

1 Phase Spaces and the Liouville Equation

emphasize the change of language from deterministic to probabilistic description.

Under the dynamics:

$$\begin{cases} m\dot{\mathbf{v}}_i = \mathbf{F}_i \\ \dot{\mathbf{x}}_i = \mathbf{v}_i \end{cases}$$

with initial data given.

What is the joint probability density of finding simultaneously the first particle at point of \mathbf{x}_1 with velocity \mathbf{v}_1 , the second particle at point of \mathbf{x}_2 with velocity \mathbf{v}_2, \dots , and N^{th} particle at \mathbf{x}_N with velocity \mathbf{v}_N ? Here "the point at \mathbf{x}_i with velocity \mathbf{v}_i " means "the point between \mathbf{x}_i and $\mathbf{x}_i + d\mathbf{x}_i$ with velocity between \mathbf{v}_i and $\mathbf{v}_i + d\mathbf{v}_i$."

The trajectory is

$$\begin{cases} \mathbf{x}_i = \mathbf{x}_i(t) \\ \mathbf{v}_i = \dot{\mathbf{x}}_i(t) \end{cases}$$

Define the probability density

$$\begin{aligned} P(\{\mathbf{x}, \mathbf{v}\}, t) &\equiv P(\mathbf{x}_1, \dots, \mathbf{x}_N; \mathbf{v}_1, \dots, \mathbf{v}_N, t) \\ &= \delta(\mathbf{x}_1 - \mathbf{x}_1(t)) \delta(\mathbf{x}_2 - \mathbf{x}_2(t)) \cdots \delta(\mathbf{x}_N - \mathbf{x}_N(t)) \\ &\quad \cdot \delta(\mathbf{v}_1 - \dot{\mathbf{x}}_1(t)) \delta(\mathbf{v}_2 - \dot{\mathbf{x}}_2(t)) \cdots \delta(\mathbf{v}_N - \dot{\mathbf{x}}_N(t)) \end{aligned}$$

A state of the system is described by a point $(\mathbf{x}_1, \dots, \mathbf{x}_N; \mathbf{v}_1, \dots, \mathbf{v}_N)$ in this $6N$ dimensional space. The space is referred to as the phase space of the dynamics.

1.1 Liouville Equation

Derivation of the Liouville Equation:

$$\begin{aligned} \frac{\partial}{\partial t} P &= - \sum_{j=1}^N \prod_{\substack{k=1 \\ k \neq j}}^N \delta(\mathbf{x}_k - \mathbf{x}_k(t)) \delta(\mathbf{v}_k - \dot{\mathbf{x}}_k(t)) \cdot \frac{\partial}{\partial \mathbf{x}_j} \delta(\mathbf{x}_j - \mathbf{x}_j(t)) \delta(\mathbf{v}_j - \dot{\mathbf{x}}_j(t)) \cdot \dot{\mathbf{x}}_j \\ &\quad - \sum_{j=1}^N \prod_{\substack{k=1 \\ k \neq j}}^N \delta(\mathbf{x}_k - \mathbf{x}_k(t)) \delta(\mathbf{v}_k - \dot{\mathbf{x}}_k(t)) \cdot \delta(\mathbf{x}_j - \mathbf{x}_j(t)) \frac{\partial}{\partial \mathbf{v}_j} \delta(\mathbf{v}_j - \dot{\mathbf{x}}_j(t)) \cdot \ddot{\mathbf{x}}_j \end{aligned}$$

Note that:

$$\dot{\mathbf{x}}_j(t) \delta(\mathbf{v}_j - \dot{\mathbf{x}}_j(t)) = \mathbf{v}_j \delta(\mathbf{v}_j - \dot{\mathbf{x}}_j(t))$$

also note that

$$\begin{cases} \ddot{\mathbf{x}}_j(t) = \frac{\mathbf{F}_i}{m} \equiv \mathbf{f}_i \\ \dot{\mathbf{x}}_j = \mathbf{v}_j \end{cases}$$

where $\mathbf{f}_i = \frac{\mathbf{F}_i}{m}$ is the force per unit mass over the j^{th} particle. Therefore,

$$\begin{aligned} \frac{\partial}{\partial t} P &= - \sum_{j=1}^N \mathbf{v}_j \frac{\partial}{\partial \mathbf{x}_j} \delta(\mathbf{x}_j - \mathbf{x}_j(t)) \delta(\mathbf{v}_j - \dot{\mathbf{x}}_j(t)) \prod_{\substack{k=1 \\ k \neq j}}^N \delta(\mathbf{x}_k - \mathbf{x}_k(t)) \delta(\mathbf{v}_k - \dot{\mathbf{x}}_k(t)) \\ &\quad - \sum_{j=1}^N \frac{\mathbf{F}_i}{m} \frac{\partial}{\partial \mathbf{v}_j} \delta(\mathbf{v}_j - \dot{\mathbf{x}}_j(t)) \delta(\mathbf{x}_j - \mathbf{x}_j(t)) \prod_{\substack{k=1 \\ k \neq j}}^N \delta(\mathbf{x}_k - \mathbf{x}_k(t)) \delta(\mathbf{v}_k - \dot{\mathbf{x}}_k(t)) \\ &= - \sum_{j=1}^N \mathbf{v}_j \frac{\partial}{\partial \mathbf{x}_j} P - \sum_{j=1}^N \frac{\mathbf{F}_i}{m} \frac{\partial}{\partial \mathbf{v}_j} P \end{aligned}$$

i.e.,

$$\frac{\partial}{\partial t} P + \sum_{j=1}^N \mathbf{v}_j \frac{\partial}{\partial \mathbf{x}_j} P + \sum_{j=1}^N \frac{\mathbf{F}_i}{m} \frac{\partial}{\partial \mathbf{v}_j} P = 0$$

which is the Liouville equation — a linear, homogeneous, first order partial differential equation.

If we know the initial state $\{\mathbf{x}_i^0, \mathbf{v}_i^0\}$, $i = 1, \dots, N$, then

$$P(\{\mathbf{x}, \mathbf{v}\}, t = 0) = \prod_{k=1}^N \delta(\mathbf{x}_k - \mathbf{x}_k^0) \delta(\mathbf{v}_k - \mathbf{v}_k^0)$$

If the initial data of the system is described by a probability density

$$\rho(\{\mathbf{x}, \mathbf{v}\}, t = 0),$$

then the evolution of this system is described by $\rho(\{\mathbf{x}, \mathbf{v}\}, t)$,

$$\rho(\{\mathbf{x}, \mathbf{v}\}, t) = \mathbf{E}(P(\{\mathbf{x}, \mathbf{v}\}, t))$$

where \mathbf{E} is the expectation operator over initial data ensemble. Therefore,

$$\frac{\partial}{\partial t} \rho + \sum_{j=1}^N \mathbf{v}_j \frac{\partial}{\partial \mathbf{x}_j} \rho + \sum_{j=1}^N \mathbf{f}_i \frac{\partial}{\partial \mathbf{v}_j} \rho = 0$$

1.1.1 Hamiltonian Dynamics

Under the Hamiltonian dynamics:

$$\begin{cases} \dot{p}_i = -\frac{\partial H}{\partial q_i} \\ \dot{q}_i = \frac{\partial H}{\partial p_i} \end{cases} \quad (1)$$

$i = 1, 2, \dots, 3N$.
e.g.

$$H = \frac{p^2}{2m} + V(q)$$

$$\begin{cases} \dot{p} = -\frac{\partial H}{\partial q} = -\frac{d}{dq}V(q) \\ \dot{q}_i = \frac{\partial H}{\partial p_i} = \frac{p}{m} \end{cases}$$

Note that H is independent of the time derivative of p_i and q_i . If H is explicitly time-independent, then Eq.(1) is time reversal symmetric. As a consequence of this symmetry, we have

1. The locus of a representative point is either a simple closed curve or a curve that never intersects itself.
2. The loci of two distinct representative points never intersect.

Then the Liouville Theorem is

$$\frac{\partial}{\partial t}\rho + \sum_{j=1}^{3N} \left(\dot{p}_j \frac{\partial}{\partial p_j} \rho + \dot{q}_j \frac{\partial}{\partial q_j} \rho \right) = 0$$

i.e.,

$$\frac{D}{Dt}\rho = 0$$

the density of representative points remains constant along the Hamiltonian flow. This can be easily seen from the Divergence Theorem. Since

$$-\frac{d}{dt} \int_{\Gamma} d\Gamma \rho = \int_s dS \mathbf{n} \cdot \mathbf{V} \rho$$

where $\mathbf{V} = (\dot{p}_1, \dot{p}_2, \dots, \dot{p}_{3N}, \dot{q}_1, \dots, \dot{q}_{3N})$, we have

$$\int_{\Gamma} d\Gamma \left[\frac{\partial \rho}{\partial t} + \nabla \cdot (\mathbf{V}\rho) \right] = 0$$

therefore,

$$\begin{aligned} -\frac{\partial \rho}{\partial t} &= \sum_{i=1}^{3N} \left(\frac{\partial \rho}{\partial p_i} \dot{p}_i + \frac{\partial \rho}{\partial q_i} \dot{q}_i \right) \\ &\quad + \sum_{i=1}^{3N} \rho \left(\frac{\partial \dot{p}_i}{\partial p_i} + \frac{\partial \dot{q}_i}{\partial q_i} \right) \end{aligned}$$

Since a Hamiltonian system has the Liouville property:

$$\frac{\partial \dot{p}_i}{\partial p_i} + \frac{\partial \dot{q}_i}{\partial q_i} = 0, \quad \forall i$$

Hence, the Liouville equation:

$$\begin{aligned} -\frac{\partial \rho}{\partial t} &= \sum_{i=1}^{3N} \left(\frac{\partial \rho}{\partial p_i} \dot{p}_i + \frac{\partial \rho}{\partial q_i} \dot{q}_i \right) \\ \text{i.e.,} \quad \frac{D\rho}{Dt} &= 0 \end{aligned}$$

1.1.2 The General Case

It is important to realize that the Liouville equation holds for more general cases than the Hamiltonian dynamics. We summarize some relevant results below. Consider the following differential equations:

$$\frac{d}{dt} \mathbf{X} = \mathbf{F}(\mathbf{X}), \quad \mathbf{X} = (X_1, \dots, X_N) \in \mathbb{R}^N, \quad \mathbf{F} = (F_1, \dots, F_N) \quad (2)$$

with $\mathbf{X}(t=0) = \mathbf{X}_0$. An associated flow map $\Phi^t(\mathbf{X})|_{t \geq 0}$

$$\Phi^t : \mathbb{R}^N \mapsto \mathbb{R}^N$$

then is defined by

$$\begin{aligned} \frac{d}{dt} \Phi^t(\mathbf{X}) &= \mathbf{F}(\Phi^t(\mathbf{X})) \\ \Phi^t(\mathbf{X})|_{t=0} &= \mathbf{X}_0 \end{aligned}$$

If the initial ensemble of the system (2) is described by a probability density function $\rho_0(\mathbf{X})$ at $t=0$. Then, under the flow $\Phi^t(\mathbf{X})|_{t \geq 0}$, the evolution of this ensemble is described by a density $\rho(\mathbf{X}, t)$, which is the pull-back of the initial probability density $\rho_0(\mathbf{X})$ with the flow map $\Phi^t(\mathbf{X})$, i.e.,

$$\rho(\mathbf{X}, t) \equiv \rho_0 \left((\Phi^t)^{-1}(\mathbf{X}) \right).$$

Liouville Property If the vector field $\mathbf{F}(\mathbf{X})$ satisfies the divergence-free condition, i.e.,

$$\nabla_{\mathbf{x}}\mathbf{F} = \sum_{j=1}^N \frac{\partial F_j}{\partial X_j} = 0$$

the vector field $\mathbf{F}(\mathbf{X})$ is said to have the Liouville property. Then, we have

1. $\Phi^t(\mathbf{X})$ is volume preserving (or measure preserving) on the phase space, i.e.,

$$\det(\nabla_{\mathbf{x}}\Phi^t(\mathbf{X})) = 1$$

for all time $t \geq 0$

2. $\rho(\mathbf{X},t)$ satisfies the Liouville equation:

$$\frac{\partial}{\partial t}\rho + \mathbf{F} \cdot \nabla_{\mathbf{x}}\rho = 0,$$

which shows that $\rho(\mathbf{X},t)$ is a probability density function for all time.

2 The Equilibrium State of an Ideal Gas

What is a state of equilibrium? Recall Maxwellian distribution — the one-particle distribution of ideal gas.

The ideal gas is a model gas in which the potential energy of intermolecular forces is negligible outside a core of strong repulsive force.

We assume that the number N of molecules in a box is large, $N \gg 1$. Under the normal condition, $N \sim 10^{20}$ in a volume of 1cm^3 .

For monatoms, there is no internal degrees of freedom (e.g., unlike, say, oxygen molecules, O_2 , there is a vibration mode between two oxygen atoms in the molecule) and the state of molecules can be completely specified by their three spatial coordinates and three velocity components. These are the molecules we will consider below.

Physical Intuition: An equilibrium state is a state whose macroscopic observables (which are the averaged microscopic quantities with the details of molecular interactions coarse-grained out) remains constant in macroscopic times. A macroscopic state can be described by a probability density ρ of certain microscopic states and the equilibrium condition requires that

$$\frac{\partial \rho}{\partial t} = 0 \tag{3}$$

If there is no external field, then we can show that $\frac{\partial \rho}{\partial x_i} = 0$, i.e., the gas is homogeneous in space. We note that this $\rho(\{\mathbf{x}_k, \mathbf{v}_k\}, t)$ is a coarse-grained probability density function describing a macroscopic state of a gas with the details of molecular interactions averaged out. It is different from the one obtained by averaging over the initial data (as we have done above in obtaining Liouville equation for the general situation), therefore, it need not satisfy the Liouville equation. However, since we can show that this coarse-grained ρ actually is spatially uniform (see below), then it satisfies the Liouville equation trivially.

We now consider the equilibrium state of an ideal gas in a closed system — a closed system is one which does not exchange energy nor particles with other systems. Obviously, for a closed system, the total energy of all the particles is conserved,

$$E_{total} = \text{constant in time.}$$

We consider the gas is in a box (denoted by region R) with specular reflections for particles colliding with the boundary, i.e.,

$$\begin{aligned} \mathbf{v}_i \cdot \mathbf{n} &> 0 \text{ for } \mathbf{x}_i \in \partial R \\ \rho(\mathbf{x}_1, \dots, \mathbf{x}_N, \mathbf{v}_1, \dots, \mathbf{v}_N, t) &= \rho(\mathbf{x}_1, \dots, \mathbf{x}_N, \mathbf{v}_1, \dots, \mathbf{v}_i - 2\mathbf{n}(\mathbf{n} \cdot \mathbf{v}_i), \dots, \mathbf{v}_N, t) \end{aligned}$$

for the box at rest.

Since a particle of an ideal gas has only kinetic energy:

$$E_i = \frac{1}{2} m \mathbf{v}_i^2$$

Clearly, this boundary condition conserves the energy of each particle which collides with the wall because

$$\begin{aligned} (\mathbf{v}_i - 2\mathbf{n}(\mathbf{n} \cdot \mathbf{v}_i))^2 &= \mathbf{v}_i^2 - 4(\mathbf{n} \cdot \mathbf{v}_i)(\mathbf{n} \cdot \mathbf{v}_i) + 4(\mathbf{n} \cdot \mathbf{v}_i)^2 \\ &= \mathbf{v}_i^2 \end{aligned}$$

The momentum is not conserved for this particle.

Note that, corresponding to a macrostate, there are many microstates.

For a collision between any pair of particles, i , and j , inside the region R , in addition to the momentum conservation:

$$m\mathbf{v}'_1 + m\mathbf{v}'_2 = m\mathbf{v}_1 + m\mathbf{v}_2$$

we have the energy conservation:

$$\frac{1}{2} m \mathbf{v}'_1{}^2 + \frac{1}{2} m \mathbf{v}'_2{}^2 = \frac{1}{2} m \mathbf{v}_1^2 + \frac{1}{2} m \mathbf{v}_2^2$$

where the primed quantities denote the ones after collision. Therefore, the total energy is conserved (note that the total momentum is not conserved because of the boundary). Since

these collisions do not manifest themselves macroscopically, we postulate that the coarse-grained ρ is a function of the total energy

$$E = \sum_{i=1}^N \frac{1}{2} m \mathbf{v}_i^2$$

only. We denote the average energy per mass as

$$\varepsilon = \frac{E}{Nm} = \frac{1}{Nm} \sum_{i=1}^N \frac{1}{2} m \mathbf{v}_i^2 = \frac{1}{N} \sum_{i=1}^N \frac{1}{2} \mathbf{v}_i^2$$

then we have

$$\rho_N = C_N \delta\left(\sum_{i=1}^N \mathbf{v}_i^2 - 2N\varepsilon\right), \quad (4)$$

where C_N is a normalization and is determined by

$$\int C_N \rho d\Gamma = 1$$

where $d\Gamma$ is a volume element in the phase space. We note that in the coarse-grained picture of the N -partical distributions, Eq. (4) expresses the fact that all the coarse-grained systems of the same energy are equally likely to occur.

Microcanonical Ensembles

Eq. (4) can also be understood as follows: For a given total energy for an isolated system, all possible microstates are equally likely to occur, that is, the ensemble of all microstates are uniformly distributed over the energy surface determined by the total energy. This hypothesis is the fundamental assumption of equilibrium statistical mechanics.

Now we proceed to study the consequence of Eq. (4). We have

$$C_N \int_{\mathbb{R}^{3N}} \delta\left(\sum_{i=1}^N \mathbf{v}_i^2 - 2N\varepsilon\right) d\mathbf{v}_1 \cdots d\mathbf{v}_N \int_{R^N} d\mathbf{x}_1 \cdots d\mathbf{x}_N = 1 \quad (5)$$

where $\int_{R^N} d\mathbf{x}_1 \cdots d\mathbf{x}_N = V^N$, V is the volume of the box. Using the polar coordinates:

$$\sum_{i=1}^N \mathbf{v}_i^2 = r^2, \quad d\mathbf{v}_1 \cdots d\mathbf{v}_N = r^{3N-1} dr d^{3N}\Omega$$

where $d^{3N}\Omega$ is the surface element of the unit sphere in $3N$ dimension. We can easily evaluate the surface area of the unit sphere in N -Dimension.

$$A_N \equiv \int d^N\Omega = \frac{2\pi^{N/2}}{\Gamma\left(\frac{N}{2}\right)}.$$

Then, Eq. (5) is

$$C_N V^N \int_0^\infty \delta(r^2 - 2N\varepsilon) r^{3N-1} dr \int d^{3N}\Omega = 1 \quad (6)$$

Using the property of the δ -function,

$$\delta(x^2 - a^2) = \frac{1}{2|a|} [\delta(x - a) + \delta(x + a)]$$

Eq. (6) becomes

$$\begin{aligned} C_N V^N \frac{1}{2} (2N\varepsilon)^{(3N-2)/2} A_{3N} &= 1 \\ C_N &= 2V^{-N} (2N\varepsilon)^{-(3N-2)/2} A_{3N}^{-1} \end{aligned}$$

and

$$\rho_N = \frac{2}{A_{3N} (2N\varepsilon)^{(3N-2)/2} V^N} \delta\left(\sum_{i=1}^N \mathbf{v}_i^2 - 2N\varepsilon\right)$$

However, this expression of ρ_N still does not tell us much. Note that this ρ_N is an N -particle probability density function. If we are interested in one-particle properties, then, we can ask the question what is the probability density of finding a molecule (regardless which molecule) that has velocity lying in $[\mathbf{v}, \mathbf{v}+d\mathbf{v}]$ and its position lying in $[\mathbf{x}, \mathbf{x}+d\mathbf{x}]$ without any regard of other particles. Without loss of generality, this particle can be labeled as particle #1. Clearly, the one-particle probability density is

$$\begin{aligned} \rho_N^{(1)}(\mathbf{x}_1, \mathbf{v}_1) &\equiv \int_{\mathbb{R}^{3N-3}} d\mathbf{v}_2 d\mathbf{v}_3 \cdots d\mathbf{v}_N \int_{R^{\otimes(N-1)}} d\mathbf{x}_2 d\mathbf{x}_3 \cdots d\mathbf{x}_N \rho_N \\ &= V^{N-1} C_N \int_{\mathbb{R}^{3N-3}} \delta\left(\sum_{i=1}^N \mathbf{v}_i^2 - 2N\varepsilon\right) d\mathbf{v}_2 d\mathbf{v}_3 \cdots d\mathbf{v}_N \end{aligned}$$

Again using the polar coordinates for this space \mathbb{R}^{3N-3} :

$$\sum_{i=2}^N \mathbf{v}_i^2 = r^2, \quad d\mathbf{v}_2 \cdots d\mathbf{v}_N = r^{3N-4} dr d^{3N-3}\Omega$$

therefore

$$\begin{aligned} \rho_N^{(1)} &= V^{N-1} C_N A_{3N-3} \int \delta(r^2 - (2N\varepsilon - \mathbf{v}_1^2)) r^{3N-4} dr \\ &= A_{3N-3} A_{3N}^{-1} V^{-1} (2N\varepsilon)^{-(3N-2)/2} (2N\varepsilon - \mathbf{v}_1^2)^{(3N-5)/2} \quad \text{for } \mathbf{v}_1^2 < 2N\varepsilon \end{aligned}$$

For $\mathbf{v}_1^2 < 2N\varepsilon$, we have

$$\begin{aligned} \rho_N^{(1)}(\mathbf{x}_1, \mathbf{v}_1) &= A_{3N-3} A_{3N}^{-1} V^{-1} (2N\varepsilon)^{-(3N-2)/2} (2N\varepsilon - \mathbf{v}_1^2)^{(3N-5)/2} \\ &= \left(\frac{3}{4\pi\varepsilon}\right)^{3/2} V^{-1} \left(1 - \frac{\mathbf{v}_1^2}{2N\varepsilon}\right)^{(3N-5)/2} \frac{\Gamma\left(\frac{3}{2}N\right)}{\left(\frac{3}{2}N\right)^{3/2} \Gamma\left(\frac{3N-3}{2}\right)} \end{aligned}$$

since $A_N = \frac{2\pi^{N/2}}{\Gamma(\frac{N}{2})}$.

For $\mathbf{v}_1^2 > 2N\varepsilon$, we have

$$\rho_N^{(1)}(\mathbf{x}_1, \mathbf{v}_1) = 0.$$

Note that:

1. $\rho_N^{(1)}$ is \mathbf{x}_1 -independent, i.e., the particle is uniformly distributed in space and it can be anywhere at random.
2. As $N \rightarrow \infty$,

$$\rho_\infty^{(1)} = \lim_{N \rightarrow \infty} \rho_N^{(1)} = \left(\frac{3}{4\pi\varepsilon}\right)^{3/2} V^{-1} \exp\left(-\frac{3\mathbf{v}^2}{4\varepsilon}\right)$$

we will show later that

$$\varepsilon = \frac{3}{2} \frac{k_B T}{m}$$

where $k_B = 1.38 \times 10^{-23} \text{ J K}^{-1}$ is the Boltzmann constant. Therefore,

$$\rho_\infty^{(1)}(\mathbf{v}) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \frac{1}{V} \exp\left(-\frac{m\mathbf{v}^2}{2k_B T}\right)$$

which is the Maxwellian distribution.

We can proceed to the two-particle probability density, i.e., of finding particle #1 with its velocity in $[\mathbf{v}_1, \mathbf{v}_1 + d\mathbf{v}_1]$ and location in $[\mathbf{x}_1, \mathbf{x}_1 + d\mathbf{x}_1]$ and finding particle #2 with its velocity in $[\mathbf{v}_2, \mathbf{v}_2 + d\mathbf{v}_2]$ and location in $[\mathbf{x}_2, \mathbf{x}_2 + d\mathbf{x}_2]$. Obviously, the distribution is

$$\rho_N^{(2)}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{v}_1, \mathbf{v}_2) \equiv \int_{\mathbb{R}^{3N-6}} d\mathbf{v}_3 d\mathbf{v}_4 \cdots d\mathbf{v}_N \int_{R^{\otimes(N-2)}} d\mathbf{x}_3 d\mathbf{x}_4 \cdots d\mathbf{x}_N \rho_N$$

For $\mathbf{v}_1^2 + \mathbf{v}_2^2 < 2N\varepsilon$, we have

$$\begin{aligned} \rho_N^{(2)}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{v}_1, \mathbf{v}_2) &= V^{N-2} C_N A_{3N-6} \frac{1}{2} (2N\varepsilon - (\mathbf{v}_1^2 + \mathbf{v}_2^2))^{(3N-8)/2} \\ &= A_{3N-6} A_{3N}^{-1} V^{-2} (2N\varepsilon)^{-(3N-4)/2} (2N\varepsilon - (\mathbf{v}_1^2 + \mathbf{v}_2^2))^{(3N-8)/2} \\ &= \left(\frac{3}{4\pi\varepsilon}\right)^3 \frac{1}{V^2} \left(1 - \frac{\mathbf{v}_1^2 + \mathbf{v}_2^2}{2N\varepsilon}\right)^{(3N-8)/2} \left(1 - \frac{2}{3N}\right) \left(1 - \frac{4}{3N}\right) \left(1 - \frac{6}{3N}\right) \end{aligned}$$

and for $\mathbf{v}_1^2 + \mathbf{v}_2^2 > 2N\varepsilon$, we have

$$\rho_N^{(2)}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{v}_1, \mathbf{v}_2) = 0$$

An extremely important result follows as the limit $N \rightarrow \infty$ is taken:

$$\begin{aligned} \rho_N^{(2)}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{v}_1, \mathbf{v}_2) &= \left(\frac{3}{4\pi\varepsilon}\right)^3 \frac{1}{V^2} \exp\left[-\frac{3}{4\varepsilon} (\mathbf{v}_1^2 + \mathbf{v}_2^2)\right] \\ &= \rho_\infty^{(1)}(\mathbf{x}_1, \mathbf{v}_1) \rho_\infty^{(1)}(\mathbf{x}_2, \mathbf{v}_2) \end{aligned}$$

i.e., the two-particle distribution becomes independent and there is no correlation between any two particles as $N \rightarrow \infty$.

Note that, in general, two particles are correlated for the finite N case. This is due to the fact that the total energy is conserved, if one particle is known to possess high velocity, then the other will likely possess low velocity.

Comment: In the above derivation, we di

Q: Ideal gas in a spherical container with specular reflection.

Question:

How much volume is "concentrated" on the surface?

In n -Dim, the unit ball has volume

$$V_n = \frac{1}{n} \frac{2\pi^{n/2}}{\Gamma\left(\frac{n}{2}\right)}$$

and the surface area on the unit sphere is

$$\frac{2\pi^{n/2}}{\Gamma\left(\frac{n}{2}\right)}$$

therefore

$$\frac{\text{Volume in the shell } dr}{\text{Volume of the unit ball}} = ndr$$

If

$$dr = \frac{1}{n}$$

then

$$dr \rightarrow 0 \quad \text{as } n \rightarrow \infty$$

and

$$\frac{\text{Volume in the shell } dr}{\text{Volume of the unit ball}} = 1$$

Homework

1. Truncated Burgers equation.

The inviscid Burger's equation is

$$\frac{\partial}{\partial t}u + \frac{1}{2}(u^2)_x = 0$$

Let $\mathcal{P}_\Lambda f = f_\Lambda$ denote the finite Fourier series truncation, i.e.,

$$\mathcal{P}_\Lambda f = f_\Lambda = \sum_{|k| \leq \Lambda} \hat{f}_k e^{ikx}$$

Here, all functions, such as, u , f are assumed to be 2π -periodic.

We define the Fourier-truncated Burgers equation as

$$\frac{\partial}{\partial t}u_\Lambda + \frac{1}{2}\mathcal{P}_\Lambda (u_\Lambda^2)_x = 0$$

and note that

$$\begin{aligned} u_\Lambda(t) &= \sum_{|k| \leq \Lambda} \hat{u}_k(t) e^{ikx} \\ \hat{u}_{-k} &= \hat{u}_k^*. \end{aligned}$$

Show that the truncated Burgers equation has a Liouville property in the variables $\{\hat{u}_k\}$, $1 \leq |k| \leq \Lambda$. (more precisely, in a_k, b_k , where $\hat{u}_k = a_k + ib_k$).

2. Given the particle number distribution of the particle in equilibrium

$$\rho(\mathbf{v}) = n \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-\frac{m\mathbf{v}^2}{2k_B T}}$$

show that the equation of state for the ideal gas is

$$p = nk_B T$$

where $n = N/V$ is the number density and p is the pressure of the gas.

3. Show that for

$$\frac{d\mathbf{X}}{dt} = F(\mathbf{X})$$

if $\nabla_X \cdot F = 0$, then

$$\det(\nabla_X \Phi^t(\mathbf{X})) = 1$$