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Information thermodynamics of transition paths between multiple mesostates

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between two mesostates generate a set of trajectories [12] or sample the flux of trajectories [11,13,14] of a given trajectory type. This generates microstate probability distributions conditioned on each trajectory type (e.g., → , → , → , →) whose average entropy over all subensembles is less than the system entropy in the full equilibrium ensemble; the reduction in entropy is the mutual information between the system microstate and trajectory type [Eq. (10c)]. By resolving one of these variables, either the current trajectory type or the system microstate, information is gained about the other.

m (system finishes a reactive trajectory from m to m). These terms are equal in magnitude and have opposite sign since the two sets of transitions leading to changes of trajectory type are

$$\dot{}^{\,\mathrm{irr}}(\boldsymbol{\Phi}, {}_{-}, {}_{+}) = \sum_{s} (s)\dot{\Sigma}_{s} \tag{25a}$$

$$= \sum_{-,+}\sum_{\boldsymbol{\phi},\boldsymbol{\phi}'} {}^{s}_{\boldsymbol{\phi}\boldsymbol{\phi}'} (\boldsymbol{\phi}', s)\left[\ln \frac{{}_{\boldsymbol{\phi}\boldsymbol{\phi}'}\pi(\boldsymbol{\phi}')}{{}_{\boldsymbol{\phi}'\boldsymbol{\phi}}\pi(\boldsymbol{\phi})} + \ln \frac{({}_{-}|\boldsymbol{\phi}')}{({}_{-}|\boldsymbol{\phi})} + \ln \frac{({}_{+}|\boldsymbol{\phi})}{({}_{+}|\boldsymbol{\phi}')}\right] \tag{25b}$$

$$= \sum_{+}\sum_{\boldsymbol{\phi}\boldsymbol{\phi}'} {}_{\boldsymbol{\phi}\boldsymbol{\phi}'}\pi(\boldsymbol{\phi}') \; ({}_{+}|\boldsymbol{\phi}) \ln \frac{({}_{+}|\boldsymbol{\phi})}{}$$

the joint entropy $(\boldsymbol{\phi}, \ _{-})$ to quantify the irreversible entropy production,

$$\dot{}_{\text{irr}}(\boldsymbol{\Phi}, \ _{-}) = \sum_{\boldsymbol{\phi},\boldsymbol{\phi}'} \sum_{-} \ _{\boldsymbol{\phi}\boldsymbol{\phi}'}\pi(\boldsymbol{\phi}') \ (\ _{-}|\boldsymbol{\phi}') \ln \frac{_{\boldsymbol{\phi}\boldsymbol{\phi}'} \ (\boldsymbol{\phi}', \ _{-})}{_{\boldsymbol{\phi}'\boldsymbol{\phi}} \ (\boldsymbol{\phi}, \ _{-})} \tag{37a}$$

$$= \sum_{\boldsymbol{\phi},\boldsymbol{\phi}' \notin m} \sum_{\neq} \ _{\boldsymbol{\phi}\boldsymbol{\phi}'}\pi(\boldsymbol{\phi}') \ (\ _{-} = m \ |\boldsymbol{\phi}')$$

$$\times \ \ln \frac{(\ _{-} = m \ |\boldsymbol{\phi}')}{(}$$

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APPENDIX B: TRAJECTORY-ORIGIN SUBENSEMBLES

The transition rate for a $\boldsymbol{\phi}' \to \boldsymbol{\phi}$ transition within a trajectory-origin subensemble is unchanged from the original system dynamics $_{\phi\phi'}$ since they are Markovian. The local detailed-balance relation that quantifies time asymmetry is

$$\frac{\bar{}_{\phi\phi'}\ (\boldsymbol{\phi}',\ _{-})}{\bar{}_{\phi'\phi}\ (\boldsymbol{\phi},\ _{-})} = \frac{(\ _{-}|\boldsymbol{\phi}')}{(\ _{-}|\boldsymbol{\phi})}. \tag{B1}$$

Therefore a $\boldsymbol{\phi}' \to \boldsymbol{\phi}$ transition where $(\ _{-}|\boldsymbol{\phi})$ changes has some time asymmetry in the trajectory-origin subensembles. The net flux for a $\boldsymbol{\phi}' \to \boldsymbol{\phi}$ transition within subensemble $_{-}$ is the difference between the forward and reverse transition frequencies:

$$\bar{}_{\phi\phi'}\ (\boldsymbol{\phi}',\ _{-}) - \bar{}_{\phi'\phi}\ (\boldsymbol{\phi},\ _{-}) = {}_{\phi\phi'}\pi(\boldsymbol{\phi}')\ (\ _{-}|\boldsymbol{\phi}') - {}_{\phi'\phi}\pi(\boldsymbol{\phi})\ (\ _{-}|\boldsymbol{\phi}) \tag{B2a}$$

$$= {}_{\phi\phi'}\pi(\boldsymbol{\phi}')[\ (\ _{-}|\boldsymbol{\phi}') - (\ _{-}|\boldsymbol{\phi})]. \tag{B2b}$$

Thus there is net flux within the subensemble toward microstates with lower values of $(\ _{-}|\boldsymbol{\phi})$; that is, a net flux away from the origin mesostate $_{-} = m$ towards the -1 other mesostates, which act as absorbing boundary conditions for dynamics in subensemble $_{-} = m$. To maintain steady state within the subensemble, trajectories are regenerated in mesostate m with flux equal to the total flux of trajectories departing $_{-} = m$ to all other mesostates,

$$\sum_{\neq} \nu_{\to}\ . \tag{B3}$$

Now consider the change in joint entropy $(\boldsymbol{\Phi},\ _{-})$. As before, the joint entropy is split into three contributions

$$0 = \mathrm{d}\ (\boldsymbol{\Phi},\ _{-}) \tag{B4a}$$

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The environment entropy change for transitions within a subensemble is

$$\dot{}^{\,\text{env}}(\Phi, \ \_) = \sum_{\phi,\phi'} \sum_{\_} \ _{\phi\phi'}\pi(\phi') \ (\ \_|\phi') \ln \frac{_{\phi\phi'}}{_{\phi'\phi}} \tag{B6a}$$

$$= \sum \ \sum_{\phi,\phi' \notin m \ \neq} \ _{\phi\phi'}\pi(\phi') \ (\ \_ = m \ |\phi') \ln \frac{_{\phi\phi'}}{_{\phi'\phi}}, \tag{B6b}$$

which is the average energy change in the system for dynamics in each trajectory-origin subensemble. This cancels the first term in the expression for subensemble entropy change (B5c), since these two contributions account for all energy changes at steady state, which by definition is zero.

The irreversible entropy production for transitions within a subensemble is

$$\dot{}^{\,\text{irr}}(\Phi, \ \_) = \sum_{\phi,\phi'} \sum_{\_} \ _{\phi\phi'}\pi(\phi') \ (\ \_|\phi') \ln \frac{_{\phi\phi'} \ (\phi', \ \_)}{_{\phi'\phi} \ (\phi, \ \_)} \tag{B7a}$$

$$= \sum \ \sum_{\phi,\phi' \notin m \ \neq} \ _{\phi\phi'}\pi(\phi') \ (\ \_ = m \ |\phi') \ln \frac{(\ \_ = m \ |\phi')}{(\ \_ = m \ |\phi)} \tag{B7b}$$

$$= - \ \dot{}^{\,\Phi}[\Phi; \ \_] \tag{B7c}$$

$$\geqslant 0, \tag{B7d}$$

where $\sum_{\phi,\phi' \notin m \ \neq}$ indicates a sum over microstates ϕ and ϕ', neither of which is in any mesostate m other than m, and $\dot{}^{\,\Phi}[\Phi; \ \_]$ is the information change due to system transitions within the same trajectory-origin subensemble.

The irreversible entropy production within a subensemble $\_ = m$ is

$$(\ \_ = m \ )\dot{\Sigma}_m = \sum_{\phi,\phi' \notin m \ \neq} \ _{\phi\phi'}\pi(\phi') \ (\ \_ = m \ |\phi') \ln \frac{(\ \_ = m \ |\phi')}{(\ \_ = m \ |\phi)}. \tag{B8}$$

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