Equilibrium, local equilibrium, nonequilibrium

Typical particle Hamiltonian:

$$\hat{H} = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} + \sum_{i<j} u(\vec{x}_i - \vec{x}_j)$$

Full N-body dist$^{\underline{ns}}$:

$$\rho_N(\vec{x}_1, \ldots, \vec{x}_N; \vec{p}_1, \ldots, \vec{p}_N) = \frac{1}{N!} \begin{cases} Z_N^{-1} e^{-\beta \hat{H}_N} & \text{OCE} \\ \Xi^{-1} e^{\beta \mu N} e^{-\beta \hat{H}_N} & \text{GCE} \end{cases}$$

Then

$$\underset{\uparrow \text{ dimensionless}}{\rho_N(\{\vec{x}_i\}; \{\vec{p}_i\})} \prod_{j=1}^{N} \frac{d^d x_j \, d^d p_j}{h^d} = \begin{cases} \text{prob to find \#1 within} \\ d^d x_1 \text{ of } \vec{x}_1 \text{ and within} \\ d^d p_1 \text{ of } \vec{p}_1, \text{ etc.} \end{cases}$$

Nonequilibrium: $\rho_N = \rho_N(\{\vec{x}_i\}; \{\vec{p}_i\}, t)$ is time-dependent. General nonequilibrium problem is hopeless – need to compute avgs by integrating over $\mathcal{O}(N_A)$ coordinates. But in our applications typically external drives occur over large scales, and scattering processes then work to establish local equilibria in which there are <u>local</u> values for intensive thermodynamic quantities such as $T(\vec{r})$, $\mu(\vec{r})$, and $\vec{V}(\vec{r})$ (local velocity field).

The K-body distribution

$$f_K(\vec{r}_1, \ldots, \vec{r}_K, \vec{\pi}_1, \ldots, \vec{\pi}_K, t) \equiv \sum_{\{j_1, \ldots, j_K\}}{}' \langle \delta(\vec{r}_1 - \vec{x}_{j_1}(t)) \cdots$$

← all indices distinct

$$\delta(\vec{r}_K - \vec{x}_{j_K}(t))\, \delta(\vec{\pi}_1 - \vec{p}_{j_1}(t)) \cdots \delta(\vec{\pi}_K - \vec{p}_{j_K}(t)) \rangle$$

$$= \frac{N!\, h^{-Kd}}{(N-K)!} \int \prod_{i=K+1}^{N} d\mu_i\, \rho_N(\vec{r}_1, \ldots, \vec{r}_K, \vec{x}_{K+1}, \ldots, \vec{x}_N ; \vec{\pi}_1, \ldots, \vec{\pi}_K, \vec{p}_{K+1}, \ldots, \vec{p}_N)$$

$$d\mu_i = h^{-d} d^d x_i\, d^d p_i$$

We'll mostly be interested in $K = 1$:

$$f(\vec{r}, \vec{\pi}) = N h^{-d} \int \prod_{i=2}^{N} d\mu_i\, \rho_N(\vec{r}, \vec{x}_2, \ldots, \vec{x}_N ; \vec{\pi}, \vec{p}_2, \ldots, \vec{p}_N)$$

called the (diagonal elements of the) 1-body density matrix.

Symmetry $\Rightarrow$ $\rho_N(\sigma\{\vec{x}_j\}, \sigma\{\vec{p}_j\}, t) = \rho_N(\{\vec{x}_j\}, \{\vec{p}_j\}, t)$

where $\{\vec{x}_j\} = \{\vec{x}_1, \ldots, \vec{x}_N\}$ and $\sigma\{\vec{x}_j\} = \{x_{\sigma(1)}, \ldots, x_{\sigma(N)}\}$

with $\sigma \in S_N$ is a permutation of the N labels.

Then we have "sum rules":

$$\int \prod_{i=1}^{K} d^d r_i \, d^d \pi_i \; f_K(\{\vec{r}_j\}, \{\vec{\pi}_j\}, t) = \frac{N!}{(N-K)!}$$

Thus with $f(\vec{r}, \vec{p}, t) = f_1(\vec{r}, \vec{p}, t)$ we have

$$\int d^d r \, d^d p \, f(\vec{r}, \vec{p}, t) = N$$

1-body number density: $n(\vec{r}, t) = \int d^d p \, f(\vec{r}, \vec{p}, t)$

and so $\int d^d r \, n(\vec{r}, t) = N$.

Currents

We've already defined

$$\vec{j}(\vec{r}, t) = \int d^d p \, f(\vec{r}, \vec{p}, t) \frac{\vec{p}}{m}$$

$$\vec{j}_\varepsilon(\vec{r}, t) = \int d^d p \, f(\vec{r}, \vec{p}, t) \, \varepsilon(\vec{p}) \frac{\vec{p}}{m}$$

Equilibrium dist$^{\underline{n}}$ for ballistic particles:

$$f^0(\vec{r},\vec{p}) = \frac{n}{(2\pi m k_B T)^{d/2}}\, e^{-\vec{p}^{\,2}/2mk_BT}$$
$$= h^{-d}\, z\, e^{-\vec{p}^{\,2}/2mk_BT} \quad ; \quad z = e^{\beta\mu} = n\lambda_T^d$$

Recall $\vec{j}_q = T\vec{j}_s = \vec{j}_\varepsilon - \mu\vec{j}$

from local thermodynamics $dq = T\,ds = d\varepsilon - \mu\,dn$.

Derivation of Boltzmann Eq$^{\underline{n}}$

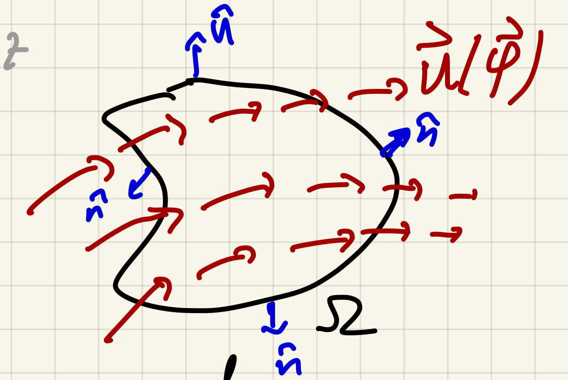
Recall $f(\vec{r},\vec{p},t)\, d^3r\, d^3p = \begin{cases} \#\text{ particles within } d^3r \text{ of } \vec{r} \\ \text{and } d^3p \text{ of } \vec{p} \text{ at time } t \end{cases}$

Let $\vec{\varphi} = (x, y, z, p_x, p_y, p_z)$ be the 6-dim^l <u>phase space</u> position and $\vec{u} = \dot{\vec{\varphi}} = (\dot{x}, \dot{y}, \dot{z}, \dot{p}_x, \dot{p}_y, \dot{p}_z)$ be the <u>phase space velocity vector</u>. The dist$^{\underline{n}}$ must obey the continuity equation,

$$\frac{\partial f}{\partial t} + \vec{\nabla}\cdot(\vec{u} f) = 0$$

Integrating over a region Ω gives

$$0 = \int_\Omega dV \left[\frac{\partial f}{\partial t} + \vec{\nabla}\cdot(\vec{u} f)\right] \qquad \leftarrow dV = dx\,dy\,dz\,dp_x\,dp_y\,dp_z$$



$$= \frac{d}{dt}\int_\Omega dV f + \int_\Omega dV\, \vec{\nabla}\cdot(\vec{u} f)$$

diff' surface area

outward normal

$$= \frac{d}{dt} Q_\Omega + \int_{\partial\Omega} d\Sigma\, \hat{n}\cdot\vec{u} f = \frac{dQ_\Omega}{dt} + \int_{\partial\Omega} d\Sigma\, \hat{n}\cdot\vec{j}$$

"charge" in Ω — boundary of Ω — current $\vec{j} = \vec{u} f$

Thus,

$$\frac{dQ_\Omega}{dt} = -\int_{\partial\Omega} d\Sigma\, \hat{n}\cdot\vec{j}$$

Just like in E&M!

The dynamics of $\vec{\varphi}(t)$ are Hamiltonian:

$$\dot{\vec{r}} = \frac{\partial H}{\partial \vec{p}} \quad , \quad \dot{\vec{p}} = -\frac{\partial H}{\partial \vec{r}}$$

$$H = \varepsilon(\vec{p}) + U(\vec{r})$$

Hamiltonian flow is <u>incompressible</u>:

$$\vec{\nabla}\cdot\vec{u} = \frac{\partial \dot{r}^\alpha}{\partial r^\alpha} + \frac{\partial \dot{p}^\alpha}{\partial p^\alpha}$$

$$\dot{r}^\alpha = \frac{\partial H}{\partial p^\alpha} \quad , \quad \dot{p}_\alpha = -\frac{\partial H}{\partial r^\alpha}$$

So $$\vec{\nabla}\cdot\vec{u} = \frac{\partial}{\partial r^\alpha}\frac{\partial H}{\partial p^\alpha} + \frac{\partial}{\partial p^\alpha}\left(-\frac{\partial H}{\partial r^\alpha}\right) = 0$$

if $H(\vec{p}, \vec{r})$ is a smooth f^n of its arguments.

Thus the continuity eqn simplifies:

$$0 = \frac{\partial}{\partial t} + \vec{\nabla}\cdot(\vec{u}f) = \frac{\partial}{\partial t} + f\,\cancel{\vec{\nabla}\cdot\vec{u}} + \vec{u}\cdot\vec{\nabla}f$$

$$\Rightarrow \quad \frac{Df}{Dt} = \frac{\partial f}{\partial t} + \vec{u}\cdot\vec{\nabla}f = 0$$

The operator $\frac{D}{Dt} = \frac{\partial}{\partial t} + \vec{u}\cdot\vec{\nabla}$ is called the <u>convective derivative</u>. It evaluates change in time measured in a frame which moves with the local velocity $\vec{u}(\vec{\varphi})$:

$$\frac{d}{dt} f(\vec{r}(t), \vec{p}(t), t) = \frac{\partial f}{\partial \vec{r}} \cdot \frac{d\vec{r}}{dt} + \frac{\partial f}{\partial \vec{p}} \cdot \frac{d\vec{p}}{dt} + \frac{\partial f}{\partial t} = \frac{Df}{Dt}$$

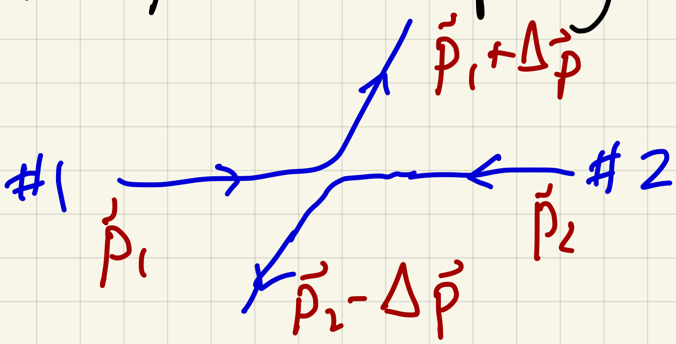
The equation $\frac{Df}{Dt} = 0$ is known as the <u>collisionless</u> <u>Boltzmann</u> <u>eqn</u> (CBE). It can be written as

$$\frac{\partial f}{\partial t} + \overbrace{\dot{\vec{r}} \cdot \frac{\partial f}{\partial \vec{r}} + \dot{\vec{p}} \cdot \frac{\partial f}{\partial \vec{p}}}^{(df/dt)_{\text{streaming}}} = 0$$

To complete the derivation, we add the <u>collision</u> <u>term</u> to the RHS

$$\frac{\partial f}{\partial t} + \dot{\vec{r}} \cdot \frac{\partial f}{\partial \vec{r}} + \dot{\vec{p}} \cdot \frac{\partial f}{\partial \vec{p}} = \left(\frac{df}{dt}\right)_{\text{collision}}$$

In collisions, two particles rapidly exchange momenta:



Collisions are assumed to occur locally in space.