Lecture Notes on:

“NonEquilibrium Statistical Mechanics and Lyapunov Instability”

by

Denis J. Evans and Debra J. Searles
Research School of Chemistry
Canberra, ANU, ACT 2601
Australia

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Liouville Equation for N-particle distribution function

$$\frac{\partial f(\boldsymbol{\Gamma},t)}{\partial t} = -\frac{\partial}{\partial \boldsymbol{\Gamma}} \bullet [\dot{\boldsymbol{\Gamma}} f(\boldsymbol{\Gamma},t)] \equiv -i\mathit{L} f(\boldsymbol{\Gamma},t) \tag{1}$$

Equation of motion of phase function

$$\frac{dA(\boldsymbol{\Gamma})}{dt} = \dot{\boldsymbol{\Gamma}} \bullet \frac{\partial A(\boldsymbol{\Gamma})}{\partial \boldsymbol{\Gamma}} \equiv iLA(\boldsymbol{\Gamma}) \tag{2}$$

So,

$$iL = \dot{\boldsymbol{\Gamma}} \bullet \frac{\partial}{\partial \boldsymbol{\Gamma}} \ldots, \quad i\mathit{L} = \frac{\partial}{\partial \boldsymbol{\Gamma}} \bullet \dot{\boldsymbol{\Gamma}} \ldots, \quad i\mathit{L} - iL = \frac{\partial}{\partial \boldsymbol{\Gamma}} \bullet \dot{\boldsymbol{\Gamma}} \equiv \Lambda(\boldsymbol{\Gamma}) \tag{3}$$

and since,

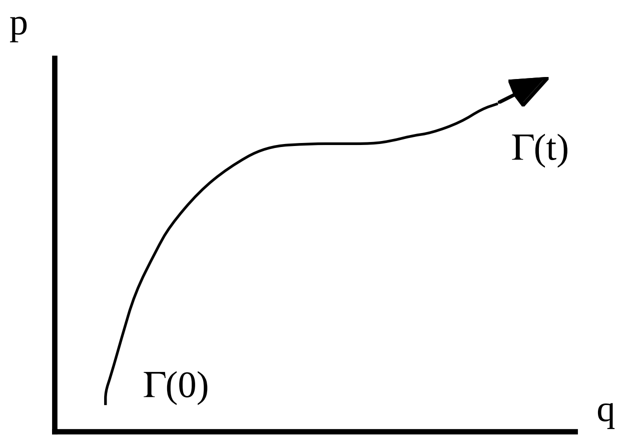
$$\frac{df}{dt} = [\frac{\partial}{\partial t} + \dot{\boldsymbol{\Gamma}} \bullet \frac{\partial}{\partial \boldsymbol{\Gamma}}] f = -f\Lambda \tag{4}$$

Λ is called the *phase space compression factor*. The formal solution of the equations of motion,

$$f(\mathbf{\Gamma},t)=\exp[-i\mathit{L}t]f(\mathbf{\Gamma},0)=\sum_{n=0}^{\infty}\frac{(-i\mathit{L}t)^n}{n!}f(\mathbf{\Gamma},0) \qquad (5)$$

and

$$A(\mathbf{\Gamma}(t))=\exp[+iLt]A(\mathbf{\Gamma}(0))=\sum_{n=0}^{\infty}\frac{(iLt)^n}{n!}A(\mathbf{\Gamma}(0)) \qquad (6)$$



Response theory

Consider an initial equilibrium ensemble:

$$f(\mathbf{\Gamma},0)=\frac{\exp[-\beta H_0(\mathbf{\Gamma})]}{\int d\mathbf{\Gamma}\,\exp[-\beta H_0(\mathbf{\Gamma})]} \tag{7}$$

$$f(\mathbf{\Gamma},t)=\exp[-(iL+\Lambda)t]f(\mathbf{\Gamma},0) \tag{8}$$

Now employ a *Dyson decomposition*

$$\begin{aligned}&\exp[-(iL+\Lambda)t]\\&=\exp[-iLt]-\int_0^t ds\,\exp[-(iL+\Lambda)s]\Lambda\exp[-iL(t-s)]\end{aligned} \tag{9}$$

Substitute recursively,

$$\begin{aligned}&\exp[-(iL+\Lambda)t]\\&=\exp[-iLt]\\&-\int_0^t ds_1\,\exp[-iLs_1]\Lambda\exp[-iL(t-s_1)]\\&+\int_0^t ds_1\int_0^{s_1} ds_2\,\exp[-iLs_2]\Lambda\exp[-iL(s_1-s_2)]\Lambda\exp[-iL(t-s_1)]\\&-.....\end{aligned} \tag{10}$$

Equations of motion

$$\frac{d\mathbf{q}_i}{dt} = \frac{\mathbf{p}_i}{m} + C_i \mathbf{F}_e$$

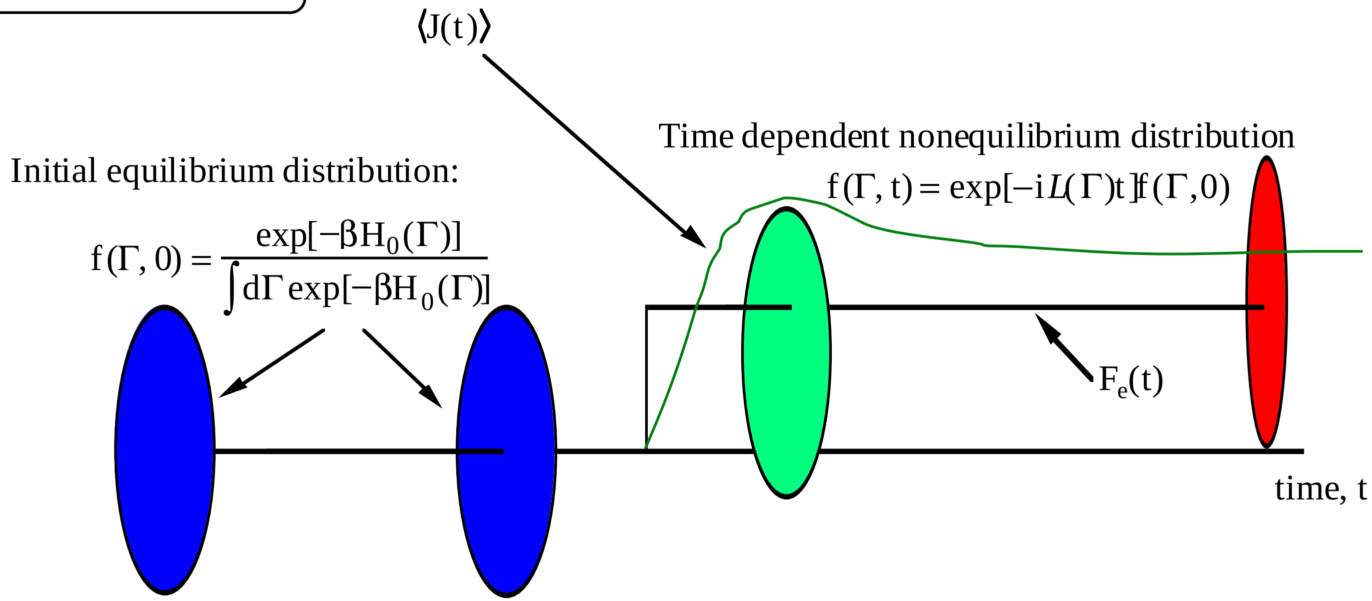
$$\frac{d\mathbf{p}_i}{dt} = \mathbf{F}_i + D_i \mathbf{F}_e - \alpha \mathbf{p}_i$$

Heat Q, is removed by the thermostat to ensure the possibility of a nonequilibrium steady state. J is called the dissipative flux. The momenta appearing in the equations of motion are peculiar.

α is chosen to keep the peculiar kinetic energy, K, constant:

Gaussian Thermostat

$$\frac{dQ}{dt} = -2K\alpha = -\mathbf{J} \bullet \mathbf{F}_e$$



$$
\begin{aligned}
&\exp[-(iL+\Lambda)t] \\
&= \exp[-iLt] \\
&-\int_0^t ds_1\, \Lambda(-s_1)\exp[-iLt] \\
&+\int_0^t ds_1 \int_0^{s_1} ds_2 \Lambda(-s_2)\Lambda(-s_1)\exp[-iLt] \\
&-..... \\
&= \exp[-\int_0^t ds\, \Lambda(-s)]\exp[-iLt]
\end{aligned} \tag{11}
$$

Substituting into the equation for the distribution function gives,

$$
f(\mathbf{\Gamma},t) = \exp[-\int_0^t ds\, \Lambda(s)]\exp[-\beta H_0(-t)] \tag{12}
$$

For isokinetic equations of motion,

$$
\begin{aligned}
\dot{\mathbf{q}}_i &= \frac{\mathbf{p}_i}{m} + C_i \mathbf{F}_e \\
\dot{\mathbf{p}}_i &= \mathbf{F}_i + D_i \mathbf{F}_e - \alpha \mathbf{p}_i
\end{aligned} \tag{13}
$$

From equations of motion,

$$\frac{dH_0}{dt} = \frac{dH_0}{dt}^{ad} + \frac{dH_0}{dt}^{therm}$$
$$= -\mathbf{J}(\mathbf{\Gamma}).\mathbf{F}_e - 2K\alpha \qquad (14)$$

and

$$\Lambda = 3N\alpha + O(1) \qquad (15)$$

This leads to the so-called *Kawasaki* expression for the nonequilibrium distribution function,

$$f(\mathbf{\Gamma},t) = \exp[-\beta\int_0^t ds\ \mathbf{J}(-s)\bullet\mathbf{F}_e]f(\mathbf{\Gamma},0) \qquad (16)$$

We can use this to compute averages,

$$< B(t) >= \int d\mathbf{\Gamma}\ f(\mathbf{\Gamma},t)B(\mathbf{\Gamma})$$
$$= \int d\mathbf{\Gamma}\ B(\mathbf{\Gamma})\exp[-\beta\int_0^t ds\ \mathbf{J}(-s)\bullet\mathbf{F}_e]f(\mathbf{\Gamma},0) \qquad (17)$$

$$d < B(t) > / dt = -\beta \int d\mathbf{\Gamma}\, B(\mathbf{\Gamma})\mathbf{J}(-t) \bullet \mathbf{F}_e f(\mathbf{\Gamma}, t)$$

$$= -\beta \int d\mathbf{\Gamma}\, B(t)\mathbf{J}(0) \bullet \mathbf{F}_e f(\mathbf{\Gamma}, 0) \qquad (18)$$

Yielding the *Transient Time Correlation Function* expression for an average,

$$< B(t) >= -\beta \mathbf{F}_e \bullet \int_0^t ds < \mathbf{J}(0)B(s) > \qquad (19)$$

In the small field limit we can linearise both Kawasaki and TTCF giving, the *Linear Response formula*

$$\lim_{F_e \to 0} < B(t) >= -\beta \mathbf{F}_e \bullet \int_0^t ds < \mathbf{J}(0)B(s) >_{eq} \qquad (20)$$

Green-Kubo Relations for linear thermal Transport Coefficients

1 Self Diffusion coefficient

$$D = \frac{1}{3}\int_0^{\infty} ds < \mathbf{v}_i(0) \bullet \mathbf{v}_i(t) >_{eq} \tag{21}$$

2 Thermal Conductivity

$$\lambda = \frac{V}{3k_B T^2}\int_0^{\infty} ds < \mathbf{J}_Q(0) \bullet \mathbf{J}_Q(t) >_{eq} \tag{22}$$

3 Shear Viscosity

$$\eta = \frac{V}{k_B T}\int_0^{\infty} ds < P_{xy}(0) P_{xy}(t) >_{eq} \tag{23}$$

4 Bulk Viscosity

$$\eta_V = \frac{1}{V k_B T}\int_0^{\infty} ds < [p(0)V(0) - < pV >][p(t)V(t) - < pV >] >_{eq} \tag{24}$$

NEMD Algorithms for Navier-Stokes transport coefficients.

SLLOD algorithm for shear viscosity

$$\dot{\mathbf{q}}_i = \frac{\mathbf{p}_i}{m} + \mathbf{i}\gamma y_i$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \mathbf{i}\gamma p_{yi} - \alpha\mathbf{p}_i \text{, which is equivalent to: } \ddot{\mathbf{q}}_i = \frac{\mathbf{F}_i}{m} + \mathbf{i}\gamma\delta(t) y_i \qquad (25)$$

satisfies AIΓ and the dissipative flux is $P_{xy}V$. The shear viscosity, η, is computed as,

$$\eta = -\lim_{\gamma\to 0}\lim_{t\to\infty} \frac{\frac{1}{t}\int_0^t ds\, P_{xy}(s)}{\gamma}$$

SLLOD algorithm for viscous flow

$$\dot{\mathbf{q}}_i = \frac{\mathbf{p}_i}{m} + \mathbf{q}_i \bullet \nabla\mathbf{u}$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \mathbf{p}_i \bullet \nabla\mathbf{u} - \alpha\mathbf{p}_i \qquad (26)$$

satisfies AIΓ and the dissipative flux is $\mathbf{P}V$.

Colour Conductivity algorithm for self diffusion

$$\dot{\mathbf{q}}_i = \frac{\mathbf{p}_i}{m}$$
$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \mathbf{i} c_i F_c - \alpha(\mathbf{p}_i - \mathbf{i} c_i J_x / \rho) \tag{27}$$

where

$$J_{cx} = \frac{1}{V}\sum_{i=1}^{N} c_i \dot{x}_i \quad \text{and} \quad \sum_{i=1}^{N} (\mathbf{p}_i - \mathbf{i} c_i J_{cx} / \rho)^2 / m = 3Nk_B T \tag{28}$$

satisfies AIΓ and the dissipative flux is $J_x V$. The self diffusion coefficient,D,

$$D = \lim_{F\to 0}\lim_{t\to\infty} \frac{1}{\beta\rho t} \frac{\int_0^t ds\, J_{cx}(s)}{F_c}$$

Evans Heat flow algorithm

$$\dot{\mathbf{q}}_i = \frac{\mathbf{p}_i}{m}$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - (E_i - \overline{E})\mathbf{F}_Q + \frac{1}{2}\sum_{j=1}^{N}\mathbf{F}_{ij}\mathbf{q}_{ij} \bullet \mathbf{F}_Q - \frac{1}{2N}\sum_{j,k=1}^{N}\mathbf{F}_{jk}\mathbf{q}_{jk} \bullet \mathbf{F}_Q - \alpha\mathbf{p}_i \qquad (29)$$

where

$$\overline{E} = \{\sum_{i=1}^{N}\frac{p_i^2}{2m} + \frac{1}{2}\sum_{i,j}^{N}\Phi_{ij}\}/N ,$$

satisfies AIΓ and the dissipative flux is $\mathbf{J}_Q V$,

where $\mathbf{J}_Q$ is the heat flux vector, $\mathbf{J}_Q V = \sum_i \frac{\mathbf{p}_i E_i}{m} - \frac{1}{2}\sum_{i,j}^{N}\mathbf{q}_{ij}\mathbf{F}_{ij} \bullet \frac{\mathbf{p}_i}{m}$.

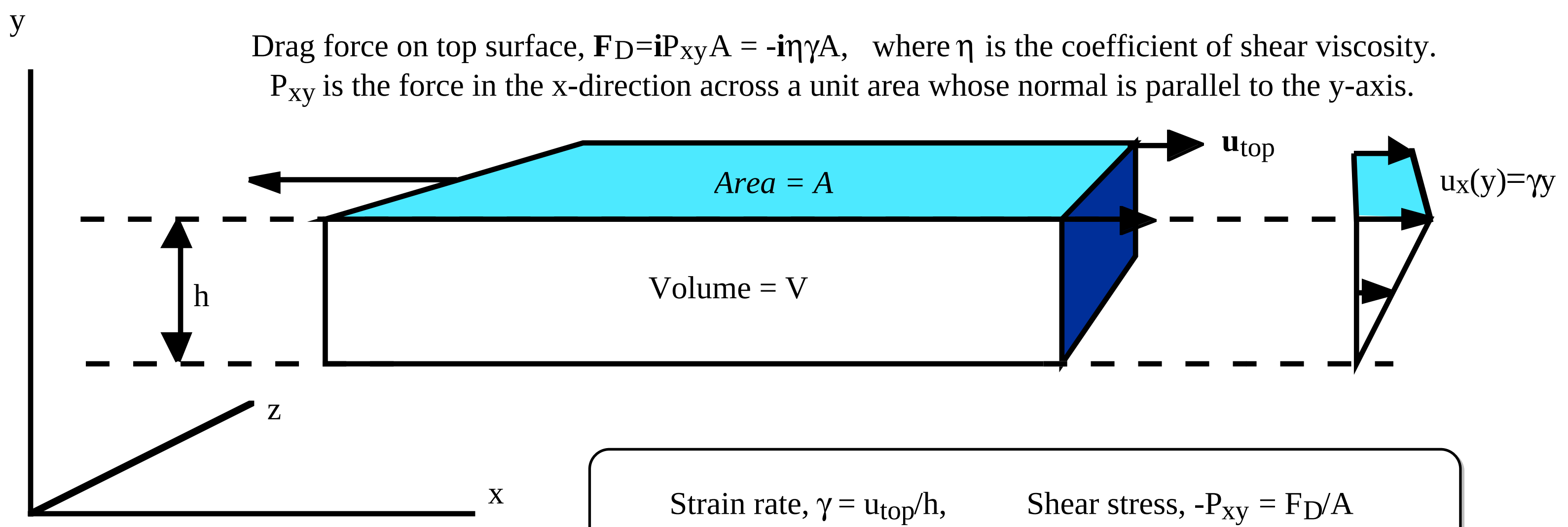
The thermal conductivity, λ, can be computed,

$$\lambda = \lim_{F\to 0}\lim_{t\to\infty}\frac{1}{Tt}\frac{\int_0^t ds\, J_{Qx}(s)}{F_{Qx}} \qquad (30)$$

Note: NEMD algorithms and Green Kubo relations are also known for thermal and mutual diffusion (Soret and Dufour effects) in non-ideal binary mixtures, and for the 12 or so viscosity coefficients of nematic liquid crystals.

Newton's Constitutive Relation for Shear Flow

Drag force on top surface, $\mathbf{F}_D = \mathbf{i}P_{xy}A = -\mathbf{i}\eta\gamma A$, where η is the coefficient of shear viscosity.
P_{xy} is the force in the x-direction across a unit area whose normal is parallel to the y-axis.



Strain rate, $\gamma = u_{top}/h$, Shear stress, $-P_{xy} = F_D/A$

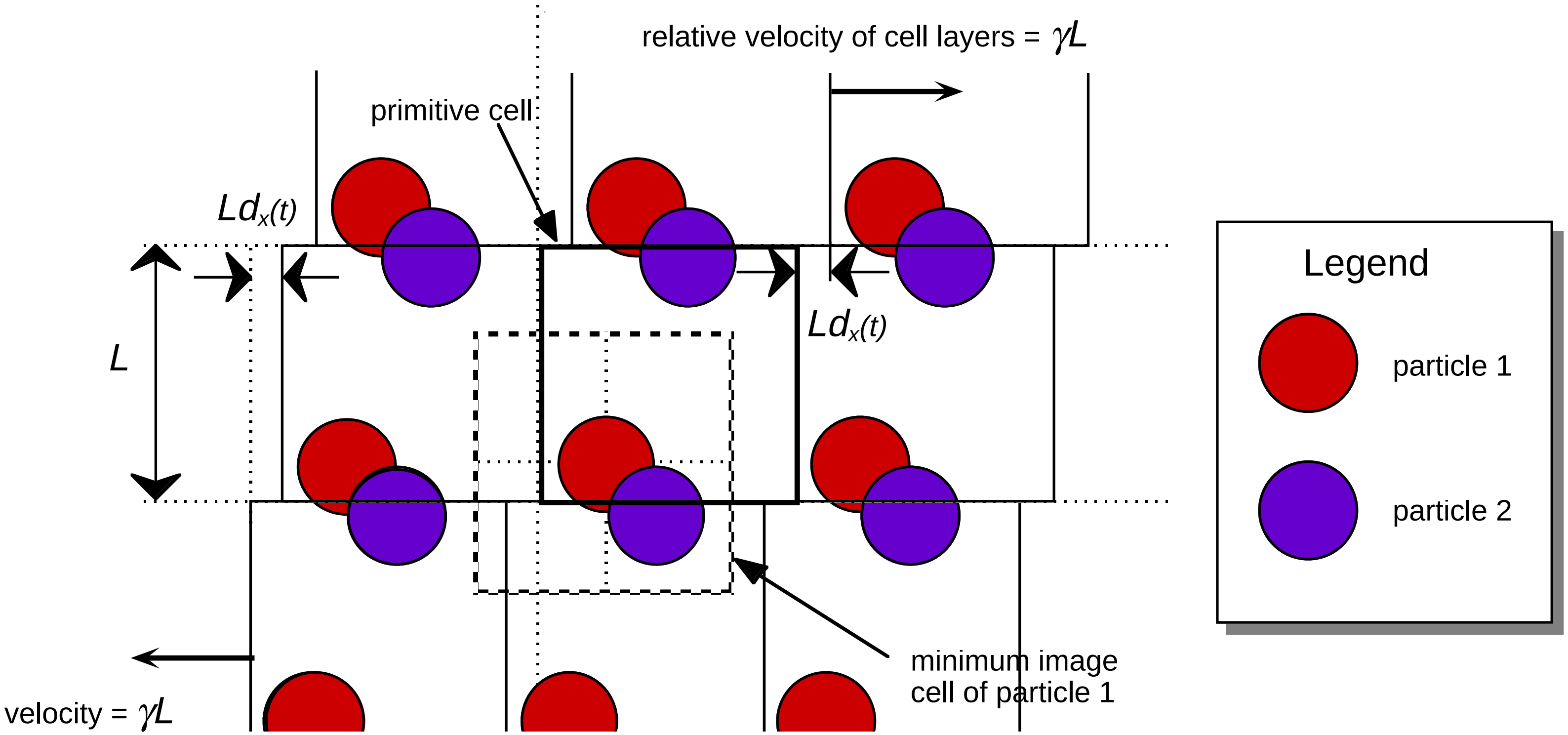
Viscosity, η = Shear stress/strain rate

In a *Newtonian* fluid η is independent of γ.

Viscous heating = work done =
force x velocity = $F_D.u_{top} = P_{xy}.A.\gamma.h = P_{xy}.\gamma.V$

Shearing Periodic BoundaryConditions

Lees-Edwards Periodic Boundary Conditions



Lees-Edwards periodic boundary conditions are non-autonomous. The coordinates in the primitive cell are *insufficient* to calculate trajectories or thermophysical phase variables. For example the pressure tensor can be written.

$$P_{xy} = \frac{1}{V}\left\langle \sum_{i=1}^{N}\left(\frac{p_{xi}p_{yi}}{m} - \frac{1}{2}\sum_{\substack{j=1\\ j\neq i}}^{N} y_{ij}F_{xij}(x_i, x_j, y_i, y_j, d_x(t)) \right) \right\rangle$$

$$= \frac{1}{V}\left\langle \sum_{i=1}^{N}\left(\frac{p_{xi}p_{yi}}{m} - \frac{1}{2}\sum_{\substack{j=1\\ j\neq i}}^{N} \left[x_{ij}F_{yij}(x_{ij}, y_{ij})\right] \right) \right\rangle$$

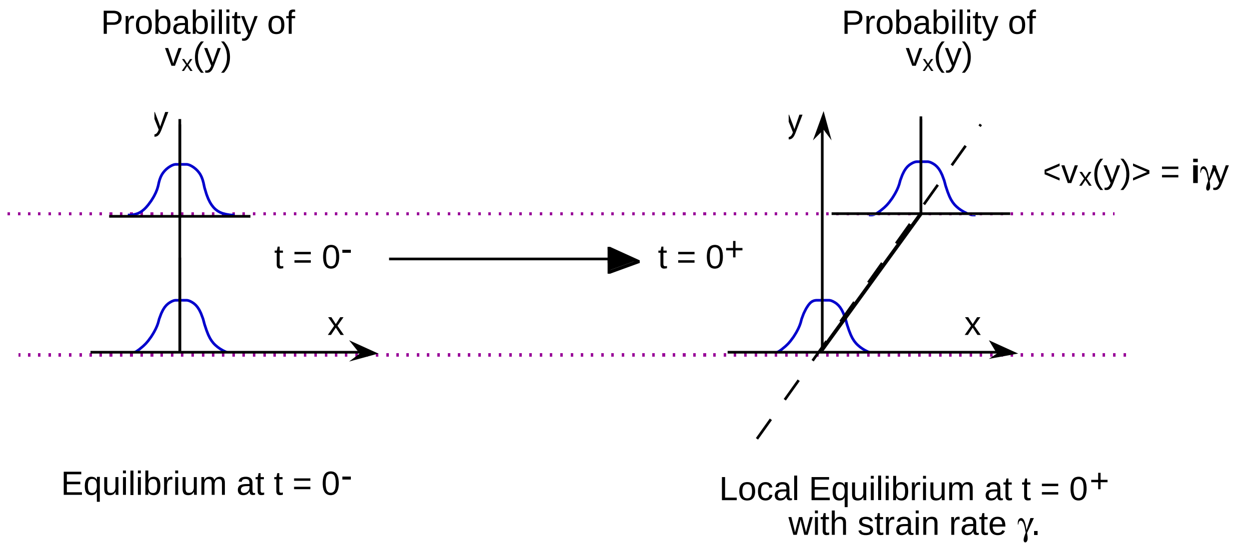
The motion of a unit cell of N particles under SLLOD dynamics but employing Lees-Edwards periodic boundary conditions, is *identical* to the motion one would observe for an infinite periodic array of particles evolving under SLLOD but without reference to the boundary conditions. If the initial infinite system is periodic, SLLOD dynamics will preserve that symmetry forever [1]. Lees-Edwards periodic boundary conditions are the natural generalisation of periodic boundary conditions to shear flow.

SLLOD algorithm for shear viscosity

$$\dot{\mathbf{q}}_i = \frac{\mathbf{p}_i}{m} + \mathbf{i}\gamma y_i$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \mathbf{i}\gamma p_{yi} - \alpha \mathbf{p}_i, \text{ which is equivalent to: } \ddot{\mathbf{q}}_i = \frac{\mathbf{F}_i}{m} + \mathbf{i}\gamma\delta(t) y_i \qquad (25)$$

SLLOD changes an equilibrium distribution at $t = 0^-$, to a *local* equilibrium distribution.



The SLLOD equations of motion (25) are equivalent to Newton's equations for $t > 0^+$, with a linear shift applied to the initial x-velocities of the particles.