be used here, several efficient and numerically stable approaches are detailed in [9]. Note that the $\hat{Z}_{s_i}$ are only determined up to a multiplicative constant, such that only ratios $\hat{Z}_{s_i}/\hat{Z}_{s_j}$ are meaningful.

For an arbitrary path ensemble $P[X] = Z^{-1}q[X]$, we can estimate the normalization constant Z up to the same normalization constant without further iteration by

$$\hat{Z} = \sum_{n=1}^N \frac{q[X_n]}{\sum_{k=1}^K N_k\, \hat{Z}_{s_k}^{-1}\, q_{s_k}[X_n]} \tag{22}$$

For some path ensemble $P_s[X]$ in particular, even if no samples are collected from this path ensemble, this reduces to

$$\hat{Z}_s = \sum_{n=1}^N \left[\sum_{k=1}^K N_k\, \hat{Z}_{s_k}^{-1}\, e^{-(s_k - s)K[X_n]}\right]^{-1} \tag{23}$$

Path expectations $\langle \mathcal{F}\rangle$ for a path function $\mathcal{F}[X]$ for an arbitrary path ensemble $P[X] = Z^{-1}q[X]$ can also be easily computed. Define a the normalized weight function

$$w_n = \hat{Z}^{-1} \frac{q[X_n]}{\sum_{k=1}^K N_k\, \hat{Z}_{s_k}^{-1}\, q_{s_k}[X_n]} \tag{24}$$

Note that, because of the large dynamic range that can be assumed by quantities like w_n and Z_s, it is more numerically stable to work with their logarithms.

The path average estimate $\bar{\mathcal{F}} \approx \langle \mathcal{F} \rangle$ is then given by

$$\bar{\mathcal{F}} = \sum_{n=1}^{N} w_n \, \mathcal{F}[X_n] \tag{25}$$

For example, we estimate $\langle U_s \rangle_s$ by

$$\langle U_s \rangle_s \approx \sum_{n=1}^{N} w_{ns} \, U_s[X_n] \tag{26}$$

where the s-dependent weight w_{ns} has simple form:

$$w_{ns} = \hat{Z}_s^{-1} \left[\sum_{k=1}^{K} N_k \, \hat{Z}_{s_k}^{-1} \, e^{-(s_k - s) K[X_n]} \right]^{-1} \tag{27}$$

This allows us to estimate the relative entropy between two s-ensembles as

$$\begin{aligned} \Delta \hat{S}(s_1, s_2) = &\sum_{n=1}^{N} \left(w_{ns_2} \, U_{s_2}[X_n] - w_{ns_1} \, U_{s_1}[X_n] \right) \\ &+ \ln(\hat{Z}_{s_2} / \hat{Z}_{s_1}) \end{aligned} \tag{28}$$

or the relative entropy of the subset of equilibrium trajectories with $K[X] > K_*$ for $s = 0$ by

$$\Delta S_* = \sum_{n=1}^{N} (w_{n*} - w_{n0}) \, U_0[X_n] + \ln(\hat{Z}_* / \hat{Z}_0) \tag{29}$$

where w_{n*} and Z_* contain contributions from only those trajectories with $K[X] > K_*$:

$$w_{n*} = \hat{Z}_*^{-1} \, \chi_*[X] \left[\sum_{k=1}^{K} N_k \, \hat{Z}_{s_k}^{-1} \, e^{-s_k K[X_n]} \right]^{-1} \tag{30}$$

$$Z_* = \sum_{n=1}^{N} \chi_*[X] \left[\sum_{k=1}^{K} N_k \, \hat{Z}_{s_k}^{-1} \, e^{-s_k K[X_n]} \right]^{-1} \tag{31}$$

Estimation of the statistical error in these estimates (through estimation of the asymptotic variance) is more involved, but mechanically straightforward; the procedure is described in detail and illustrated in [4]. The algebra is lengthy and unilluminating, but the Python `pymbar` package [available at `http://www.simtk.org/home/pymbar`] has a function to do this analysis automatically.

OTHER OBSERVABLES

(There is a slight change of notation here.)

Expected activity as a function of field s

We can estimate $\langle K \rangle_s$ as

$$\langle K \rangle_s \approx \sum_{n=1}^{N} w_n(s) \, K[X_n] \tag{32}$$

where

$$\begin{aligned} w_n(s) &= \hat{Z}(s)^{-1} \left[\sum_{k=1}^{K} N_k \, \hat{Z}_k^{-1} \, e^{-(s_k - s) K[X_n]} \right]^{-1} \\ \hat{Z}(s) &= \sum_{n=1}^{N} \left[\sum_{k=1}^{K} N_k \, \hat{Z}_k^{-1} \, e^{-(s_k - s) K[X_n]} \right]^{-1} \end{aligned} \tag{33}$$

Susceptibility

We can also estimate the susceptibility, $\chi(s) \equiv -\partial \langle K \rangle_s / \partial s$, in either of two mathematically (but not numerically) equivalent ways. Differentiating our estimate of $\langle K \rangle_s$ produces an estimator expression

$$\begin{aligned} \chi(s) &= \frac{\partial \langle K \rangle_s}{\partial s} \\ &\approx \sum_{n=1}^{N} \frac{\partial w_n}{\partial s}(s) \, K[X_n] \end{aligned} \tag{34}$$

where the weight derivatives are given by

$$\frac{\partial w_n}{\partial s}(s) = w_n(s) \left(-K[X_n] + \langle K \rangle_s \right) \tag{35}$$

Alternatively, the mathematically equivalent fluctuation form of $\chi(s)$ can be used,

$$\begin{aligned} \chi(s) &= \langle (K - \langle K \rangle_s) \rangle_s \\ &= \left\langle K^2 \right\rangle_s - \langle K \rangle_s \end{aligned} \tag{36}$$

and the two moments estimated separately. While this expression may run into numerical precision issues if $\left\langle K^2 \right\rangle$ and $\langle K \rangle^2$ are individually large but have a small difference, their uncertainties can be propagated to produce an uncertainty estimate for $\chi(s)$ (see Ref. [4]).

Probability density of K

The probability density $p(K; s)$ or free energy $f(K; s) = -\ln p(K; s)$ can also be estimated by use of the functional $\mathcal{F}[X] \equiv h(K[X] - K')$, where $h(x)$ here denotes a positive kernel localized around $x = 0$, normalized such that $\int dx \, h(x) = 1$, such as a top-hat function or Gaussian:

$$p(K'; s) \approx \langle h(K[X] - K') \rangle_s \tag{37}$$

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