Phase Space Volumes and Liouville's Theorem

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1 Coordinate transformation in phase space for Hamiltonian and non-Hamiltonian system

Since the mapping function of the point x_0 to x_t is one-to-one, the mapping is equivalent to a coordinate transformation on the phase space from initial phase space coordinate to final coordinate

$$dx_t = Jdx_0 \tag{1}$$

where J is the Jacobian of the transformation and $J_{kl} = \frac{\partial x_t^k}{\partial x_0^l}$. The determinant of J is named

$$J(x_t; x_0) = det(J) \tag{2}$$

Since J is diagonal, it has eigenvalue λ_k and $ln(J)$ has eigenvalue $ln(\lambda)$, so

$$\begin{aligned} e^{Tr[ln(J)]} &= e^{\sum_k ln(\lambda_k)} \\ &= \prod_k \lambda_k \\ &= det(J) \end{aligned} \tag{3}$$

Then

$$\begin{aligned} \frac{d}{dt} J(x_t; x_0) &= \frac{d}{dt} e^{Tr[ln(J)]} \\ &= e^{Tr[ln(J)]} Tr\left[\frac{dJ}{dt} J^{-1}\right] \\ &= J(x_t; x_0) \sum_{k,l} \left[\frac{dJ_{kl}}{dt} J^{-1}_{lk}\right] \\ &= J(x_t; x_0) \sum_{k,l} \left[\frac{\partial \dot{x}_t^k}{\partial x_0^l} \frac{\partial x_0^l}{\partial x_0^k}\right] \\ &= J(x_t; x_0) \sum_k \frac{\partial \dot{x}_t^k}{\partial x_0^k} \end{aligned} \tag{4}$$

For a system evolving under Hamilton equation, the phase space compressibility $\kappa(x_t,t) = \nabla \cdot x_t = \sum_k \frac{\partial \dot{x}_t^k}{\partial x_0^k} = 0$. the equation of motion for the Jacobian reduced to

$$\frac{d}{dt} J(x_t; x_0) = 0 \tag{5}$$

This equation implies that the Jacobian is a constant at all time. Since the initial value of $J(x_t; x_0)$ is 1, it remains 1 at all time. It implies that the phase space volume is a constant, which is known as the Liouville's theorem.
For a non-Hamilton system, if there's a function $\omega(x_t,t)$ such that $\kappa(x_t,t) = \frac{d}{dt}\omega(x_t,t)$,

$$J(x_t; x_0) = \exp[\omega(x_t,t) - \omega(x_0,0)] \tag{6}$$

and the phase space volume element evolve according to

$$\exp[-\omega(x_t,t)]dx_t = \exp[-\omega(x_0,0)]dx_0 \tag{7}$$

The equation constitutes a generalized Liouville theorem which implies a weighted phase space volume is conserved. So the phase space does not follow the usual laws of Euclidean geometry. The phase space volume can be denoted as $\sqrt{g(x)}dx$, where $g(x)$ is the determinant of a second-rank tensor $g_{ij}(x)$ known as the **metric tensor**.
The Jacobian can be as a statement of the fact of the coordinate transformation $x_0 \to x_t$

$$J(x_t; x_0) = \frac{\sqrt{g(x_0,0)}}{\sqrt{g(x_t,t)}} \tag{8}$$

where

$$\sqrt{g(x_t,t)} = e^{-\omega x_t, t} \tag{9}$$

The implication of the equation is that any phase space integral that represents an ensemble average should be performed using $\sqrt{g}$ as the volume element.

2 Generalization of the Liouville equation in non-Hamiltonian system

Assume a system interacting with its surroundings and possibly subject to driving force is described bt non-Hamiltonian microscopic equation of the form

$$\dot{x} = \xi(x,t) \tag{10}$$

Consider an ensemble described by a distribution function $f : R^{n+1} \to R^1$, which is a function of n coordinate and time t. A continuity equation for f can be derived whose condition is that the rate if change of the number of ensemble members within volume Ω is balanced by the flux of members through the surface bounding Ω, which is expressed mathematically as

$$\begin{aligned} -\frac{d}{dt}\int_{\Omega} f(x,t)\sqrt{g(x,t)}dx &= \int_{\partial\Omega} \tilde{\sigma}\hat{n}\cdot\xi f \\ &= \int_{\Omega} \mathcal{L}_{\xi}(fg(x,t)dx) \end{aligned} \tag{11}$$

where $\tilde{\sigma}$ is the surface $n-1$ form and $\hat{n}$ is the unit normal one-form to the surface. The surface integral has been converted to a volume integral via a generalization of the divergence theorem to manifolds with nontrivial metrics using Lie derivative $\mathcal{L}_{\xi}$ along the vector ξ.

The equation hold independent of the choice of Ω and thus implies the local continuity condition

$$\int_{\Omega}\left(\frac{\partial}{\partial t}+\mathcal{L}_{\xi}\right)(f(x,t)\sqrt{g(x,t)}dx) = 0 \tag{12}$$

To project the equation onto a coordinate basis, we first apply the Leibniz rule, $\mathcal{L}_{\xi}(f\sqrt{g}dx) = \sqrt{g}dx(\mathcal{L}_{\xi}f) + f\mathcal{L}_{\xi}(\sqrt{g}dx$, to the Lie derivative on the product. The action of the Lie derivative on the scalar and on the volume form is

$$\begin{aligned} \mathcal{L}_{\xi}f &= \xi^{i}\frac{\partial f}{\partial x^{i}} \\ \mathcal{L}_{\xi}\epsilon_{i_1\cdots 1_n} &= \dot{x}^{k}\frac{\partial\sqrt{g}}{\partial x^{k}}\epsilon_{i_1\cdots 1_n} + \sqrt{g}\frac{\partial\xi^{i}}{\partial x^{k}}\epsilon_{i_1\cdots 1_n} \end{aligned} \tag{13}$$

where the component representation of the wedge product is given by $\epsilon_{i_1\cdots 1_n}$, the Levi-Civita tensor.

Combining he last two equations gives the general form for the continuity equation in an arbitrary coordinate basis

$$\left[\frac{\partial}{\partial t}(f(x,t)\sqrt{g(x,t)}) + \frac{\partial\xi^{i}}{\partial x^{k}}\right]dx = 0 \tag{14}$$

$$\frac{\partial}{\partial t}(f(x,t)\sqrt{g(x,t)}) + \nabla\cdot(f(x,t)\sqrt{g(x,t)}) = 0 \tag{15}$$

According to equation (4) and (8), the phase space metric factor $\sqrt{g(x,t)}$ satisfies

$$\frac{d}{dt}\sqrt{g(x,t)} = -\kappa(x,t)\sqrt{g(x,t)} \tag{16}$$

The last two equations lead to an equation for $f(x,t)$ alone

$$\frac{\partial}{\partial t}f(x,t) + \xi(x,t)\cdot\nabla f(x,t) = 0 \tag{17}$$

$$\frac{d}{dt}f(x,t) = 0 \tag{18}$$

In equilibrium, both $f(x_t.t)$ and $g(x_t, t)$ have no explicit time dependence. According to equation (7), we can obtain the generalized **Liouville equation**

$$f(x_t, t)\sqrt{g(x_t, t)}dx_t = f(x_0, t)\sqrt{g(x_0, t)}dx_0 \tag{19}$$

Suppose the dynamical equations processes a set of n_c associated conservation laws or conserved quantities $\Lambda_k(x), k = 1, \cdots, n_c$, which satisfies

$$\begin{aligned} \Lambda_k(x_t) - C_k &= 0 \\ \frac{d\Lambda_k}{dt} &= 0 \end{aligned}$$

a general solution for $f(x)$ can be constructed in the form

$$f(x) = \prod_{k=1}^{n_c} \delta(\Lambda_k(x) - C_k) \tag{20}$$

3 Analysis of Different Algorithms

The microcanonical ensemble average of the function F is denoted F_{NVE}, which is defined as

$$F_{NVE}(N, V, E) \equiv [N!\Omega(N, V, E)]^{-1} \int_V d\mathbf{r}^N \int d\mathbf{p}^N \delta[\mathscr{H}(\mathbf{r}^N, \mathbf{p}^N; V) - E]F(\mathbf{r}^N, \mathbf{p}^N; V) \tag{21}$$

where

$$\Omega(N, V, E) = (N!)^{-1} \int_V d\mathbf{r}^N \int d\mathbf{p}^N \delta[\mathscr{H}(\mathbf{r}^N, \mathbf{p}^N; V) - E] \tag{22}$$

is the microcanonical ensemble partition function.
The canonical ensemble partition function is

$$Q(N, V, T) = (N!)^{-1} \int_V d\mathbf{r}^N \int d\mathbf{p}^N \exp\left[-\frac{\mathscr{H}(\mathbf{r}^N, \mathbf{p}^N; V)}{kT}\right] \tag{23}$$

The isothermal-isobaric ensemble partition function is

$$\Delta(N, P, T) = (N!)^{-1} \int_0^\infty dV \int_V d\mathbf{r}^N \int d\mathbf{p}^N \exp\left[-\frac{PV + \mathscr{H}(\mathbf{r}^N, \mathbf{p}^N; V)}{kT}\right] \tag{24}$$

The isoenthalpic-isobaric ensemble partition function is

$$\Gamma(N, P, H) = (N!)^{-1} \int_0^\infty dV \int_V d\mathbf{r}^N \int d\mathbf{p}^N \delta[\mathscr{H}(\mathbf{r}^N, \mathbf{p}^N; V) + PV - H] \tag{25}$$

3.1 The Hoover Algorithm

Hoover introduced the equations of motion as follows

$$\begin{aligned}
\dot{r}_i &= \frac{p_i}{m_i} + \frac{p_\epsilon}{W} r_i \\
\dot{p}_i &= F_i - \frac{p_\epsilon}{W} p_i - \frac{p_\xi}{Q} p_i \\
\dot{V} &= \frac{D p_\epsilon}{W} V \\
\dot{p_\epsilon} &= dV(P - P_{ext}) - \frac{p_\xi}{Q} p_\epsilon \\
\dot{\xi} &= \frac{p_\xi}{Q} \\
\dot{p_\xi} &= \sum_{i=1}^{N} \frac{p_i^2}{m_i} + \frac{p_\epsilon^2}{W} - (N_f + 1)kT
\end{aligned} \tag{26}$$

When $\sum_{i=1}^{N} F_i = 0$, there's an conserved energy

$$H' = H(p,r) + \frac{p_\epsilon^2}{2W} + \frac{p_\xi^2}{2Q} + LkT\xi + P_{ext}V \tag{27}$$

and an additional momentum conservation law

$$\mathbf{P}e^{\epsilon+\xi} = \mathbf{K} \tag{28}$$

where $\mathbf{P} = \sum_{\mathbf{i=1}}^{\mathbf{N}}$, for

$$\frac{d}{dt}\mathbf{P}e^{\epsilon+\xi} = \sum_{i=1}^{N} \left(-\frac{p_\epsilon}{W} p_i - \frac{p_\xi}{Q} p_i \right) + \mathbf{P}e^{\epsilon+\xi} \frac{\mathbf{D}\mathbf{p}_\epsilon}{\mathbf{W}} + \mathbf{P}e^{\epsilon+\xi} \frac{\mathbf{p}_\xi}{\mathbf{Q}} = \mathbf{0} \tag{29}$$

The compressibility of the equations is

$$\begin{aligned}
\kappa_{Hoover} &= \sum_{i=1}^{N} \left(\frac{\partial}{\partial r_i} \cdot \dot{r}_i + \frac{\partial}{\partial p_i} \cdot \dot{p}_i \right) + \frac{\partial}{\partial V} \dot{V} + \frac{\partial}{\partial p_\epsilon} \cdot \dot{p}_\epsilon \\
&= -\frac{(DN+1)p_\xi}{Q} + \frac{D p_\epsilon}{W} \\
&= -(DN+1)\dot{\xi} + D\dot{\epsilon}
\end{aligned} \tag{30}$$

We can obtain the phase space metric

$$\sqrt{g_{Hoover}} = \frac{1}{V} e^{DN+1} \tag{31}$$

Only taking the conserved energy into consideration, the partition function becomes

$$\begin{aligned}
\Omega_{T,P_{ext}}(N,E) = &\frac{e^{\beta E}}{LkT} \int dp_\xi e^{\beta p_\xi^2/2Q} \int dp_\epsilon e^{-\beta p_\epsilon^2/2W} \\
&\int dV \frac{1}{V} e^{-\beta P_{ext} V} \int d^N p \int d^N r e^{-\beta H(p,r)}
\end{aligned} \tag{32}$$

Due to the presence of the $\frac{1}{V}$ factor in the volume integration, the volume distribution is incorrect. The difficulty arises from the equations of motion don't have the desired compressibility.

3.2 The MTK Algorithm

Martyna, Tobias and Klein introduced an algorithm which has been proved to yield a correct volume distribution.

$$\begin{aligned}
\dot{r}_i &= \frac{p_i}{m_i} + \frac{p_\epsilon}{W} r_i \\
\dot{p}_i &= F_i - \left(1 + \frac{D}{N_f}\right) \frac{p_\epsilon}{W} p_i - \frac{p_\xi}{Q} p_i \\
\dot{V} &= \frac{dp_\epsilon}{W} V \\
\dot{p_\epsilon} &= dV(P - P_{ext}) + \frac{D}{N_f} \sum_{i=1}^{N} \frac{p_i^2}{m_i} - \frac{p_\xi}{Q} p_\epsilon \\
\dot{\xi} &= \frac{p_\xi}{Q} \\
\dot{p_\xi} &= \sum_{i=1}^{N} \frac{p_i^2}{m_i} + \frac{p_\epsilon^2}{W} - (N_f + 1)kT
\end{aligned} \tag{33}$$

Compared to Hoover's algorithm, this one add a term to yield an extra$-\frac{dp_\epsilon}{W}$ in the compressibility. The p_ϵ equation has been modified to ensure the energy conservation.
Other thermostat with better behavior can replace the Nosé-Hoover thermostat.