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

$$dx_t = J dx_0 \tag{1}$$

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

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

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

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

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

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

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

$$\Lambda_k(x_t) - C_k = 0$$
$$\frac{d\Lambda_k}{dt} = 0$$

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

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

The isothermal-isobaric ensemble partition function is

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

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

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

The compressibility of the equations is

$$\begin{aligned}
\kappa_{Hoover} &= \sum_{i=1}^{N} \left(\frac{\partial}{\partial r_i} \cdot \dot{r}_i + \frac{\partial}{\partial p_i} \cdot \dot{p}_i \right) + \frac{\partial}{\partial V} \dot{V} + \frac{\partial}{\partial p_\epsilon} \cdot \dot{p}_\epsilon \\
&= -\frac{(DN + 1) p_\xi}{Q} + \frac{D p_\epsilon}{W} \\
&= -(DN + 1)\dot{\xi} + D\dot{\epsilon}
\end{aligned} \tag{27}$$

We can obtain the phase space metric

$$\sqrt{g_{Hoover}} = \frac{1}{V} eDN + 1 \tag{28}$$

3.2 The MTK Algorithm

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