Constant Pressure Dynamics by extended system method

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The expression of pressure

Since the kinetic energy is a universal term that appears in all Hamiltonian, we can introduce the configuration partition function

$$Z(N, V, T) = \int_{D(V)} dr_1 \cdots dr_N \, exp\big[- \beta U(r_1, \cdot, r_N)\big] \qquad (1)$$

And the pressure is

$$P = kT \frac{\partial}{\partial V} lnQ(N, V, T) = \frac{kT}{Z(N, V, T)} \frac{\partial Z(N, V, T)}{\partial V} \qquad (2)$$

The volume dependence is contained in the integration limit, so that the volume differentiation cannot be easily performed.
So we can introduce the scaled coordinates with the definition

$$s_i = \frac{1}{V^{1/3}} r_i \qquad (3)$$

Perform the change of variables in $Z(N, V, T)$ yields

$$Z(N, V, T) = V^N \int ds_1 \cdots ds_N \, exp\big[- \beta U(V^{1/3}s_1, \cdots, V^{1/3}s_N)\big] \qquad (4)$$

Thus the pressure can be easily calculated as

$$
P = \frac{kT}{Z(N, V, T)} \left\{ \frac{N}{V} Z(N, V, T) - \sum_{i=1}^{N} \beta V^N \int ds_1 \cdots ds_N \frac{1}{3V} \right.
$$

$$
\left. \left[V^{1/3} s_i \cdot \frac{\partial U}{\partial V^{1/3} s_i} \right] exp\left[- \beta U(V^{1/3} s_1, \cdots, V^{1/3} s_N) \right] \right\} \tag{5}
$$

$$
= \frac{kTN}{V} - \frac{1}{3V} \int dr_1 \cdots dr_N \left[\sum_{i=1}^{N} r_i \cdot F_1 \right] exp\left[- \beta U(r_1, \cdots, r_N) \right]
$$

$$
= \frac{1}{3V} \left\langle \sum_{i=1}^{N} \left[\frac{p_i^2}{m_i} + r_i \cdot F_1 \right] \right\rangle \tag{6}
$$

The quantity in the angle bracket is an instantaneous estmator $\mathcal{P}(r, p)$ for the pressure

$$
\mathcal{P}(r, p) = \frac{1}{3V} \sum_{i=1}^{N} \left[\frac{p_i^2}{m_i} + r_i \cdot F_1 \right] \tag{7}
$$

If the potential has an explicit volume dependence, there would be an extra term in equation (5), and the result is modified to read

$$
\mathcal{P}(r, p) = \frac{1}{3V} \sum_{i=1}^{N} \left[\frac{p_i^2}{m_i} + r_i \cdot F_1 \right] - \frac{\partial U}{\partial V} \tag{8}
$$

Isobaric phase space distribution and partition function

Assume two system coupled to a common thermal reservoir so that each system is described by a canonical distribution at temperature T. System 2 act as a barostat whose number of particles and volume is much larger than system 1, respectively. If the volume of each system were fixed, the total canonical partition function would be

$$Q(N, V, T) = C_N \int dx_1 dx_2 e^{-\beta \mathscr{H}_1(x_1) + \mathscr{H}_2(x_2)}$$

$$= g(N, N_1, N_2) C_{N_1} \int dx_1 de^{-\beta \mathscr{H}_1(x_1)} C_{N_2} \int dx_2 de^{-\beta \mathscr{H}_2(x_2)} \qquad (9)$$

Where $g(N, N_1, N_2)$ is an overall normalization constant.
The canonical phase space distribution function $f(x)$ of combined system 1 and 2 is

$$f(x) = \frac{C_N e^{-\beta \mathscr{H}}}{Q(N, V, T)} \qquad (10)$$

To determine the distribution function of system 1, we need to integrate over the phase space of system 2

$$f_1(x_1, V_1) = \frac{g(N, N_1, N_2)}{Q(N, V, T)} C_{N_1} de^{-\beta \mathcal{H}_1(x_1)} C_{N_2} \int dx_2 de^{-\beta \mathcal{H}_2(x_2)}$$

$$= \frac{Q_2(N - N_1, V - V_1, T)}{Q(N, V, T)} g(N, N_1, N_2) C_{N_1} de^{-\beta \mathcal{H}_1(x_1)} \quad (11)$$

Express the partition function in terms of Helmholtz free energies according to $Q(N, V, T) = e^{\beta A(N, V, T)}$,

$$\frac{Q_2(N_2, V - V_1, T)}{Q(N, V, T)} = e^{\beta[A(N - N_1, V - V_1, T) - A(N, V, T)]} \quad (12)$$

Expand $A(N - N_1, V - V_1, T)$ to first order

$$A(N - N_1, V - V_1, T) \approx A(N, V, T) - N_1 \Big(\frac{\partial A}{\partial N} \Big) \Big|_{N_1 = 0, V_1 = 0} - V_1 \Big(\frac{\partial A}{\partial V} \Big) \Big|_{N_1 = 0, V_1 = 0}$$

$$= A(N, V, T) - \mu N_1 + PV_1 \quad (13)$$

So

$$f_1(x_1, V_1) = g(N, N_1, N_2) e^{\beta \mu N_1} e^{-\beta PV_1} e^{-\beta \mathcal{H}_1} \quad (14)$$

which means the distribution can of the system can be obtained.

If we focus on the system and drop the extraneous "1" subscript, the equation can be rearranged as

$$e^{-\beta\mu N} \int_0^\infty dV \int dx f(x, V) = I_N \int_0^\infty dV \int dx e^{-\beta[\mathscr{H} + pV]} \quad (15)$$

which defines the partition function of the isothermal-isobaric ensemble as

$$\Delta(N, P, T) = I_N \int_0^\infty dV \int dx e^{-\beta[\mathscr{H} + pV]} \quad (16)$$

Coordinate transformation in phase space

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

$$dx_t = Jdx_0 \tag{17}$$

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

$$J(x_t; x_0) = det(J) \tag{18}$$

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

$$e^{Tr[ln(J)]} = e^{\sum_k ln(\lambda_k)} = \prod_k \lambda_k = det(J) \tag{19}$$

Then

$$\frac{d}{dt} J(x_t; x_0) = e^{Tr[ln(J)]} Tr\left[\frac{dJ}{dt} J^{-1}\right] = J(x_t; x_0) \sum_{k,l} \left[\frac{\partial \dot{x}_t^k}{\partial x_0^l} \frac{\partial x_0^l}{\partial x_0^k}\right]$$

$$= J(x_t; x_0) \sum_k \frac{\partial \dot{x}_t^k}{\partial x_0^k} \tag{20}$$

For a system evolving under **Hamilton equation**, the phase space compressibility

$$\kappa(x_t, t) = \nabla \cdot x_t = \sum_k \frac{\partial \dot{x}_t^k}{\partial x_0^k} = 0 \tag{21}$$

The equation of motion for the Jacobian reduced to

$$\frac{d}{dt} J(x_t; x_0) = 0 \tag{22}$$

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 $\kappa(x_t, t) = \frac{d}{dt}\omega(x_t, t)$,

$$J(x_t; x_0) = \exp[\omega(x_t, t) - \omega(x_0, 0)] \tag{23}$$

and the phase space volume element evolve according to

$$\exp[-\omega(x_t, t)]dx_t = \exp[-\omega(x_0, 0)]dx_0 \tag{24}$$

The equation constitutes a **generalized Liouville theorem** which implies a weighted phase space volume is conserved which 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 $x_0 \to x_t$

$$J(x_t; x_0) = \frac{\sqrt{g(x_0, 0)}}{\sqrt{g(x_t, t)}} \tag{25}$$

where

$$\sqrt{g(x_t, t)} = e^{-\omega x_t, t} \tag{26}$$

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.

Generalization of the Liouville equation

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

$$\dot{x} = \xi(x, t) \tag{27}$$

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. From a continuity equation we can obtain

$$\frac{\partial}{\partial t}(f(x, t)\sqrt{g(x, t)}) + \nabla \cdot (f(x, t)\sqrt{g(x, t)}) = 0 \tag{28}$$

According to last section, the phase space metric factor $\sqrt{g(x, t)}$ satisfies

$$\frac{d}{dt}\sqrt{g(x, t)} = -\kappa(x, t)\sqrt{g(x, t)} \tag{29}$$

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

$$\frac{\partial}{\partial t}f(x, t) + \xi(x, t) \cdot \nabla f(x, t) = 0, \qquad \frac{d}{dt}f(x, t) = 0 \tag{30}$$

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**

$$f(x_t, t)\sqrt{g(x_t, t)}dx_t = f(x_0, t)\sqrt{g(x_0, t)}dx_0 \tag{31}$$

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

$$f(x) = \prod_{k=1}^{n_c} \delta(\Lambda_k(x) - C_k) \tag{32}$$

The Hoover Algorithm

Hoover introduced the equations of motion as follows

$$\dot{r}_i = \frac{p_i}{m_i} + \frac{p_\epsilon}{W} r_i \qquad \dot{p}_i = F_i - \frac{p_\epsilon}{W} p_i - \frac{p_\xi}{Q} p_i$$

$$\dot{V} = \frac{Dp_\epsilon}{W} V \qquad \dot{p}_\epsilon = dV(P - P_{ext}) - \frac{p_\xi}{Q} p_\epsilon \qquad (33)$$

$$\dot{\xi} = \frac{p_\xi}{Q} \qquad \dot{p}_\xi = \sum_{i=1}^{N} \frac{p_i^2}{m_i} + \frac{p_\epsilon^2}{W} - (N_f + 1)kT$$

There's an conserved energy

$$H' = H(p, r) + \frac{p_\epsilon^2}{2W} + \frac{p_\xi^2}{2Q} + LkT\xi + P_{ext}V \qquad (34)$$

and when $\sum_{i=1}^{N} F_i = 0$, an additional momentum conservation law $\quad \mathbf{P}e^{\epsilon+\xi} = \mathbf{K} \quad$ for

$$\frac{d}{dt}\mathbf{P}e^{\epsilon+\xi} = \sum_{i=1}^{N} \left(-\frac{p_\epsilon}{W} p_i - \frac{p_\xi}{Q} p_i \right) + \mathbf{P}e^{\epsilon+\xi} \frac{\mathbf{D}p_\epsilon}{\mathbf{W}} + \mathbf{P}e^{\epsilon+\xi} \frac{p_\xi}{\mathbf{Q}} = \mathbf{0} \qquad (35)$$

📄 William G. Hoover. Physical Review A 31, 1685 (1985).

The compressibility of the equations is

$$\kappa_{Hoover} = \sum_{i=1}^{N} \left(\frac{\partial}{\partial r_i} \cdot \dot{r}_i + \frac{\partial}{\partial p_i} \cdot \dot{p}_i \right) + \frac{\partial}{\partial V} \dot{V} + \frac{\partial}{\partial p_\epsilon} \cdot \dot{p}_\epsilon$$
$$= -\frac{(DN+1)p_\xi}{Q} + \frac{Dp_\epsilon}{W} \tag{36}$$
$$= -(DN+1)\dot{\xi} + D\dot{\epsilon}$$

We can obtain the phase space metric

$$\sqrt{g_{Hoover}} = \frac{1}{V} e^{(DN+1)\xi} \tag{37}$$

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

$$\Omega_{T,P_{ext}}(N,E) = \frac{e^{\beta E}}{LkT} \int dp_\xi e^{\beta p_\xi^2/2Q} \int dp_\epsilon e^{-\beta p_\epsilon^2/2W}$$
$$\int dV \frac{1}{V} e^{-\beta P_{ext} V} \int d^N p \int d^N r e^{-\beta H(p,r)} \tag{38}$$

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.

The MTK Algorithm

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

$$\dot{r}_i = \frac{p_i}{m_i} + \frac{p_\epsilon}{W} r_i \qquad \dot{p}_i = F_i - \left(1 + \frac{D}{N_f}\right) \frac{p_\epsilon}{W} p_i - \frac{p_\xi}{Q} p_i$$

$$\dot{V} = \frac{dp_\epsilon}{W} V \qquad \dot{p}_\epsilon = dV(P - P_{ext}) + \frac{D}{N_f} \sum_{i=1}^{N} \frac{p_i^2}{m_i} - \frac{p_\xi}{Q} p_\epsilon \qquad (39)$$

$$\dot{\xi} = \frac{p_\xi}{Q} \qquad \dot{p}_\xi = \sum_{i=1}^{N} \frac{p_i^2}{m_i} + \frac{p_\epsilon^2}{W} - (N_f + 1)kT \qquad (40)$$

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 thermostats with better behavior can replace the Nosé-Hoover thermostat.

📄 Glenn J. Martyna, Douglas J. Tobias and , and Michael L. Klein . The Journal of Chemical Physics 101, 4177 (1994).

Thank you for your attemtion!