An invariant manifold in molecular dynamics and its relation to continuum mechanics

"objective molecular dynamics"

Richard D. James
Department of Aerospace Engineering and Mechanics
University of Minnesota
Joint work with Kaushik Dayal, Traian Dumitrica, Stefan Müller

Examples of isometry groups

- Translation group

$$G_T = \{t_1^p t_2^q t_3^r : p, q, r \in \mathbb{Z}\} = \{(\mathbf{I}|p\mathbf{e}_1 + q\mathbf{e}_2 + r\mathbf{e}_3) : p, q, r \in \mathbb{Z}\}$$

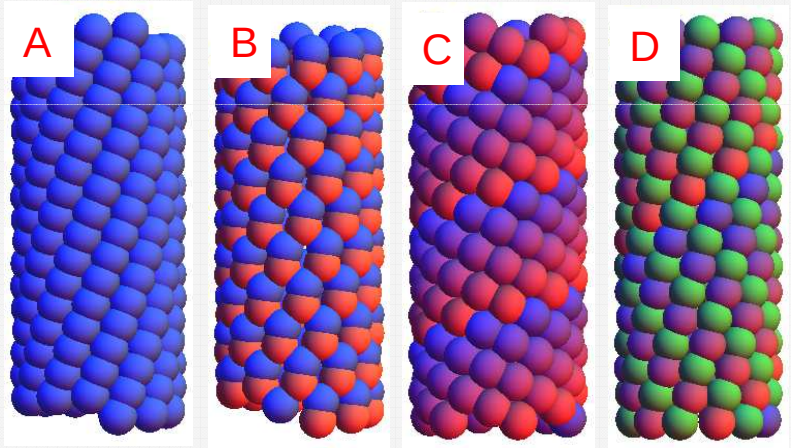
- Theorem: If a discrete group of isometries does not contain a translation and does not consist entirely of rotations, it is expressible in one of the forms

A $\{h^p : p \in \mathbb{Z}\}$,

B $\{h^p f^m : p \in \mathbb{Z},\ m = 1, 2\}$,

C $\{h^p g^q : p \in \mathbb{Z},\ q = 1, \ldots, n\}$,

D $\{h^p g^q f^m : p \in \mathbb{Z},\ q = 1, \ldots, n,\ m = 1, 2\}$,



where

1. $h = (\mathbf{R}_\theta|\tau\mathbf{e} + (\mathbf{R}_\theta - \mathbf{I})\mathbf{x}_0\}$, $\mathbf{R}_\theta\mathbf{e} = \mathbf{e}$, $|\mathbf{e}| = 1$, $\mathbf{x}_0 \cdot \mathbf{e} = 0$, $\mathbf{e}, \mathbf{x}_0 \in \mathbb{R}^3$, $\tau \neq 0$, and θ is an irrational multiple of 2π.

2. $g = (\mathbf{R}_\psi|(\mathbf{R}_\psi - \mathbf{I})\mathbf{x}_0)$, $\mathbf{R}_\psi\mathbf{e} = \mathbf{e}$, is a proper rotation with angle $\psi = 2\pi/n$, $n \in \mathbb{Z}$, $n \neq 0$.

3. $f = (\mathbf{R}|\,(\mathbf{R} - \mathbf{I})\mathbf{x}_1)$, $\mathbf{R} = -\mathbf{I} + 2\mathbf{e}_1 \otimes \mathbf{e}_1$, $|\mathbf{e}_1| = 1, \mathbf{e} \cdot \mathbf{e}_1 = 0$ and $\mathbf{x}_1 = \mathbf{x}_0 + \xi\mathbf{e}$, for some $\xi \in \mathbb{R}$.

A time-dependent invariant manifold of the equations of molecular dynamics

$$\mathbf{y}_k(t),\ k = 1, \ldots, M$$

simulated atoms

$$G = \{g_1, g_2, \ldots, g_N\}$$

a discrete group of isometries (*N* can be infinite)

$$\mathbf{y}_{i,k}(t) = g_i(\mathbf{y}_k(t)),$$

all of the atoms

$$i = 1, \ldots, N,\ k = 1, \ldots, M$$

The elements g_i can depend on t>0, but this time dependence must be consistent with

$$\frac{d^2\mathbf{y}_{j,k}(t)}{dt^2} = \frac{d^2}{dt^2} g_j(\mathbf{y}_k(t)) = \mathbf{Q}_j \frac{d^2\mathbf{y}_k(t)}{dt^2}$$

$$g_j = (\mathbf{Q}_j|\mathbf{c}_j) \in G,\ j = 1, \ldots, N,\ k = 1, \ldots, M$$

Atomic forces

The force on atom i, k is denoted by the suggestive notation $-\partial\varphi/\partial\mathbf{y}_{i,k} : \mathbb{R}^{3N} \to \mathbb{R}^3$

The force satisfies

- Frame-indifference $\mathbf{Q} \in \mathrm{O}(3),\ \mathbf{c} \in \mathbb{R}^3$

$$\mathbf{Q}\frac{\partial\varphi}{\partial\mathbf{y}_{i,k}}(\ldots,\mathbf{y}_{i_1,1},\ldots\mathbf{y}_{i_1,M},\ldots,\mathbf{y}_{i_2,1},\ldots\mathbf{y}_{i_2,M},\ldots)$$
$$= \frac{\partial\varphi}{\partial\mathbf{y}_{i,k}}(\ldots,\mathbf{Q}\mathbf{y}_{i_1,1}+\mathbf{c},\ldots\mathbf{Q}\mathbf{y}_{i_1,M}+\mathbf{c},\ldots,\mathbf{Q}\mathbf{y}_{i_2,1}+\mathbf{c},\ldots\mathbf{Q}\mathbf{y}_{i_2,M}+\mathbf{c},\ldots)$$

(These conditions satisfied, e.g., by the Hellmann-Feynman force based on Born-Oppenheimer quantum mechanics)

- Permutation invariance

$$\frac{\partial\varphi}{\partial\mathbf{y}_{\Pi(i,k)}}(\ldots,\mathbf{y}_{i_1,1},\ldots\mathbf{y}_{i_1,M},\ldots,\mathbf{y}_{i_2,1},\ldots\mathbf{y}_{i_2,M},\ldots)$$
$$= \frac{\partial\varphi}{\partial\mathbf{y}_{i,k}}(\ldots,\mathbf{y}_{\Pi(i_1,1)},\ldots\mathbf{y}_{\Pi(i_1,M)},\ldots,\mathbf{y}_{\Pi(i_2,1)},\ldots\mathbf{y}_{\Pi(i_2,M)},\ldots)$$

where Π is a permutation that preserves species.

Preservation of species means that if $(i,k) = \Pi(j,\ell)$ then the species (i.e., atomic mass and number) of atom i, k is the same as the species of atom j, ℓ.

Potential energy

These conditions can be found by formally differentiating the frame-indifference and permutation invariance of the potential energy,

$$\begin{aligned}
&\varphi(\ldots, \mathbf{y}_{i_1,1}, \ldots, \mathbf{y}_{i_1,M}, \ldots, \mathbf{y}_{i_2,1}, \ldots \mathbf{y}_{i_2,M}, \ldots) \\
&\quad = \varphi(\ldots, \mathbf{y}_{\Pi(i_1,1)}, \ldots \mathbf{y}_{\Pi(i_1,M)}, \ldots, \mathbf{y}_{\Pi(i_2,1)}, \ldots, \mathbf{y}_{\Pi(i_2,M)}, \ldots) \\
&\quad = \varphi(\ldots, \mathbf{Q}\mathbf{y}_{i_1,1} + \mathbf{c}, \ldots \mathbf{Q}\mathbf{y}_{i_1,M} + \mathbf{c}, \ldots, \mathbf{Q}\mathbf{y}_{i_2,1} + \mathbf{c}, \ldots, \mathbf{Q}\mathbf{y}_{i_2,M} + \mathbf{c}, \ldots)
\end{aligned}$$

(but of course this calculation would not make sense when $N = \infty$)

Theorem

Assume the restrictions on the potential energy above and let $G = \{g_1, g_2, \ldots, g_N\}$ be a time-dependent discrete group of isometries satisfying the restriction on the time-dependence given above. If $\mathbf{y}_k(t),\ k = 1, \ldots, M$ satisfy the equations of molecular dynamics, i.e.,

$$\begin{aligned} m_k \ddot{\mathbf{y}}_k &= -\frac{\partial \varphi}{\partial \mathbf{y}_{1,k}}(\ldots, \mathbf{y}_{i,1}, \ldots, \mathbf{y}_{i,M},\ \mathbf{y}_{i+1,1}, \ldots \mathbf{y}_{i+1,M}, \ldots) \\ &= -\frac{\partial \varphi}{\partial \mathbf{y}_{1,k}}(\ldots, g_i(\mathbf{y}_1), \ldots, g_i(\mathbf{y}_M),\ g_{i+1}(\mathbf{y}_1), \ldots g_{i+1}(\mathbf{y}_M), \ldots) \end{aligned}$$

$$\mathbf{y}_k(0) = \mathbf{y}_k^0, \quad \dot{\mathbf{y}}_k(0) = \mathbf{v}_k^0, \quad k = 1, \ldots, M$$

then $\mathbf{y}_{j,k}(t)$ also satisfy the equations of molecular dynamics:

$$m_k \ddot{\mathbf{y}}_{j,k}(t) = -\frac{\partial \varphi}{\partial \mathbf{y}_{j,k}}(\ldots, \mathbf{y}_{i,1}(t), \ldots, \mathbf{y}_{i,M}(t), \mathbf{y}_{i+1,1}(t), \ldots, \mathbf{y}_{i+1,M}(t), \ldots)$$

Proof

There is a permutation Π, depending on the choice of g, such that

$$\mathbf{y}_{\Pi(i,k)}(t) = g(\mathbf{y}_{i,k}(t)),\ i = 1, \ldots, N,\ k = 1, \ldots, M$$

Fix $j \in \{1, \ldots, N\}$ and choose $g = g_j^{-1} = (\mathbf{Q}_j^T | -\mathbf{Q}_j^T \mathbf{c}_j)$

The corresponding permutation Π satisfies $\Pi(j,k) = (1,k)$

$$\begin{aligned}
m_k \ddot{\mathbf{y}}_{j,k}(t) &= m_k \mathbf{Q}_j \ddot{\mathbf{y}}_k(t) = -\mathbf{Q}_j \frac{\partial \varphi}{\partial \mathbf{y}_{1,k}}(\ldots, \mathbf{y}_{i,1}(t), \ldots, \mathbf{y}_{i,M}(t), \mathbf{y}_{i+1,1}(t), \ldots, \mathbf{y}_{i+1,M}(t), \ldots) \\
&= -\mathbf{Q}_j \frac{\partial \varphi}{\partial \mathbf{y}_{\Pi(j,k)}}(\ldots, \mathbf{y}_{i,1}(t), \ldots, \mathbf{y}_{i,M}(t), \mathbf{y}_{i+1,1}(t), \ldots, \mathbf{y}_{i+1,M}(t), \ldots) \\
&= -\mathbf{Q}_j \frac{\partial \varphi}{\partial \mathbf{y}_{j,k}}(\ldots, \mathbf{y}_{\Pi(i,1)}(t), \ldots, \mathbf{y}_{\Pi(i,M)}(t), \ldots, \mathbf{y}_{\Pi(i+1,1)}(t), \ldots, \mathbf{y}_{\Pi(i+1,M)}(t), \ldots) \\
&= -\mathbf{Q}_j \frac{\partial \varphi}{\partial \mathbf{y}_{j,k}}(\ldots, g_j^{-1}(\mathbf{y}_{i,1}(t)), \ldots, g_j^{-1}(\mathbf{y}_{i,M}(t)), g_j^{-1}(\mathbf{y}_{i+1,1}(t)), \ldots, g_j^{-1}(\mathbf{y}_{i+1,M}(t)), \ldots) \\
&= -\mathbf{Q}_j \frac{\partial \varphi}{\partial \mathbf{y}_{j,k}}(\ldots, \mathbf{Q}_j^T \mathbf{y}_{i,1}(t) - \mathbf{Q}_j^T \mathbf{c}_j, \ldots, \mathbf{Q}_j^T \mathbf{y}_{i,M}(t) - \mathbf{Q}_j^T \mathbf{c}_j, \\
&\qquad \mathbf{Q}_j^T \mathbf{y}_{i+1,1}(t) - \mathbf{Q}_j^T \mathbf{c}_j, \ldots, \mathbf{Q}_j^T \mathbf{y}_{i+1,M}(t) - \mathbf{Q}_j^T \mathbf{c}_j, \ldots) \\
&= -\frac{\partial \varphi}{\partial \mathbf{y}_{j,k}}(\ldots, \mathbf{y}_{i,1}(t), \ldots, \mathbf{y}_{i,M}(t), \mathbf{y}_{i+1,1}(t), \ldots, \mathbf{y}_{i+1,M}(t), \ldots)
\end{aligned}$$

Allowed time dependence of the group elements $g_j = (\mathbf{Q}_j|\mathbf{c}_j),\ \mathbf{Q}_j \in \mathrm{O}(3),\ \mathbf{c}_j \in \mathbb{R}^3$

$$(d/dt)\mathbf{Q}_j = \mathbf{Q}_j\mathbf{W}_j \text{ (no sum), where } \mathbf{W}_j = -\mathbf{W}_j^T$$

The permitted time-dependence,

$$\frac{d^2}{dt^2}\left(\mathbf{Q}_j\mathbf{y}_k + \mathbf{c}_j\right) = \mathbf{Q}_j\frac{d^2\mathbf{y}_k(t)}{dt^2}$$

that is,

$$\ddot{\mathbf{c}}_j = -\mathbf{Q}_j(\mathbf{W}_j^2\mathbf{y}_k + \dot{\mathbf{W}}_j\mathbf{y}_k + 2\mathbf{W}_j\dot{\mathbf{y}}_k)$$

$$k = 1, \ldots, M,\ t > 0$$

This is satisfied (in the absence of excessive assumptions on the solution) if and only if

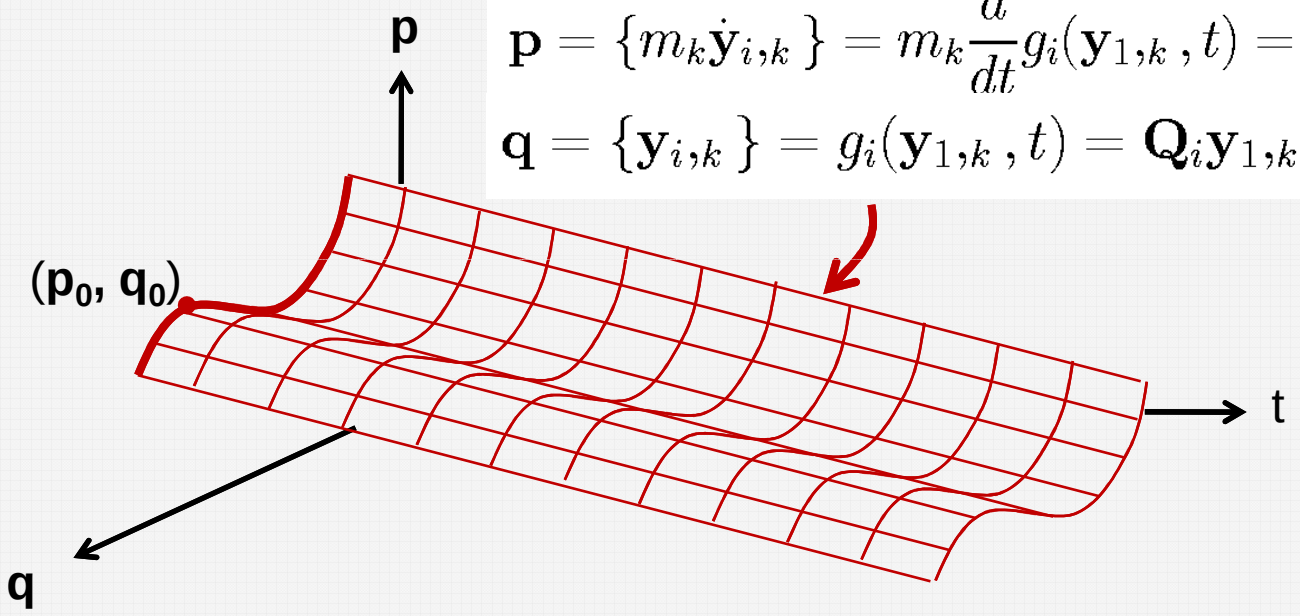
$$\ddot{\mathbf{c}}_j = 0 \quad \text{and} \quad \mathbf{W}_j = 0$$

That is, $\mathbf{Q}_j \in \mathrm{O}(3)$ must be constant and $\mathbf{c}_j = \mathbf{a}_j t + \mathbf{b}_j$ must be an affine function of t

The invariant manifold is independent of the material

$$\mathbf{p} = \{m_k \dot{\mathbf{y}}_{i,k}\} = m_k \frac{d}{dt} g_i(\mathbf{y}_{1,k}, t) = m_k \mathbf{Q}_i \dot{\mathbf{y}}_{1,k} + m_k \mathbf{a}_i$$

$$\mathbf{q} = \{\mathbf{y}_{i,k}\} = g_i(\mathbf{y}_{1,k}, t) = \mathbf{Q}_i \mathbf{y}_{1,k} + \mathbf{a}_i t + \mathbf{b}_i$$



Relation to experimental science?

Simplest case - translation group

affine in t

$$G_T = \{(\mathbf{I}|\, \nu^1\mathbf{e}_1 + \nu^2\mathbf{e}_2 + \nu^3\mathbf{e}_3) : \nu^1, \nu^2, \nu^3 \in \mathbb{Z}\}$$

discrete translation group

$$\mathbf{y}_{\nu,k}(t), \quad \nu \in \mathbb{Z}^3,\ k = 1, \ldots, M,\ t > 0$$

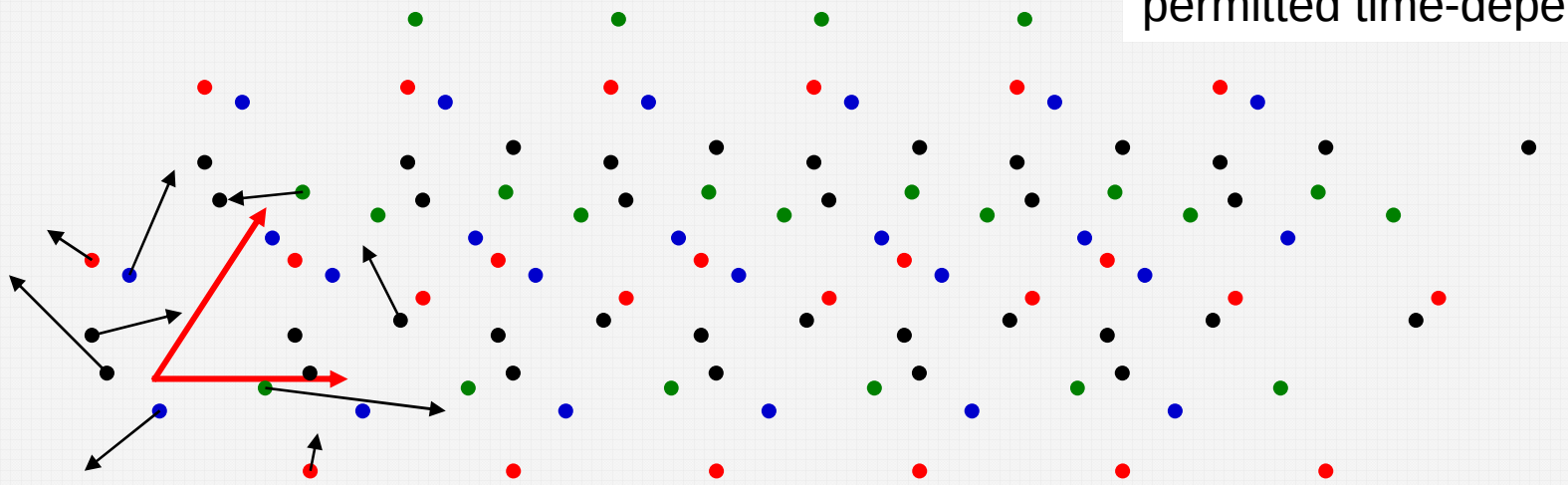
all of the atoms

$$\mathbf{y}_k(t) = \mathbf{y}_{(0,0,0),k}(t),\ k = 1, \ldots, M$$

simulated atoms

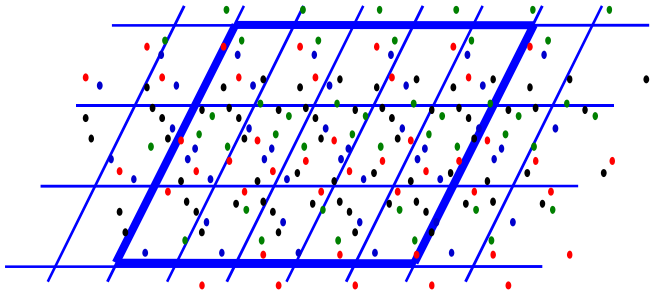
$$\mathbf{y}_{\mu,k}(t) = g_\mu(\mathbf{y}_k(t)) = \mathbf{y}_k(t) + \mu^i\mathbf{e}_i + \mu^i t\mathbf{A}\mathbf{e}_i = \mathbf{y}_k(t) + (\mathbf{I} + t\mathbf{A})(\mu^i\mathbf{e}_i)$$

permitted time-dependence



Passage to continuum level

$$\mathbf{y}_{\mu,k}(t) = \mathbf{y}_k(t) + (\mathbf{I} + t\mathbf{A})(\mu^i \mathbf{e}_i)$$



Assume ("no body force")

$$\frac{\text{force on a collection of } n^3 \text{ unit cells}}{n^3} \longrightarrow 0$$

→ center of mass of simulated atoms moves with constant velocity

Assume this velocity is zero. The centers of mass of the images lie on a grid moving according to

→ $$\mathbf{y}(\mathbf{x}, t) = (\mathbf{I} + t\mathbf{A})\mathbf{x}$$ "affine motion"

The macroscopic motion describes not the motion of the average position, but the motion of the **mass averaged position**

Viscometric flows

Constitutive equation for the Cauchy stress

$$\sigma(\mathbf{y},t) = -p\mathbf{I} + \Sigma(\mathbf{F}_t(\mathbf{y},\cdot))$$

"relative deformation gradient"

Ordinary Lagrangian description of motion

$$\mathbf{y} : \Omega \times (0,\infty) \to \mathbb{R}^3 \qquad \mathbf{y}(\mathbf{x},t)$$

Formula for the relative deformation gradient

$$\mathbf{F}_t(\mathbf{z},\tau) = \nabla_{\mathbf{z}}(\mathbf{y}(\mathbf{y}^{-1}(\mathbf{z},t),\tau))$$

Definition of a viscometric flow

$$\mathbf{F}_t(\mathbf{y},\tau) = \mathbf{Q}_t(\mathbf{y},\tau)(\mathbf{I} + (\tau - t)\mathbf{M}_t(\mathbf{y})), \quad \operatorname{rank}\mathbf{M}_t \le 1,\ \mathbf{Q}_t \in \mathrm{O}(3)$$

$$\tau \le t,\ t > 0,\ \mathbf{y} \in \Omega_t$$

Relation between the invariant manifold and viscometric flows

$$\mathbf{y}_{\mu,k}(t) = \mathbf{y}_k(t) + (\mathbf{I} + t\mathbf{A})(\mu^i \mathbf{e}_i)$$

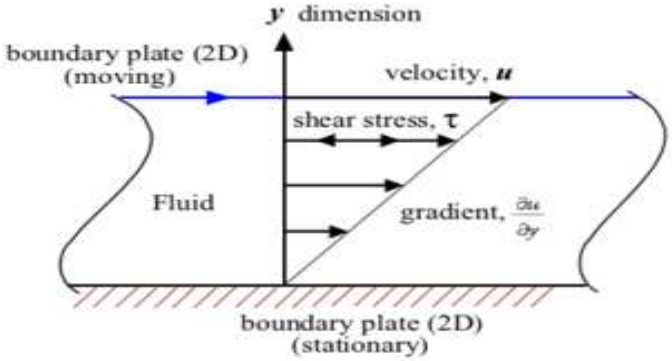
$$\mathbf{y}(\mathbf{x}, t) = (\mathbf{I} + t\mathbf{A})\mathbf{x}$$ “affine motion”

For “simple fluids” $\sigma(\mathbf{y}, t) = -p\mathbf{I} + \Sigma(\mathbf{F}_t(\mathbf{y}, \cdot))$

For the invariant solutions $\mathbf{F}_t(\mathbf{y}, \tau) = (\mathbf{I} + \tau\mathbf{A})(\mathbf{I} + t\mathbf{A})^{-1}$

- Viscometric flows $\cap \{ \mathbf{y}(\mathbf{x}, t) = (\mathbf{I} + t\mathbf{A})\mathbf{x} \}$

=



Viscometry

Lagrangian

$$\mathbf{y}(\mathbf{x},t) = (\mathbf{I} + t\mathbf{A})\mathbf{x}$$

Eulerian

$$\mathbf{v}(\mathbf{y},t) = \mathbf{A}(\mathbf{I} + t\mathbf{A})^{-1}\mathbf{y}$$

- Most viscometric flows (i.e. cone and plate flow) are only exact solutions (for some fluids) with inertia and thermodynamics neglected

- $\mathbf{v}(\mathbf{y},t) = \mathbf{A}(\mathbf{I} + t\mathbf{A})^{-1}\mathbf{y}$ is an exact solution of the equations of motion of **every** accepted model of fluid

$$\rho(\mathbf{v}_t + \nabla\mathbf{v}\mathbf{v}) = \nabla\cdot\sigma = 0$$

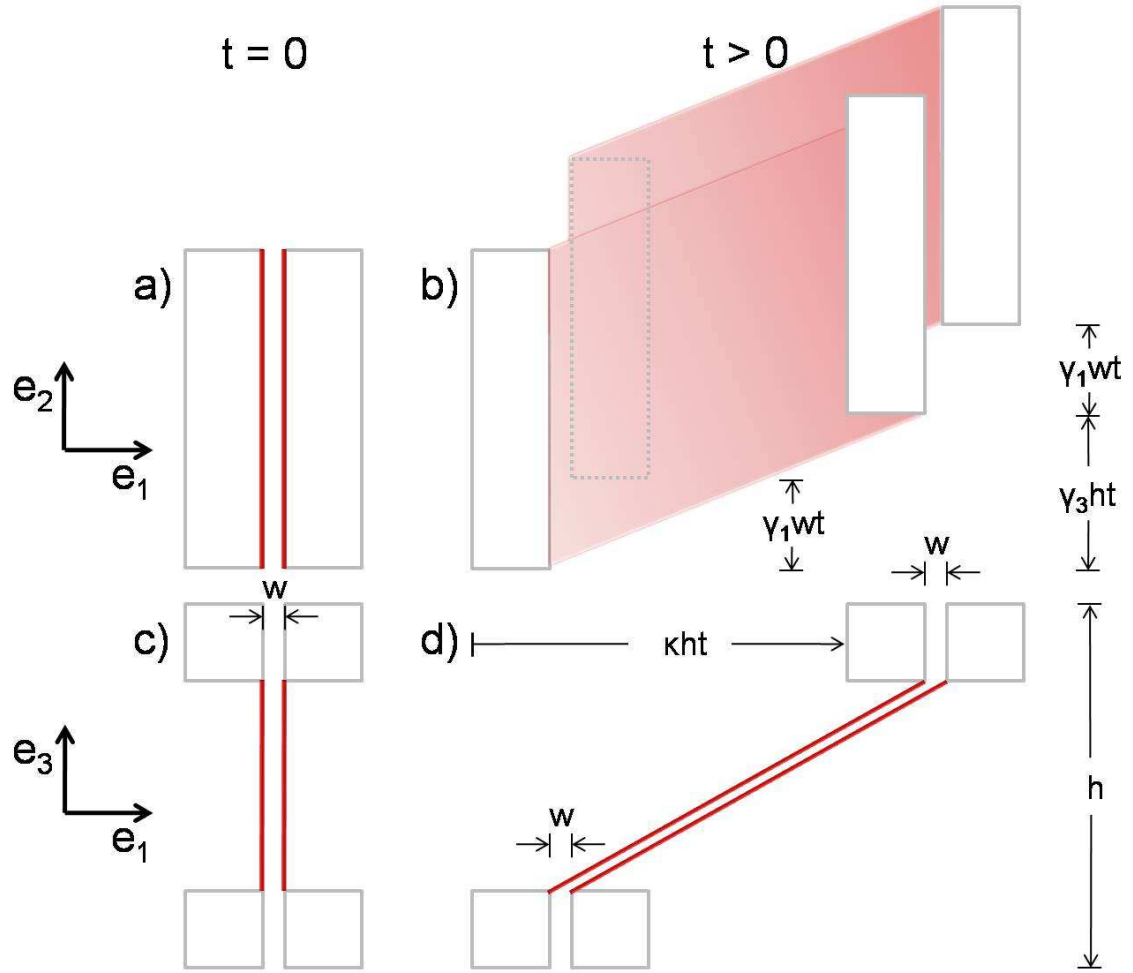
because

$$\rho(\mathbf{v}_t + \nabla\mathbf{v}\mathbf{v}) = \rho(-\mathbf{A}(\mathbf{I}+\mathbf{A}t)^{-1}\mathbf{A}(\mathbf{I}+\mathbf{A}t)^{-1}\mathbf{y} + \mathbf{A}(\mathbf{I}+\mathbf{A}t)^{-1}\mathbf{A}(\mathbf{I}+\mathbf{A}t)^{-1}\mathbf{y}) = 0$$

- It makes sense to base experimental fluid mechanics on $\mathbf{v}(\mathbf{y},t) = \mathbf{A}(\mathbf{I} + t\mathbf{A})^{-1}\mathbf{y}$ rather than viscometric flows

A “theoretical viscometer”

Caveat: it could be difficult to actually build this viscometer



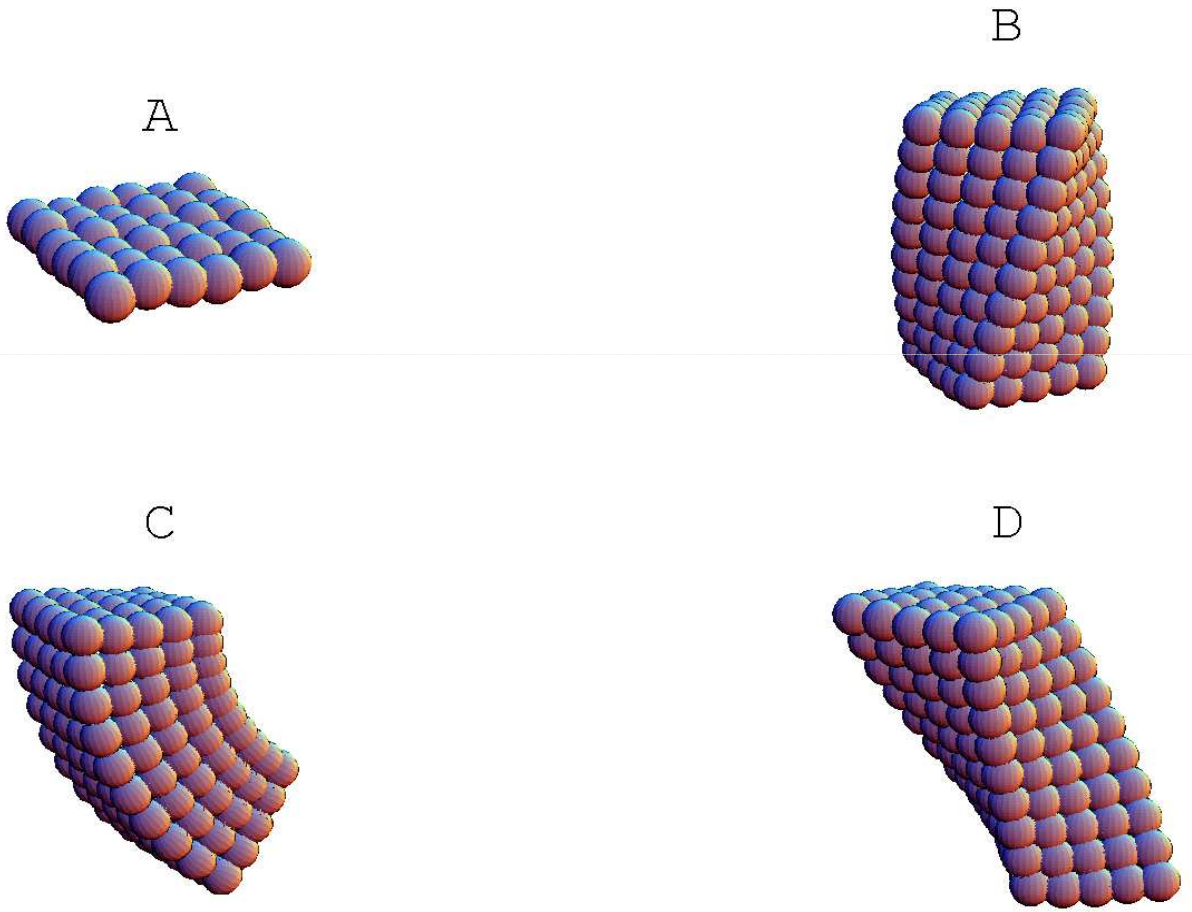
My attempt at a design: this corresponds to the general isochoric case (e.g.,incompressible fluid), in which case

$$\mathbf{A} = \begin{pmatrix} 0 & 0 & \kappa \\ \gamma_1 & 0 & \gamma_3 \\ 0 & 0 & 0 \end{pmatrix}$$

in a suitable orthonormal basis

Other groups besides the translation group

(joint work with Traian Dumitrica, Kaushik Dayal)



Objective MD study of a carbon nanotube under torsion

- Three-body Tersoff potential for carbon
- Twist was controlled by controlling the group parameters
- The groups chosen were various subgroups of the following group listed earlier:

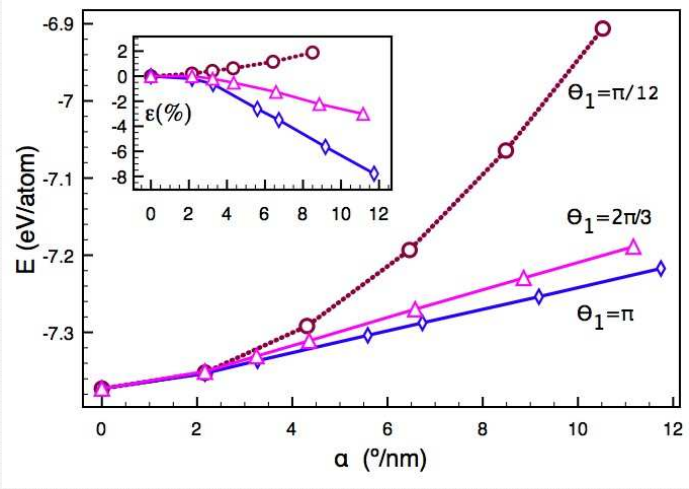
$$\{h^p g^q : p \in \mathbb{Z},\, q = 1, \ldots, n\}$$

1. $h = (\mathbf{R}_\theta | \tau\mathbf{e} + (\mathbf{R}_\theta - \mathbf{I})\mathbf{x}_0\}$, $\mathbf{R}_\theta\mathbf{e} = \mathbf{e}$, $|\mathbf{e}| = 1$, $\mathbf{x}_0 \cdot \mathbf{e} = 0$, $\mathbf{e}, \mathbf{x}_0 \in \mathbb{R}^3$, $\tau \neq 0$, and θ is an irrational multiple of 2π.
2. $g = (\mathbf{R}_\psi | (\mathbf{R}_\psi - \mathbf{I})\mathbf{x}_0)$, $\mathbf{R}_\psi\mathbf{e} = \mathbf{e}$, is a proper rotation with angle $\psi = 2\pi/n$, $n \in \mathbb{Z}$, $n \neq 0$.

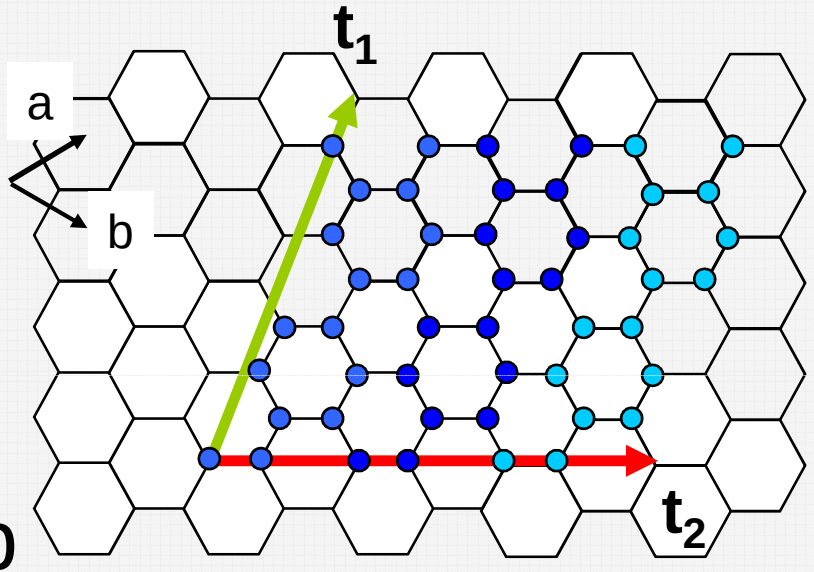
No time-dependence of the group elements

Objective MD: study of buckling of C nanotube under torsion

(12, 12) CNT



a



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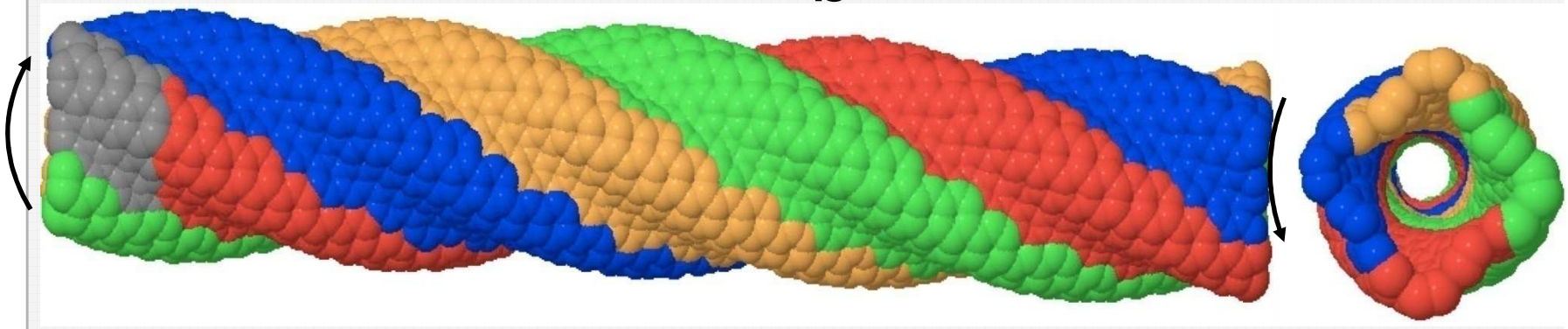
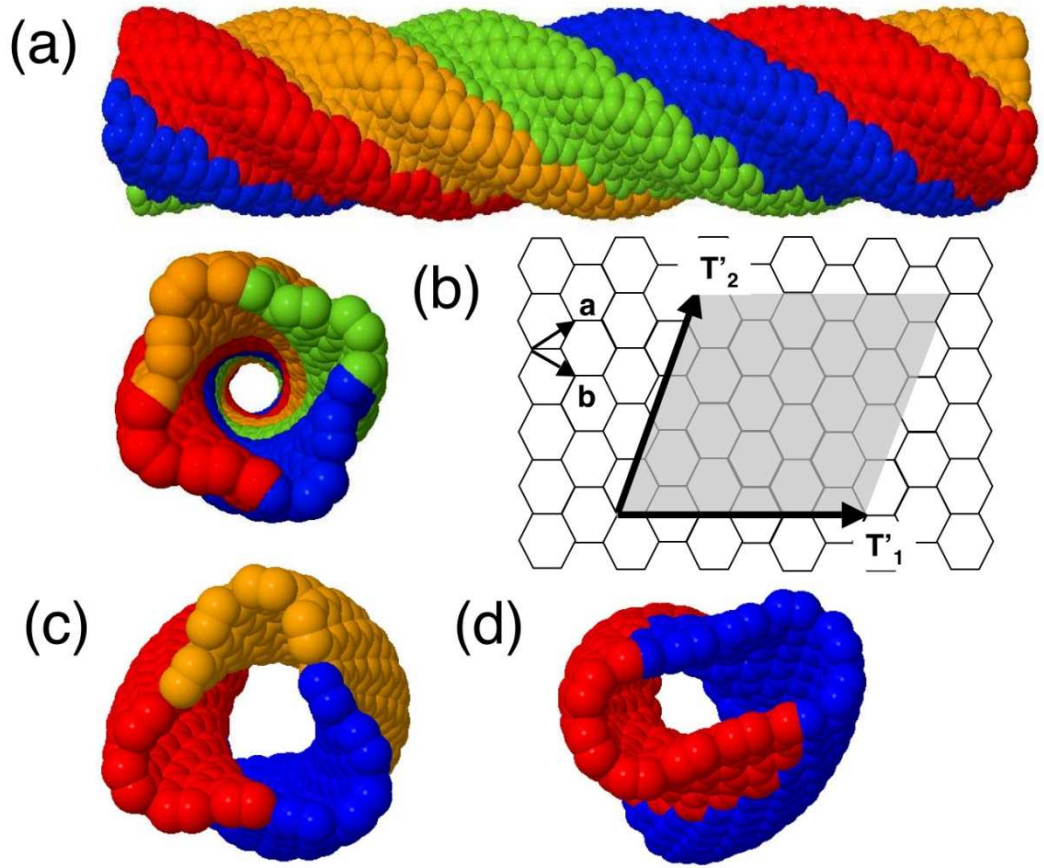
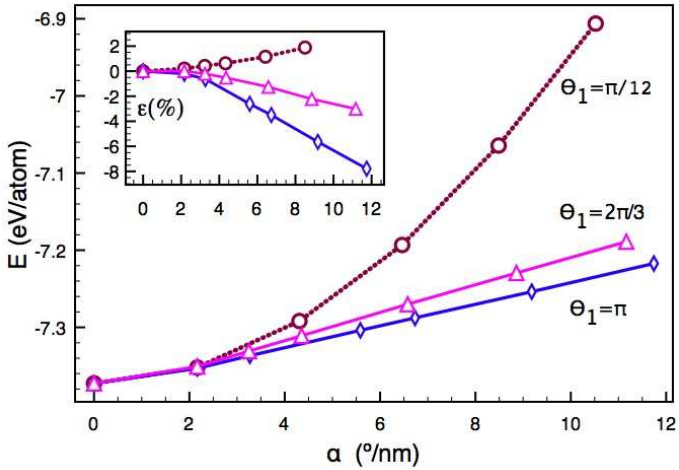


~3 deg/nm twist

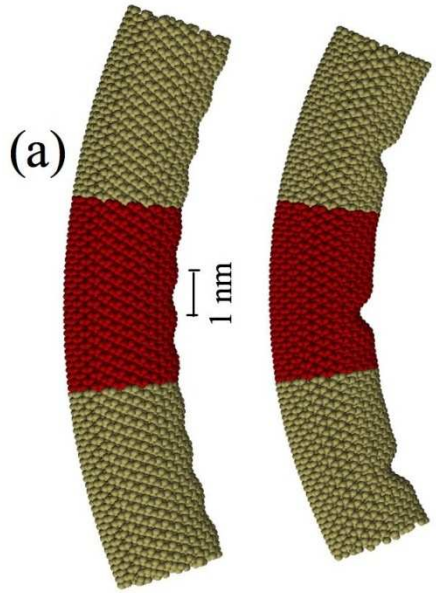
Effect of different choices of the fundamental domain

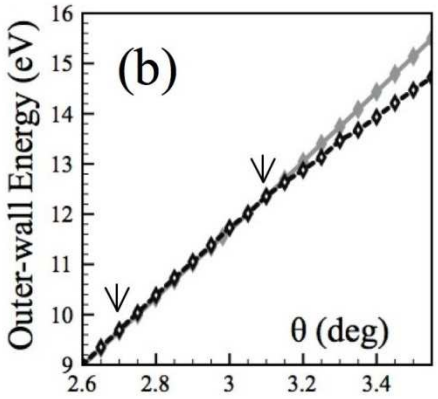


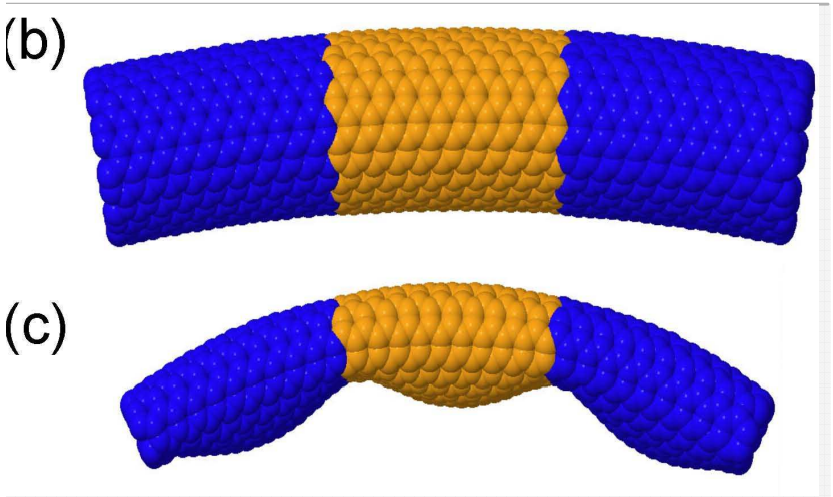
bifurcation diagram

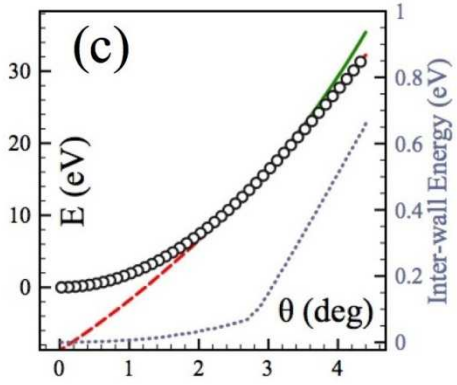


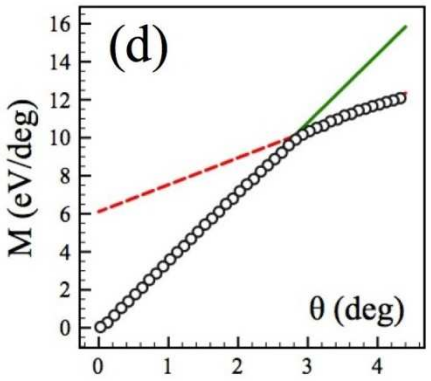
Objective MD simulation of bending of a carbon nanotube











Is there a St. Venant's principle at atomic level, with these solutions playing the role of the St. Venant solutions?

A time dependent group: “viscometry of nanostructures”

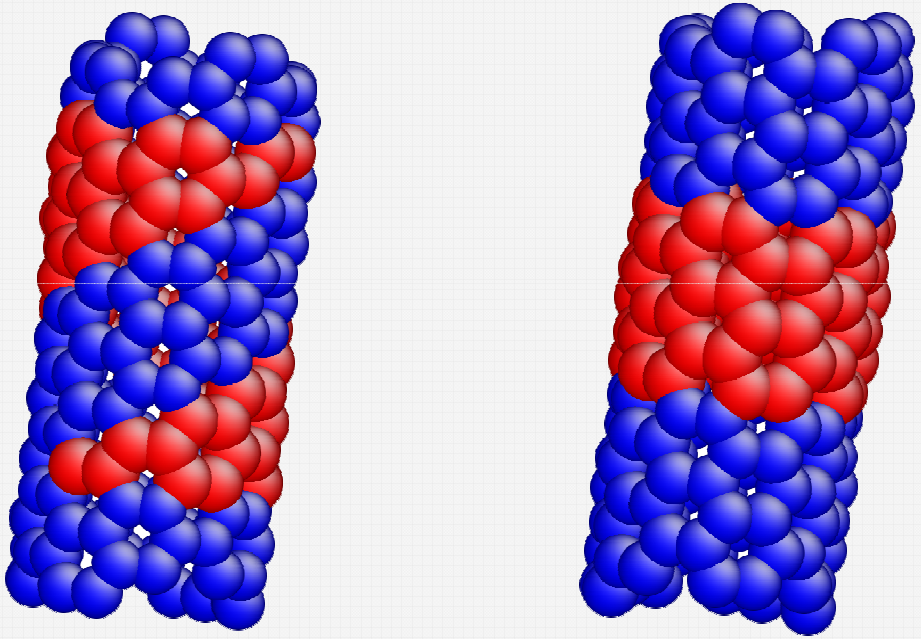
- Tersoff potential for carbon, again
- Same group as in the static simulations of the carbon nanotubes, but introduce time-dependence consistent with the main theorem

$$\{h^p g^q : p \in \mathbb{Z},\ q = 1, \ldots, n\}$$

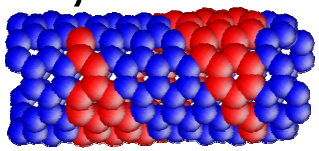
Replace $\tau = c(1 + t\,\dot{\varepsilon})$

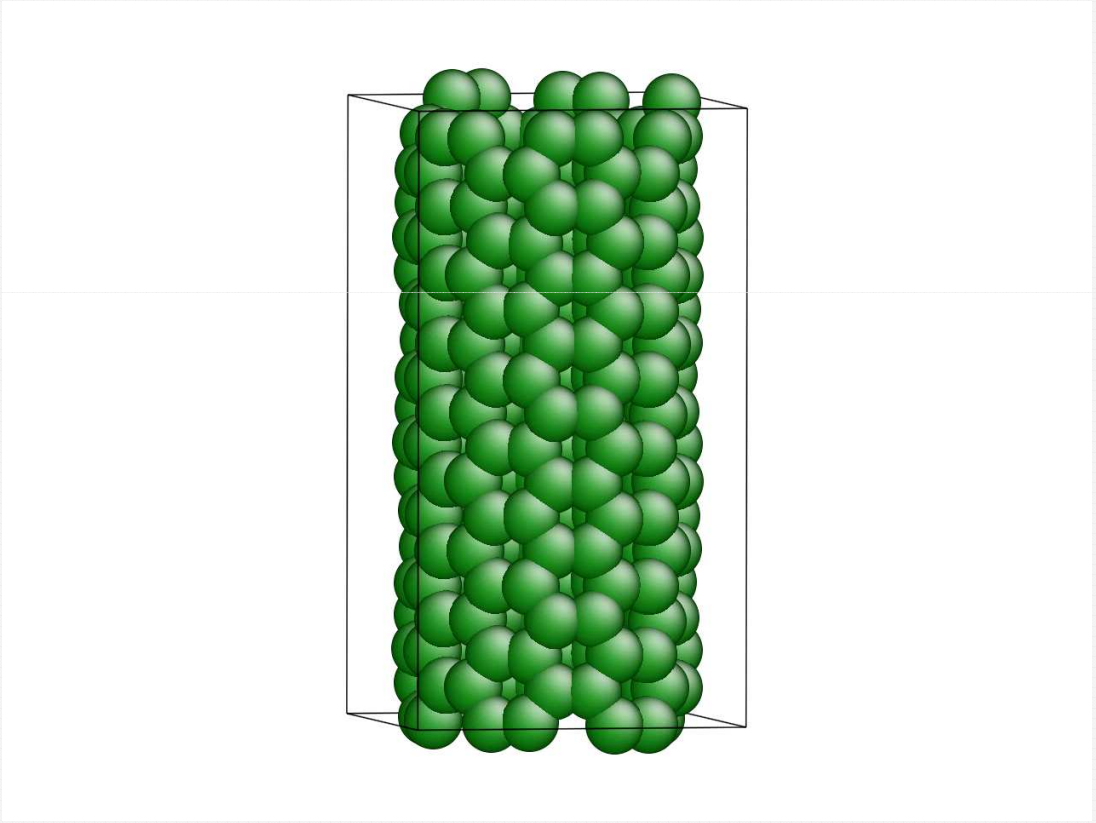
1. $h = (\mathbf{R}_\theta | \tau\mathbf{e} + (\mathbf{R}_\theta - \mathbf{I})\mathbf{x}_0\}$, $\mathbf{R}_\theta\mathbf{e} = \mathbf{e}$, $|\mathbf{e}| = 1$, $\mathbf{x}_0 \cdot \mathbf{e} = 0$, $\mathbf{e}, \mathbf{x}_0 \in \mathbb{R}^3$, $\tau \neq 0$, and θ is an irrational multiple of 2π.
2. $g = (\mathbf{R}_\psi | (\mathbf{R}_\psi - \mathbf{I})\mathbf{x}_0)$, $\mathbf{R}_\psi\mathbf{e} = \mathbf{e}$, is a proper rotation with angle $\psi = 2\pi/n$, $n \in \mathbb{Z}$, $n \neq 0$.

Two FDs used



Strain rate = 10^{-5} /ps, initial temperature = 1200K, helical FD



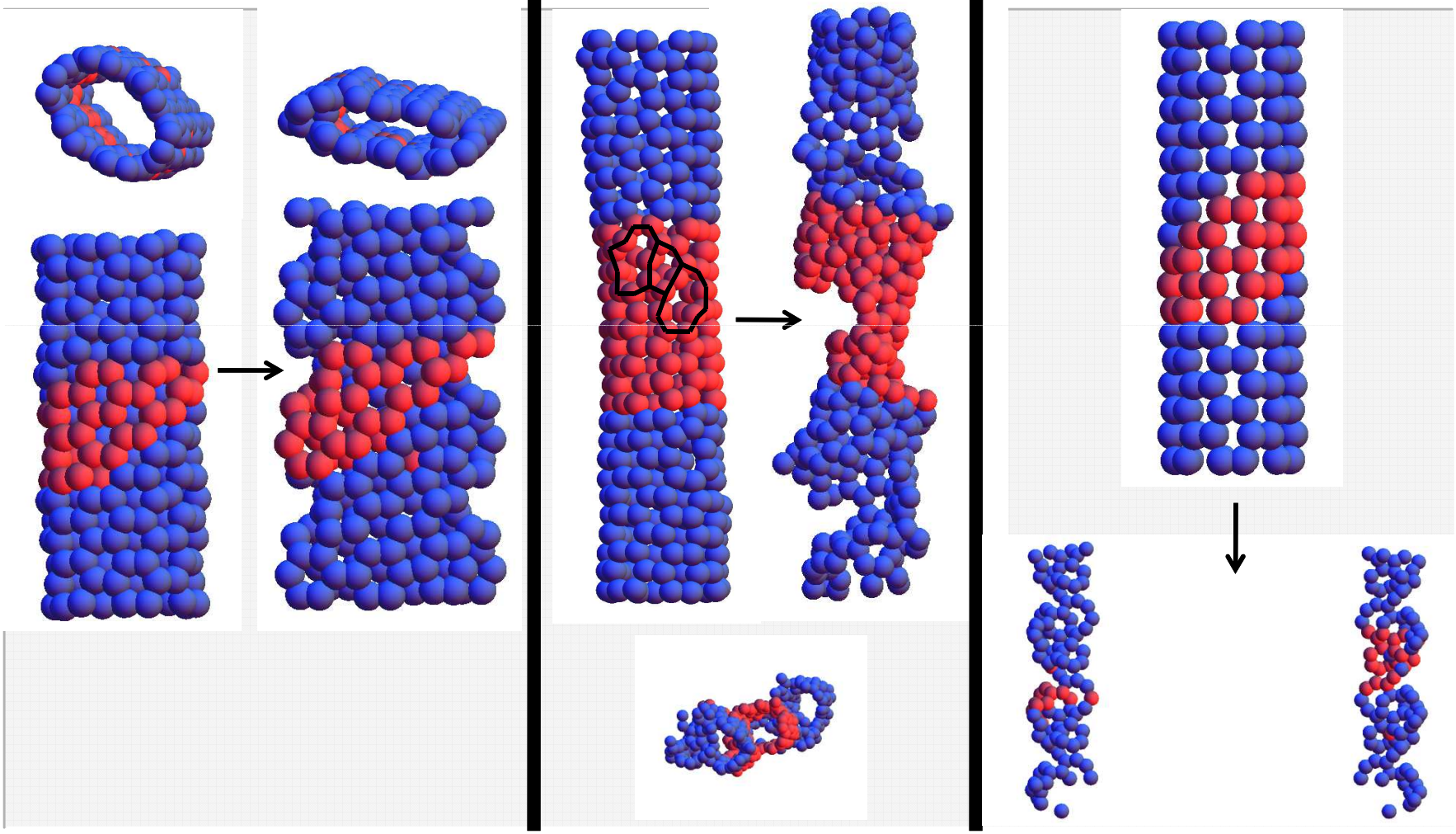


Wide variety of failure modes

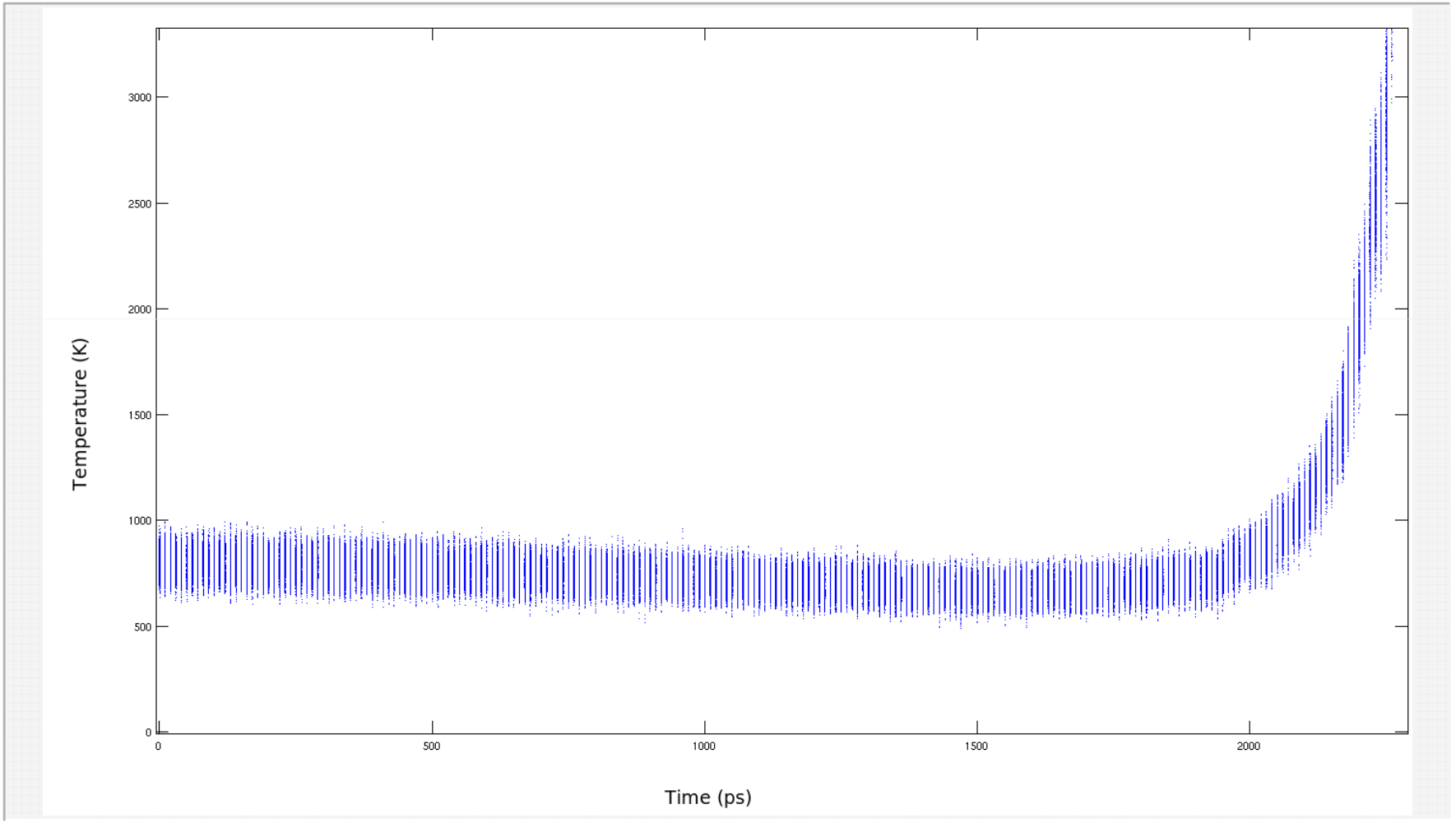
cross-sectional collapse

cavitation failure

fibrous fracture



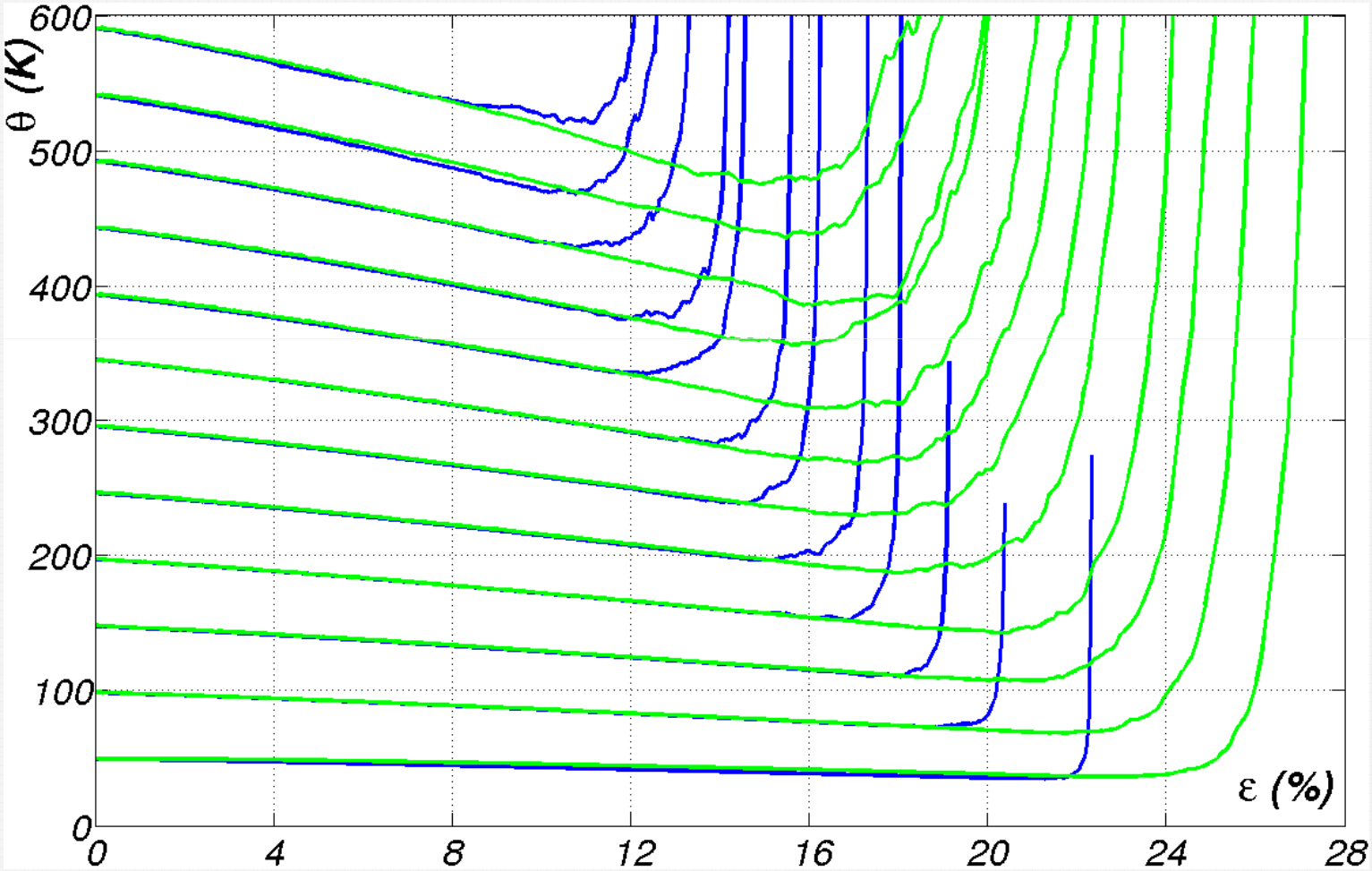
Typical temperature vs. time



Temperature replotted parametrically vs. strain at two strain rates

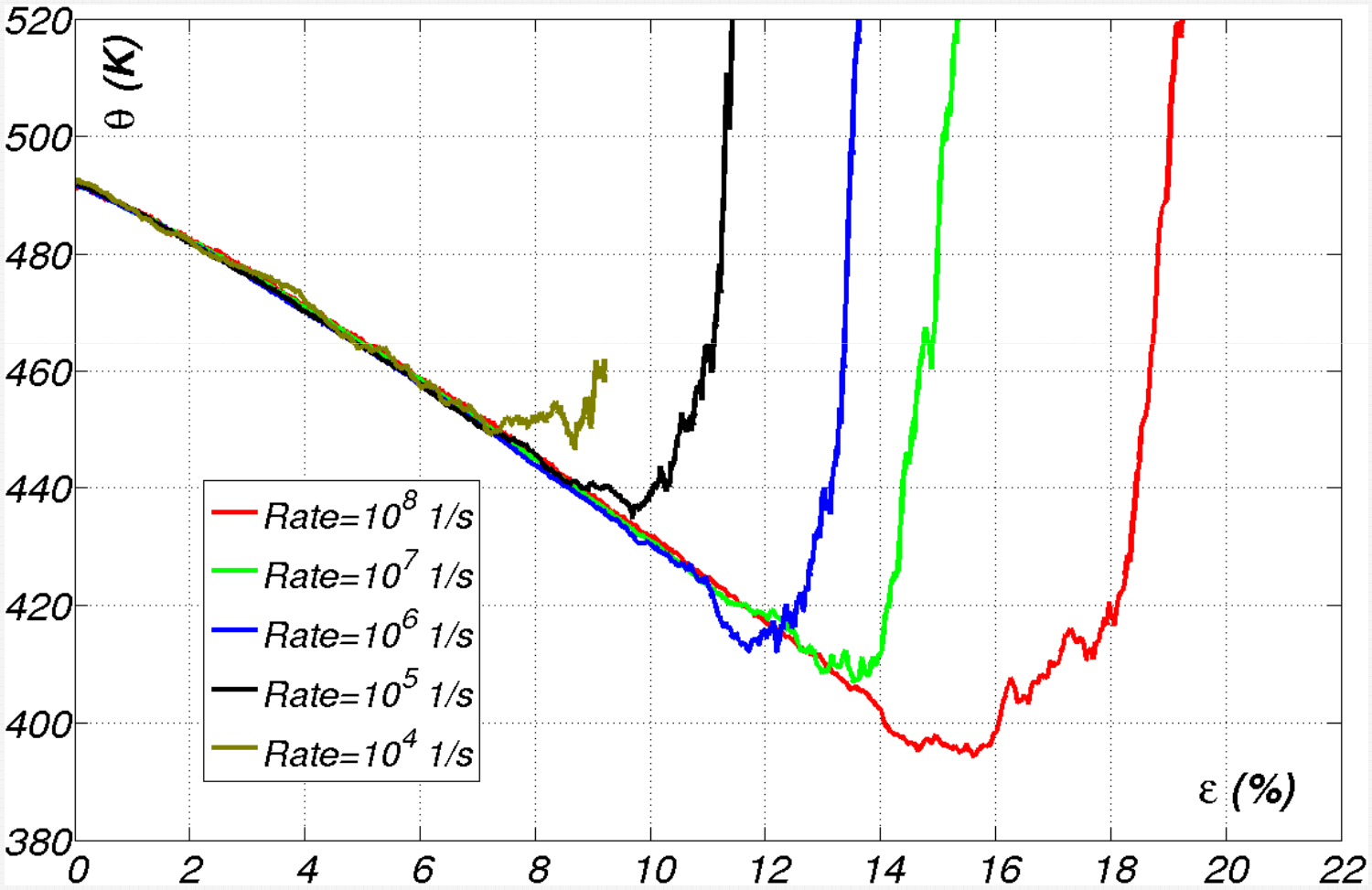
Green: 10^8 1/s. Blü: 10^6 1/s

A. Aghaei and K. Dayal



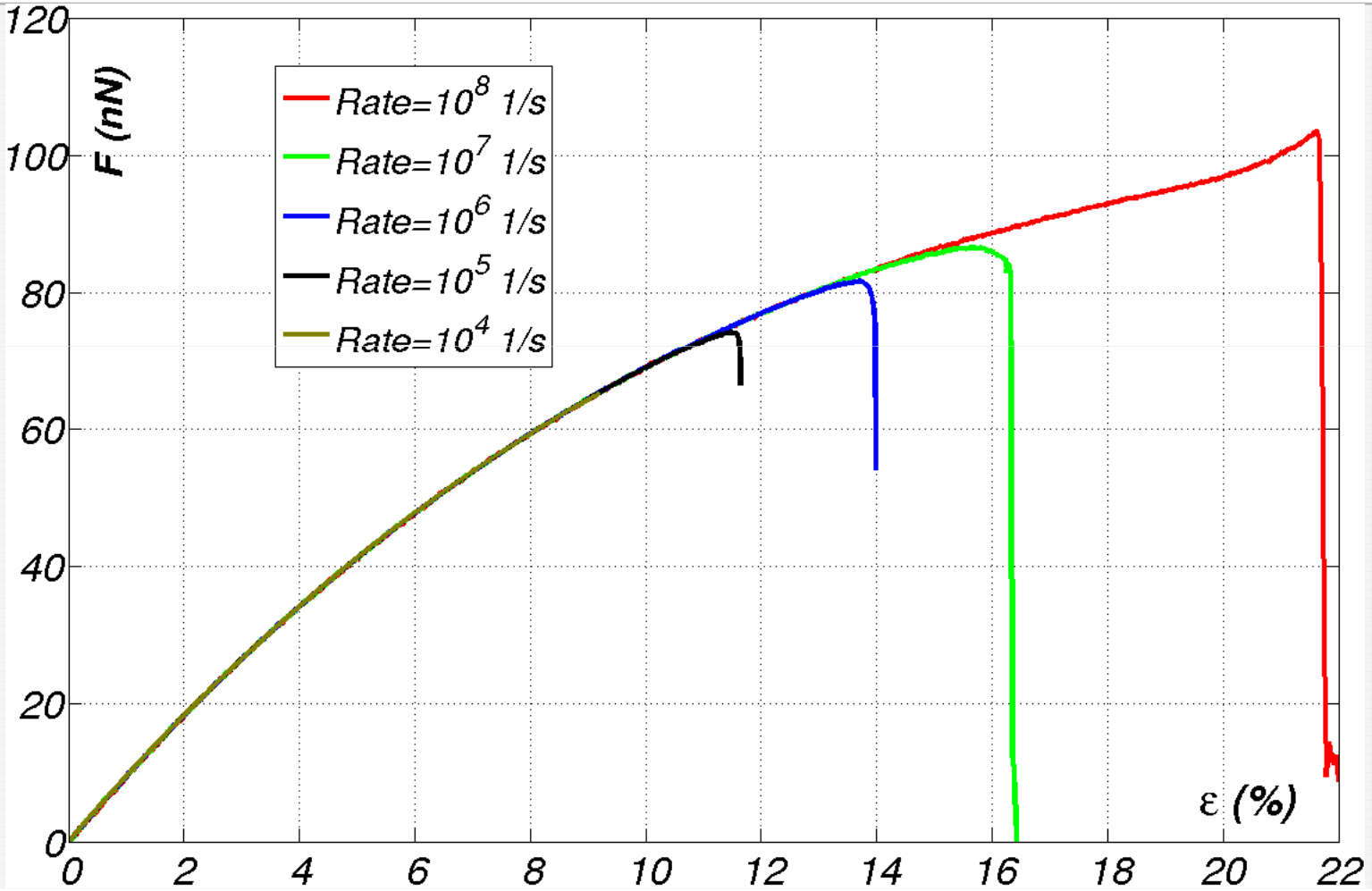
Temperature vs. strain over a wide range of strain rates

A. Aghaei and K. Dayal



Force vs. strain over the same strain rates

Initial temperature is 500K for all simulations



Maxwell-Boltzmann equation

$$f : \mathbb{R} \times \mathbb{R}^3 \times \mathbb{R}^3 \longrightarrow \mathbb{R}^{\geq}$$

$$f(t, \mathbf{y}, \mathbf{v})$$

molecular density function

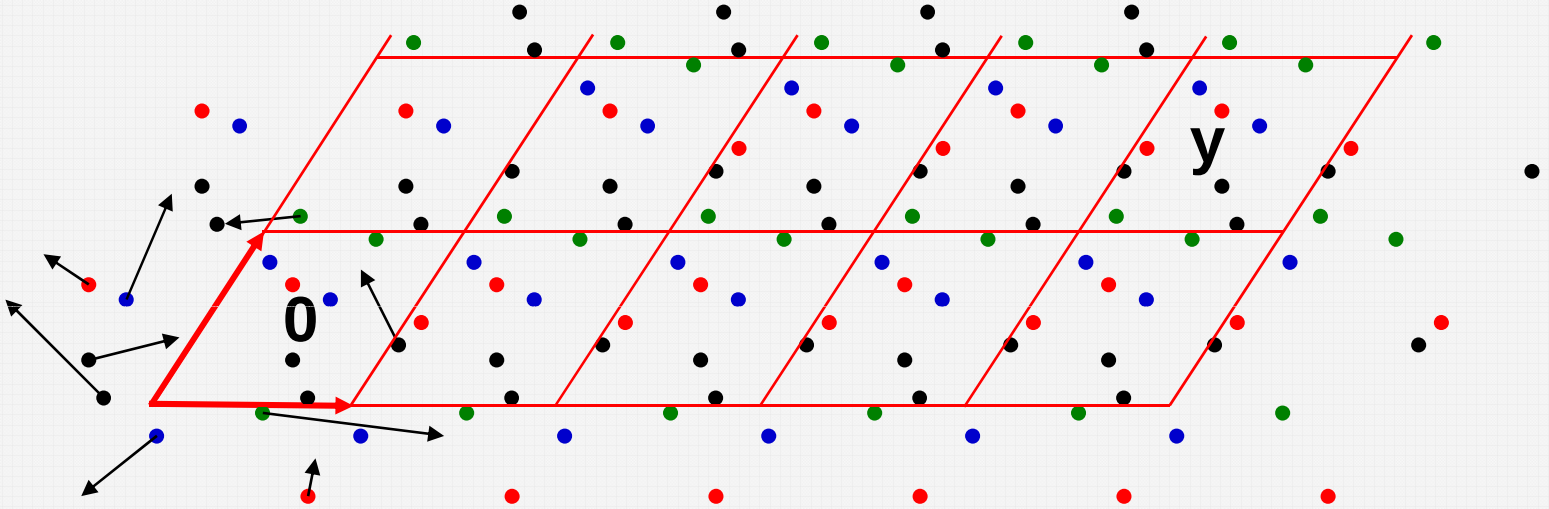
$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \frac{\partial f}{\partial \mathbf{y}} = \mathbb{C}f(\mathbf{v}) = \int_{\mathbb{R}^3} \int_{\mathcal{S}} (f'_\star f' - f_\star f)\, dS d\mathbf{v}_\star$$

Maxwell-Boltzmann equation

$$\begin{aligned} f'_\star &= f(t, \mathbf{y}, \mathbf{v}'_\star) = f(t, \mathbf{y}, \mathbf{v}_\star - ((\mathbf{v}_\star - \mathbf{v}) \cdot \mathbf{e})\mathbf{e}) \\ f' &= f(t, \mathbf{y}, \mathbf{v}') = f(t, \mathbf{y}, \mathbf{v} + ((\mathbf{v}_\star - \mathbf{v}) \cdot \mathbf{e})\mathbf{e}) \\ f_\star &= f(t, \mathbf{y}, \mathbf{v}_\star) \\ f &= f(t, \mathbf{y}, \mathbf{v}) \end{aligned}$$

Solutions on the invariant manifold have their own “statistics”

- Use translation group (i.e., gases fill volumes)



- The velocities at 0 are $\dot{\mathbf{y}}_i$, $i = 1, \ldots, M$
- The velocities at $\mathbf{y} = (\mathbf{I} + t\mathbf{A})\mathbf{x}$ are $\dot{\mathbf{y}}_i + \mathbf{A}\mathbf{x}$, $i = 1, \ldots, M$
- Or, in the Eulerian form used in the kinetic theory, the velocities at $\mathbf{y}$ are $\dot{\mathbf{y}}_i + \mathbf{A}(\mathbf{I} + t\mathbf{A})^{-1}\mathbf{y}$, $i = 1, \ldots, M$

$$f(t, \mathbf{y}, \mathbf{v} + \mathbf{A}(\mathbf{I} + t\mathbf{A})^{-1}\mathbf{y}) = f(t, 0, \mathbf{v})$$

This yields an exact reduction of the Maxwell-Boltzmann equation

(with Stefan Müller)

$$\begin{aligned} f(t,\mathbf{y},\mathbf{v}) &= f(t,0,\mathbf{v}-\mathbf{A}(\mathbf{I}+t\mathbf{A})^{-1}\mathbf{y}) \\ &= g(t,\mathbf{v}-\mathbf{A}(\mathbf{I}+t\mathbf{A})^{-1}\mathbf{y}), \qquad \mathbf{v}\in\mathbb{R}^3,\ \mathbf{y}\in\mathbb{R}^3,\ t>0 \end{aligned}$$

$g(t,\mathbf{w})$ satisfies

$$\frac{\partial g}{\partial t} - \frac{\partial g}{\partial \mathbf{w}}\cdot\mathbf{A}(\mathbf{I}+t\mathbf{A})^{-1}\mathbf{w} = \int_{\mathbb{R}^3}\int_{\mathcal{S}} (g'_\star g' - g_\star g)\, dS d\mathbf{w}_\star$$

- Includes many (all?) known exact solutions of the equations of the moments for special force laws
- Does not include the Bobylev-Krook-Wu solution

The moments of *f* (and *g*)

$(m = \text{molecular mass})$

Density	$\rho(t,\mathbf{y}) = m\,n(t,\mathbf{y}) = m\int_{\mathbb{R}^3} f(t,\mathbf{y},\mathbf{v})\,d\mathbf{v}$
Velocity	$\mathbf{u}(t,\mathbf{y}) = \frac{1}{n}\int_{\mathbb{R}^3} \mathbf{v} f(t,\mathbf{y},\mathbf{v})\,d\mathbf{v}$
Internal energy	$e(t,\mathbf{y}) = \frac{1}{n}\int_{\mathbb{R}^3} \frac{1}{2}\lvert\mathbf{v}-\mathbf{u}(t,\mathbf{y})\rvert^2 f(t,\mathbf{y},\mathbf{v})\,d\mathbf{v}$
Stress	$\mathbf{T}(t,\mathbf{y}) = -m\int_{\mathbb{R}^3} (\mathbf{v}-\mathbf{u}(t,\mathbf{y}))\otimes(\mathbf{v}-\mathbf{u}(t,\mathbf{y}))f(t,\mathbf{y},\mathbf{v})\,d\mathbf{v}$
Pressure	$p(t,\mathbf{y}) = -\frac{1}{3}\mathrm{tr}\mathbf{T}(t,\mathbf{y}) = \frac{2}{3}\rho e(t)$
Heat flux	$\mathbf{q}(t,\mathbf{y}) = m\int_{\mathbb{R}^3} \frac{1}{2}\lvert\mathbf{v}-\mathbf{u}(t,\mathbf{y})\rvert^2(\mathbf{v}-\mathbf{u}(t,\mathbf{y}))f(t,\mathbf{y},\mathbf{v})\,d\mathbf{v}$

Valüs of these moments for the invariant solutions

$$
\begin{aligned}
\rho(t,\mathbf{y}) &= \frac{\rho_0}{\det(\mathbf{I}+t\mathbf{A})}\\
\mathbf{u}(t,\mathbf{y}) &= \mathbf{A}(\mathbf{I}+t\mathbf{A})^{-1}\mathbf{y} + \text{G.T.}\\
e(t,\mathbf{y}) &= e(t)\\
\mathbf{T}(t,\mathbf{y}) &= \mathbf{T}(t)\\
p(t,\mathbf{y}) &= -\frac{1}{3}\mathrm{tr}\mathbf{T}(t) = \frac{2}{3}\rho(t)e(t)\\
\mathbf{q}(t,\mathbf{y}) &= \mathbf{q}(t)
\end{aligned}
$$

Theorem. For sufficiently regular solutions of the Maxwell-Boltzmann equation, the balance laws of continuum mechanics are satisfied by these moments:

$$
\begin{aligned}
\rho_t + \mathrm{div}(\rho\mathbf{u}) &= 0\\
\rho(\mathbf{u}_t + \nabla\mathbf{u}\mathbf{u}) &= \mathrm{div}\mathbf{T}\\
\rho(e_t + \nabla e\cdot\mathbf{u}) &= \mathbf{T}\cdot\nabla\mathbf{u} - \mathrm{div}\,\mathbf{q}
\end{aligned}
$$

The moments of *f* (and *g*)

$(m = \text{molecular mass})$

Density $\rho(t,\mathbf{y}) = m\, n(t,\mathbf{y}) = m \int_{\mathbb{R}^3} f(t,\mathbf{y},\mathbf{v})\, d\mathbf{v}$

Velocity $\mathbf{u}(t,\mathbf{y}) = \frac{1}{n} \int_{\mathbb{R}^3} \mathbf{v} f(t,\mathbf{y},\mathbf{v})\, d\mathbf{v}$

Internal energy $e(t,\mathbf{y}) = \frac{1}{n} \int_{\mathbb{R}^3} \frac{1}{2} |\mathbf{v} - \mathbf{u}(t,\mathbf{y})|^2 f(t,\mathbf{y},\mathbf{v})\, d\mathbf{v}$

Stress $\mathbf{T}(t,\mathbf{y}) = -m \int_{\mathbb{R}^3} (\mathbf{v} - \mathbf{u}(t,\mathbf{y})) \otimes (\mathbf{v} - \mathbf{u}(t,\mathbf{y})) f(t,\mathbf{y},\mathbf{v})\, d\mathbf{v}$

Pressure $p(t,\mathbf{y}) = -\frac{1}{3} \mathrm{tr}\mathbf{T}(t,\mathbf{y}) = \frac{2}{3} \rho e(t)$

Heat flux $\mathbf{q}(t,\mathbf{y}) = m \int_{\mathbb{R}^3} \frac{1}{2} |\mathbf{v} - \mathbf{u}(t,\mathbf{y})|^2 (\mathbf{v} - \mathbf{u}(t,\mathbf{y})) f(t,\mathbf{y},\mathbf{v})\, d\mathbf{v}$

Theorem. For sufficiently regular solutions of the Maxwell-Boltzmann equation, the balance laws of continuum mechanics are satisfied by these moments:

$$\begin{aligned} \rho_t + \mathrm{div}(\rho \mathbf{u}) &= 0 \\ \rho(\mathbf{u}_t + \nabla \mathbf{u}\mathbf{u}) &= \mathrm{div}\mathbf{T} \\ \rho(e_t + \nabla e \cdot \mathbf{u}) &= \mathbf{T} \cdot \nabla \mathbf{u} - \mathrm{div}\, \mathbf{q} \end{aligned}$$

H-theorem

$$H(t,\mathbf{y}) = \frac{1}{n}\int_{\mathbb{R}^3} f\log f\, d\mathbf{v} = \frac{1}{n}\int_{\mathbb{R}^3} g\log g\, d\mathbf{v}$$

H-theorem for the invariant solutions:

$$\frac{\partial H}{\partial t} \leq 0$$

Remark on H for Maxwellian densities

$$f_M = \frac{\rho}{m\left(\frac{4\pi}{3}e\right)^{3/2}} e^{\frac{-3}{4e}|\mathbf{v}-\mathbf{u}|^2}$$

Maxwellian density. Solves MBE for suitable moments. $\mathbb{C}f_M = 0$

H-theorem for Maxwellian densities:

$$H = H_M = \frac{1}{n}\int_{\mathbb{R}^3} f_M \log f_M \, d\mathbf{v} \quad \rightarrow \quad \frac{dH_M}{dt} = 0$$

Valü of H (minus entropy) for Maxwellian densities:

$$H = H_M = \frac{1}{n}\int_{\mathbb{R}^3} f_M \log f_M \, d\mathbf{v} = -\log\frac{e^{3/2}}{\rho} + const.$$

J. C. Maxwell on inverse fifth power molecules, 1866

TRANSACTIONS

OF THE

ROYAL SOCIETY

OF

LONDON.

FOR THE YEAR MDCCCLXVII.

IV. *On the Dynamical Theory of Gases.* *By* J. CLERK MAXWELL, *F.R.S. L. & E*

Received May 16,—Read May 31, 1866.

In the present paper I propose to consider the molecules of a gas, not as elastic spheres of definite radius, but as small bodies or groups of smaller molecules repelling one another with a force whose direction always passes very nearly through the centres of gravity of the molecules, and whose magnitude is represented very nearly by some function of the distance of the centres of gravity. I have made this modification of the theory in consequence of the results of my experiments on the viscosity of air at different temperatures, and I have deduced from these experiments that the repulsion is inversely as the *fifth* power of the distance.

The special invariance for inverse 5th power molecules: $(\mathbb{C}g(\lambda\,\cdot))(\mathbf{w}) = \lambda^{-3}(\mathbb{C}g)(\lambda\mathbf{w})$

Further simplification for inverse 5th power molecules

Assume $g(t, \mathbf{w}) = \xi(t) G(\eta(t)\mathbf{w})$

Choose ξ and η to remove time dependence. Get

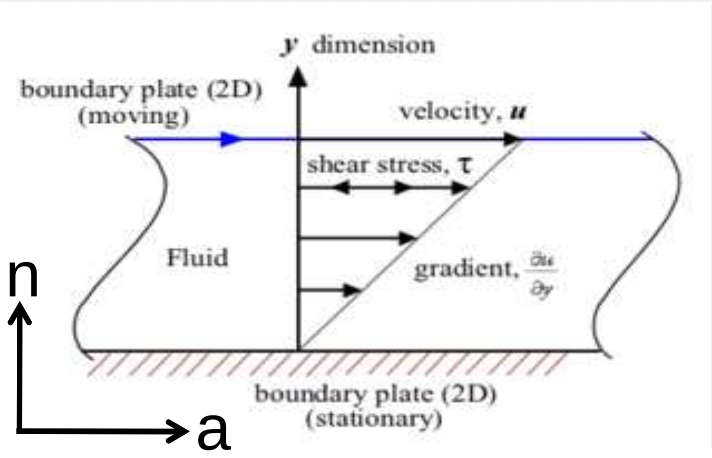
$$\operatorname{div}\left(G(t\,(\operatorname{cof}\mathbf{A}^T)^D + \beta\,\mathbf{I} - \mathbf{A}^D)\mathbf{v}\right) = \mathbb{C}G$$

$(\operatorname{cof}\mathbf{A}^T)^D = 0$ removes the time dependence.

Examples

1. $\mathbf{A} = \mathbf{a} \otimes \mathbf{n},\ \mathbf{a} \cdot \mathbf{n} = 0$

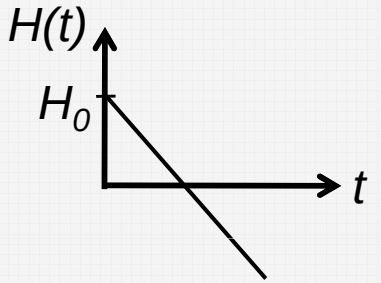
$$\mathbf{u}(\mathbf{y}, t) = \mathbf{A}(\mathbf{I} + t\mathbf{A})^{-1}\mathbf{y} = (\mathbf{n} \cdot \mathbf{y})\mathbf{a}$$



Examples, continüd

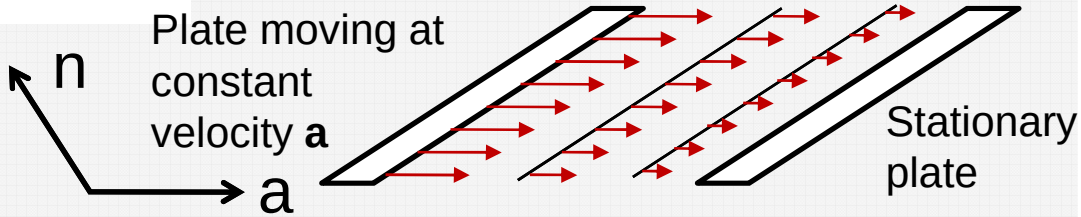
$$\rho(t) = \rho_0, \quad \mathbf{u}(t,\mathbf{y}) = \kappa y_2 \mathbf{e}_1, \quad \mathbf{T}(t) = \mathbf{T}_0 e^{-2\beta t}, \quad e(t) = -(\mathrm{tr}\mathbf{T}_0/2\rho_0)e^{-2\beta t} = \frac{3p_0}{2\rho_0}e^{-2\beta t}$$

$$H(t) = 3\beta t + H_0 = -\log\frac{e^{3/2}(t)}{\rho} + const.$$!



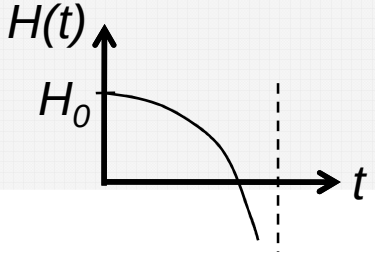
2. $\mathbf{A} = \mathbf{a} \otimes \mathbf{n}, \ \mathbf{a}\cdot\mathbf{n} \neq 0$

$$\mathbf{u}(t,\mathbf{y}) = \frac{1}{1+(\mathbf{a}\cdot\mathbf{n})t}(\mathbf{n}\cdot\mathbf{y})$$



$$\rho(t) = \frac{\rho_0}{1+(\mathbf{a}\cdot\mathbf{n})t}, \quad \mathbf{T}(t) = (1+(\mathbf{a}\cdot\mathbf{n})t)^{-\left(\frac{2\beta}{\mathbf{a}\cdot\mathbf{n}}+\frac{5}{3}\right)}\mathbf{T}_0, \quad e(t) = \frac{3p_0}{2\rho_0}(1+(\mathbf{a}\cdot\mathbf{n})t)^{-\left(\frac{2\beta}{\mathbf{a}\cdot\mathbf{n}}+\frac{2}{3}\right)}$$

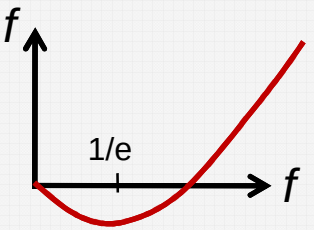
$$H(t) = \frac{3\beta}{\mathbf{a}\cdot\mathbf{n}}\log(1+(\mathbf{a}\cdot\mathbf{n})t) + H_0 = -\log\frac{e^{3/2}(t)}{\rho(t)} + const.$$!

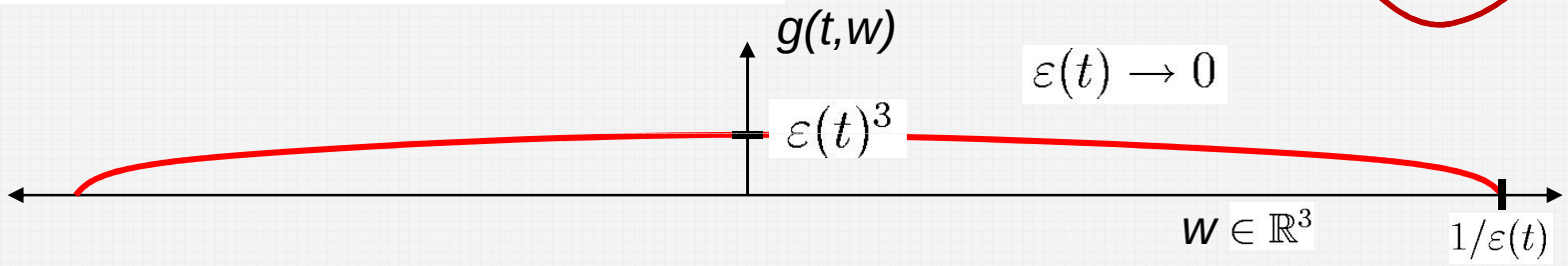


Remarks

- Consistency of behavior of H with its definition?

$$H(t,\mathbf{y}) = \frac{1}{n}\int_{\mathbb{R}^3} f \log f \, d\mathbf{v} = \frac{1}{n}\int_{\mathbb{R}^3} g \log g \, d\mathbf{v}$$





- Both the solutions of Boltzmann and the numerical results on pulling carbon nanotubes at constant strain rate suggest that there is a **statistical mechanics** for the invariant manifold. If so, it cannot be based on the invariant measure of ordinary statistical mechanics (Gibbs measure) because

$$\text{Hamiltonian} \neq \text{constant}$$