Coarse-Grained Dynamics Assuming Equal-Probability for Transient States

<table>
<thead>
<tr>
<th>著者</th>
<th>NOGAWA Tomoaki</th>
</tr>
</thead>
<tbody>
<tr>
<td>雑誌名</td>
<td>Interdisciplinary Information Sciences</td>
</tr>
<tr>
<td>卷</td>
<td>19</td>
</tr>
<tr>
<td>号</td>
<td>1</td>
</tr>
<tr>
<td>巻</td>
<td>57-60</td>
</tr>
<tr>
<td>年</td>
<td>2013-08-22</td>
</tr>
<tr>
<td>URL</td>
<td><a href="http://hdl.handle.net/10097/57193">http://hdl.handle.net/10097/57193</a></td>
</tr>
<tr>
<td>doi</td>
<td>10.4036/iis.2013.57</td>
</tr>
</tbody>
</table>
Coarse-Grained Dynamics Assuming Equal-Probability for Transient States

Tomoaki NOGAWA*

Department of Mathematics, Tohoku University, Sendai 980-8579, Japan

Received April 1, 2013; final version accepted July 2, 2013

We propose a framework to describe nonequilibrium dynamics with respect to a set of macroscopic variables by assuming that microscopic states that have the same corresponding macroscopic variables appear with equal-probability, i.e., the nonequilibrium state is treated as an extended microcanonical ensemble. The method is numerically examined by the relaxation dynamics of the two-dimensional Potts model with temperature fixed, and it is found that the two-variable (energy and magnetization) description gives much more quantitatively accurate prediction than the one-variable (energy) description, which is sufficient for equilibrium states. This means that the transient states are difficult to be approximated by the equilibrium state fixing temperature, but possible by the one fixing temperature and magnetic field.

KEYWORDS: nonequilibrium dynamics, master equation, Potts model

1. Introduction

One of the remarkable properties of equilibrium states of macroscopic systems is that when a set of extensive variables are given, realized states cannot be distinguished by macroscopic statistical measurements although they are microscopically different from each other. This is the result of the law of large numbers for microcanonical ensemble, where microcanonical ensemble means an ensemble of an isolated system in which a number of extensive variables, not necessarily including internal energy, are fixed. For instance, in a particle system where internal energy, number of particles and volume are fixed, the phase of the system and properties such as spatial correlation function of density fluctuation is uniquely determined. However, nonequilibrium states, e.g., a transient state between two equilibrium states, can take a macroscopically different states according to the history until arriving the transient state even though they have the same set of extensive variables. As well known, the time development equation derived by the Mori–Zwanzig’s projection operator method [1] is a stochastic process including a memory effect. The loss of Markovness is a result of the overreduction of the degrees of freedom of the system. To eliminate the nonuniqueness of the macroscopic state, one is required to describe the system by using larger number of extensive variables. A nonequilibrium system may require all the degrees of freedom of the system. Such a system, however, cannot be an object of statistical physics. In other words, the system that can be understood in the sense of statistical physics should be uniquely identified by a small number of extensive variables, at least approximately. In this article, we report the attempt to describe the nonlinear nonequilibrium states by identifying it with equal probability ensemble fixing extensive variables, and show the results examining how good it actually works [2].

2. Derivation of the Markov Process on Reduced Dynamics Assuming Equal-Probability for Transient States

Time evolution of the probability $p(\tilde{X}, t)$ that the system takes the microscopic state $\tilde{X} = (X_1, X_2, \ldots, X_N)$ at time $t$ is generally described by the following master equation:

$$\frac{\partial p(\tilde{X}, t)}{\partial t} = \sum_{\tilde{X}'} \left[ \tilde{w}(\tilde{b}; \tilde{X}|\tilde{X}') p(\tilde{X}', t) - \tilde{w}(\tilde{b}; \tilde{X}'|\tilde{X}) p(\tilde{X}, t) \right].$$

(2.1)

Here $\tilde{X}$ is a countable discrete state. In addition, $\tilde{w}$ is a transition probability rate at given $\tilde{b} = (b_1, b_2, \ldots, b_n)$, which is a set of intensive parameters such as temperature and pressure, given by the environment.

Let us consider the projection from a microscopic state $\tilde{X}$ to macroscopic variables $\tilde{A} = (A_1, A_2, \ldots, A_n)$ with $(n \ll N)$. We denote the surjective function as $A_\tilde{X}$. Here we suppose that $\tilde{A}$ is conjugate to $\tilde{b}$, such that the equilibrium distribution function $p_{eq}(\tilde{A})$ is proportional to the Boltzmann factor $e^{-b,A_\tilde{X}}$.

*Corresponding author. E-mail: nogawa@math.tohoku.ac.jp
The probability that the system takes \( \tilde{A} \) is given by
\[
P(\tilde{A}, t) = \sum_{\tilde{X}} p(\tilde{X}, t) \delta_{\tilde{X}, \tilde{A}}. \tag{2.2}
\]

In general, the time evolution of \( P(\tilde{A}, t) \) cannot be represented by a Markov process closed in \( \tilde{A} \) but is dependent on the history.

We assume that the all microscopic states having \( \tilde{A} \) appear with the same probability, that is,
\[
p(\tilde{X}, t) = \frac{P(\tilde{A}, t)}{g(\tilde{A})}, \quad g(\tilde{A}) \equiv \sum_{\tilde{X}} \delta_{\tilde{X}, \tilde{A}}. \tag{2.3}
\]

Here \( g(\tilde{A}) \) is a total number of states which takes \( \tilde{A} \). By multiplying \( \delta_{\tilde{X}, \tilde{A}} \) to Eq. (2.1) and taking a summation over \( \tilde{X} \), we obtain a closed equation with respect to \( P(\tilde{A}, t) \):
\[
\frac{\partial P(\tilde{A}, t)}{\partial t} = \sum_{\tilde{X}} \left[ W(\tilde{b}; \tilde{A}, \tilde{X}) P(\tilde{A}, t) - W(\tilde{b}; \tilde{X}) P(\tilde{A}, t) \right]
\]
where
\[
W(\tilde{b}; \tilde{A}, \tilde{X}) \equiv \frac{1}{g(\tilde{A})} \sum_{\tilde{X}, \tilde{X}} \delta_{\tilde{X}, \tilde{A}} \tilde{w}(\tilde{b}; \tilde{X}, \tilde{X}) \delta_{\tilde{X}, \tilde{A}} = \left\{ \delta_{\tilde{X}, \tilde{A}} \tilde{w}(\tilde{b}; \tilde{X}, \tilde{X}) \right\}_{\tilde{X}}. \tag{2.5}
\]

The macroscopic transition rate \( W \) is regarded as an expectation value of \( \tilde{w} \) in “microcanonical” equilibrium distribution of starting state \( \tilde{A} \):
\[
\langle f(\tilde{X}) \rangle_{\tilde{A}} = \frac{1}{g(\tilde{A})} \sum_{\tilde{X}} f(\tilde{X}) \delta_{\tilde{X}, \tilde{A}}. \tag{2.6}
\]

Note that we automatically obtained a Markov process by treating all states equally.

### 2.1 Case of local update

In the rest of this article, we consider the situation that the microscopic transition rate \( \tilde{w} \) can be factorized as
\[
\tilde{w}(\tilde{b}; \tilde{X}, \tilde{X}) = \tilde{w}(\tilde{b}; \tilde{A}, \tilde{X}) D(\tilde{X}|\tilde{X}). \tag{2.7}
\]
Here \( D(\tilde{X}|\tilde{X}) \) equals unity if there is a one-step transition path \( \tilde{X} \rightarrow \tilde{X} \), otherwise zero. \( \tilde{A} \) is supposed to be an accumulation of locally defined quantity, and the fact that transition rate does not explicitly depend on the value \( \tilde{A} \) itself but depends on the difference at the transition. This is the case when the dynamics is governed by short-ranged interactions. By using Eqs. (2.7) and (2.5) is rewritten as
\[
W(\tilde{b}; \tilde{A} + \Delta \tilde{A}) = \mu(\tilde{A}; \Delta \tilde{A}) w(\tilde{b}; \Delta \tilde{A}) \tag{2.8}
\]
with
\[
\mu(\tilde{A}; \Delta \tilde{A}) = \left\{ \sum_{\tilde{X}} \delta_{\tilde{X}, \tilde{A} + \Delta \tilde{A}} D(\tilde{X}|\tilde{X}) \right\}_{\tilde{A}}. \tag{2.9}
\]
Note that \( W \) is factorized into two factors; one depends on the state \( \tilde{A} \) and another depends on the environmental parameter \( \tilde{b} \). Here \( \mu \) means a probability distribution function of possible update \( \Delta \tilde{A} \) in the equal-probability ensemble with \( \tilde{A} \) fixed, and it is independent of the detail of the dynamics. This factorization Eq. (2.8) is significantly useful for the practical calculations.

### 2.2 Nonequilibrium free energy

In many cases, the width of the fluctuation of \( \tilde{A} \) can be ignored in comparison with the expectation value \( \langle \tilde{A} \rangle \) in the thermodynamic limit. The time evolution of \( \langle \tilde{A} \rangle \) is described by
\[
\frac{d \langle \tilde{A} \rangle}{dt} = \sum_{\Delta \tilde{A}} \Delta \tilde{A} \tilde{W}(\tilde{b}; \langle \tilde{A} \rangle + \Delta \tilde{A}) \equiv \tilde{V}(\tilde{b}; \langle \tilde{A} \rangle). \tag{2.10}
\]
If \( \tilde{V} \) does not have vortex in \( \tilde{A} \)-space, there exists a potential function \( F_{neq}(\tilde{b}; \langle \tilde{A} \rangle) \) that satisfies that
\[
\tilde{V}(\tilde{b}; \langle \tilde{A} \rangle) = -\frac{\partial}{\partial \langle \tilde{A} \rangle} F_{neq}(\tilde{b}; \langle \tilde{A} \rangle), \tag{2.11}
\]
and it monotonically decreases with time. Therefore we can regard this as a nonequilibrium free energy. It is important to note that \( F_{neq} \) depends on the detail of the dynamics via \( \tilde{w} \). It coincides with the equilibrium free energy only in the vicinity of the equilibrium point, namely, incide the ball with radius of \( o(N) \).
Coarse-Grained Dynamics Assuming Equal-Probability for Transient States

3. Application: Isothermal Relaxation in the Ferromagnetic Potts Model

Next we apply the method explained in the previous section to a simple model, the Potts model in two dimensions. Let $\sigma_i \in \{0, 1, 2\}$ a spin variable at the $i$th site of the $L \times L$ square lattice with a periodic boundary condition. The realization probability in canonical ensemble is proportional to the Boltzmann factor $e^{-\beta E + N_0}$. Here $\beta$ is inverse temperature, $h$ is magnetic field, $E = -\sum_{i,j} \delta_{\sigma_i \sigma_j}$ is ferromagnetic energy, and $N_0 = \sum_i \delta_{\sigma_i 0}$ is number of sites in state 0 corresponding to the order parameter. The summation over $i$ and $j$ in $E$ is taken over nearest neighbor pairs. Without magnetic field ($h = 0$), the system exhibits a second order ferromagnetic transition. In the paramagnetic phase for $\beta < \beta_c \approx 1.00505$, the system holds the symmetry among three states, and therefore $N_0/N$ equals $1/3$ where $N = L^2$. In the ferromagnetic phase for $\beta > \beta_c$, the symmetry is spontaneously broken, and $N_0/N$ is greater than $1/3$ with probability $1/3$. In the following, we restrict the phase space by eliminating the states having $N_0 < 1/3$.

For $h = 0$, the Boltzmann factor does not depend on $N_0$. The expectation values of $E$ and $N_0$ in the canonical ensemble are calculated as functions of $\beta$ as $E^{\text{can}}(\beta)$ and $N_0^{\text{can}}(\beta)$. In the thermodynamic limit, the relation between $E^{\text{can}}(\beta)$ and $N_0^{\text{can}}(\beta)$ is identical to the relation $N_0 = N_0^{\text{can}}(E)$ in the microcanonical ensemble.

Let us consider the relaxation dynamics at inverse temperature $\beta > 0$ and magnetic field $h = 0$ under the ordered initial condition: $\sigma_i = 0$ for all $i$ at $t = 0$, which is a zero temperature equilibrium state. Transition probability per unit time is given by $w(h; \Delta A) = \min[1, e^{-h \Delta A}]$. In the application of the method mentioned in §2, we consider the two cases; one-variable [$A = E$] and two-variable [$A = (E, N_0)$]. We calculate distribution function $\mu$ in the microcanonical ensemble by using the Wang–Landau sampling [3] and show the obtained time evolution of the expectation value of $E$ with one and two-variable description in Figs. 1(a) and 1(b) (solid lines), respectively. We also plot the results of the kinetic Monte-Carlo simulations (symbols) as references, i.e., the non-approximated dynamics. From Fig. 1, the relaxation of the one-variable description distinctly faster than the true one, and the approximation seems not good. The equilibrium value for $t \gg 1$ is obtained correctly. On the other hand, two-variable description provides quite large improvement. The effectiveness of the approximation does not seem to change so much below, above and near the critical point. One-variable description is, however, rather bad in the off-critical regime. We consider the reason of this in the following.

It is natural that two-variable description is better than one-variable one because the approximation of equal probability becomes better with increasing the number of extensive variables. We consider, however, there is an essential difference between one and two-variable descriptions. For one-variable case, the space of $A$ is one dimensional with the coordinate $E$. Therefore the trajectory of relaxation for all temperature is the same except the end point. Since the transient state with $E$ is unique; it is the microcanonical ensemble for $E$, there is no history dependence with respect to $\beta$. Although two-variable description is redundant to describe equilibrium ensemble with $h = 0$, it allows different trajectory in the state space $E \times N_0$ depending on $\beta$. The transient state is generally related to the extended equilibrium state with $N_0 \neq N_0^{\text{can}}(E)$ corresponding to the canonical state with $h > 0$ although the relaxation is under no magnetic field. Such state distinctly deviating from equilibrium state appears firstly for two-variable description. The choice of the variable is also important. The second variable $N_0$ corresponds to the order parameter of the ferromagnetic transition. This is a slowest variable of the present model.
4. Conclusions

In this article, we introduce the method to derive a Markov process with respect to macroscopic variables by assuming the equal-probability of microscopic transient states. We use the extended microcanonical ensemble where a few extensive variables redundant to describe equilibrium distribution. As far as in the present model, it is found that the addition of only one additional variable can recover the history dependence, and agree with non-approximated dynamics in considerably good accuracy. We expect that the present method works as well in the systems exhibiting second order transitions.

It is an interesting question whether the present method also works well for another kind of systems such as spinodal decomposition in coarsening dynamics, nucleations in first order transitions. In addition, we may be able to extend the basic idea of the present method to the nonequilibrium steady state, where we assume, for example, the equal-probability ensemble for the states with the same electric current. Another significant application is the one to the metastable state, which cannot be treated in the framework of equilibrium statistical mechanics, because equilibrium free energy is a convex function with respect to extensive variables. By considering nucleation dynamics or the glassy dynamics in kinetically constrained model, we may understand the origin of metastability in the sense of extended equilibrium state.

Acknowledgments

This work is a collaboration with Nobuyasu Ito and Hiroshi Watanabe and was partly supported by Award No. KUK-I1-523005-04 presented by King Abdullah University of Science and 524 Technology (KAUST).

REFERENCES