Objective Molecular Dynamics

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Fluid Mechanics – viscometric flows

Simple shearing flow, for example…

normal stress (non-Newtonian fluids)
Viscometric flows

Constitutive equation for the Cauchy stress

$$\sigma(y, t) = -pI + \sum(F_t(y, \cdot))$$

“relative deformation gradient”

Ordinary Lagrangian description of motion

$$y : \Omega \times (0, \infty) \rightarrow \mathbb{R}^3$$

Formula for the relative deformation gradient

$$F_t(z, \tau) = \nabla_z(y(y^{-1}(z, t), \tau))$$

Definition of a viscometric flow

$$F_t(y, \tau) = Q_t(y, \tau)(I + (\tau - t)M_t(y)), \quad \text{rank } M_t \leq 1, \quad Q_t \in O(3)$$

$$\tau \leq t, \quad t > 0, \quad y \in \Omega_t$$
Solid Mechanics – the bending and twisting of beams

- B. de St. Venant, Memoire sur la torsion des prismes, Mem. Des Savants Etrangers 14 (1855), 233-560
Bending and twisting of beams


\[ y : \Omega \rightarrow \mathbb{R}^3 \]

\[ \nabla y(x) = R(x)A(x_1, x_2) \]

or

\[ \nabla y(x) = R(x)A(x_1) \]
Main thesis of this talk

- There is a universal molecular level interpretation of these motions (universal = independent of material)

- From this viewpoint the bending and twisting of beams and viscometric flows of fluids are the same
Isometry groups

\[ g_1 = (R_1 | c_1), \quad g_2 = (R_2 | c_2) \quad g_1 g_2 = (R_1 R_2 | R_1 c_2 + c_1) \]

\[ g_1(x) = R_1 x + c_1 \quad R_1, R_2 \in O(3) \quad c_1, c_2 \in \mathbb{R}^3 \]

Iterate \( g_1 \):

\[ g_1^p(x) = \sum_{i=0}^{p-1} R_1^i c_1 + R_1^p x \]

More generally,

\[ g_1^p g_2^q g_3^r(x) = \sum_{i=0}^{p-1} R_1^i c_1 + R_1^p \sum_{i=0}^{q-1} R_2^i c_2 + R_1^p R_2^q \sum_{i=0}^{r-1} R_3^i c_3 + R_1^p R_2^q R_3^r x \]
Examples

- Translation group
  \[ G_T = \{ t_1^p t_2^q t_3^r : p, q, r \in \mathbb{Z} \} = \{ (I|p), e_1 + q, e_2 + r, e_3 ) : p, q, r \in \mathbb{Z} \} \]

- 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

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

where

1. \( h = (R_\theta | \tau, e), R_\theta e = e, |e| = 1, x_0 \cdot e = 0, e, x_0 \in \mathbb{R}^3, \tau \neq 0, \) and \( \theta \) is an irrational multiple of \( 2\pi. \)

2. \( g = (R_\psi | R_\psi, I, x_0), R_\psi e = e, \) is a proper rotation with angle \( \psi = 2\pi/n, n \in \mathbb{Z}, n \neq 0. \)

3. \( f = (R | (R-I)x_1), R = -I + 2e_1 \otimes e_1, |e_1| = 1, e \cdot e_1 = 0 \) and \( x_1 = x_0 + \xi e, \) for some \( \xi \in \mathbb{R}. \)
A time dependent invariant manifold of the equations of molecular dynamics

\[ y_k(t), \ k = 1, \ldots, M \]  

simulated atoms

\[ G = \{ g_1, g_2, \ldots, g_N \} \]  
a discrete group of isometries  
\( (N \text{ can be infinite}) \)

\[ y_{i,k}(t) = g_i(y_k(t)), \]  
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

\[ \frac{d^2 y_{j,k}(t)}{dt^2} = \frac{d^2}{dt^2} g_j(y_k(t)) = Q_j \frac{d^2 y_k(t)}{dt^2} \]

\( g_j = (Q_j | c_j) \in G, \ j = 1, \ldots, N, \ k = 1, \ldots, M \)
Atomic forces

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

The force is smooth and satisfies

■ Frame-indifference

\[
Q \frac{\partial \varphi}{\partial y_{i,k}} (\ldots, y_{i_1,1}, \ldots y_{i_1,M}, \ldots, y_{i_2,1}, \ldots y_{i_2,M}, \ldots) = \frac{\partial \varphi}{\partial y_{i,k}} (\ldots, Q y_{i_1,1} + c, \ldots Q y_{i_1,M} + c, \ldots, Q y_{i_2,1} + c, \ldots Q y_{i_2,M} + c, \ldots)
\]

■ Permutation invariance

\[
\frac{\partial \varphi}{\partial y_{\Pi(i,k)}} (\ldots, y_{i_1,1}, \ldots y_{i_1,M}, \ldots, y_{i_2,1}, \ldots y_{i_2,M}, \ldots) = \frac{\partial \varphi}{\partial y_{i,k}} (\ldots, y_{\Pi(i_1,1)}, \ldots, y_{\Pi(i_1,M)}, \ldots, y_{\Pi(i_2,1)}, \ldots, y_{\Pi(i_2,M)}, \ldots)
\]

where $\Pi$ 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 $j, \ell$. 

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

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

\[
\varphi(\ldots, Y_{i_1,1}, \ldots, Y_{i_1,M}, \ldots, Y_{i_2,1}, \ldots Y_{i_2,M}, \ldots) \\
= \varphi(\ldots, Y_{\Pi(i_1,1)}, \ldots Y_{\Pi(i_1,M)}, \ldots, Y_{\Pi(i_2,1)}, \ldots, Y_{\Pi(i_2,M)}, \ldots) \\
= \varphi(\ldots, Q_y y_{i_1,1} + c, \ldots Q_y y_{i_1,M} + c, \ldots, Q_y y_{i_2,1} + c, \ldots, Q_y y_{i_2,M} + c, \ldots)
\]

( 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 \( y_k(t), k = 1, \ldots, M \) satisfy the equations of molecular dynamics, i.e.,

\[
m_k \ddot{y}_k(t) = - \frac{\partial \varphi}{\partial y_{0,k}} (\ldots, y_{i,1}(t), \ldots, y_{i,M}(t), y_{i+1,1}(t), \ldots, y_{i+1,M}(t), \ldots)
\]

\[
= - \frac{\partial \varphi}{\partial y_{0,k}} (\ldots, g_i(y_1(t)), \ldots, g_i(y_M(t)), g_{i+1}(y_1(t)), \ldots, g_{i+1}(y_M(t)), \ldots)
\]

\[
y_k(0) = y_k^0, \quad \dot{y}_k(0) = v_k^0, \quad k = 1, \ldots, M
\]

then \( y_{j,k}(t) \) also satisfy the equations of molecular dynamics:

\[
m_k \ddot{y}_{j,k}(t) = - \frac{\partial \varphi}{\partial y_{j,k}} (\ldots, y_{i,1}(t), \ldots, y_{i,M}(t), y_{i+1,1}(t), \ldots, y_{i+1,M}(t), \ldots)
\]
Proof

There is a permutation $\Pi$, depending on the choice of $g$, such that

$$y_{\Pi(i,k)}(t) = g(y_{i,k}(t)), \quad i = 1, \ldots, N, \quad k = 1, \ldots, M$$

Fix $j \in \{1, \ldots, N\}$ and choose $g = g_j^{-1} = (Q_j^T| - Q_j^T c_j)$

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

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

$$= -Q_j \frac{\partial \varphi}{\partial y_{\Pi(i,k)}} (\ldots, y_{\Pi(i,1)}(t), \ldots, y_{\Pi(i,M)}(t), \ldots, y_{\Pi(i+1,1)}(t), \ldots, y_{\Pi(i+1,M)}(t), \ldots)$$

$$= -Q_j \frac{\partial \varphi}{\partial y_{j,k}} (\ldots, g_j^{-1}(y_{i,1}(t)), \ldots, g_j^{-1}(y_{i,M}(t)), g_j^{-1}(y_{i+1,1}(t)), \ldots, g_j^{-1}(y_{i+1,M}(t)), \ldots)$$

$$= -Q_j \frac{\partial \varphi}{\partial y_{j,k}} (\ldots, Q_j^T y_{i,1}(t) - Q_j^T c_j, \ldots, Q_j^T y_{i,M}(t) - Q_j^T c_j, \ldots, Q_j^T y_{i+1,1}(t) - Q_j^T c_j, \ldots, Q_j^T y_{i+1,M}(t) - Q_j^T c_j, \ldots)$$

$$= - \frac{\partial \varphi}{\partial y_{j,k}} (\ldots, y_{i,1}(t), \ldots, y_{i,M}(t), y_{i+1,1}(t), \ldots, y_{i+1,M}(t), \ldots)$$

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Allowed time dependence of the group elements \( g_j = (Q_j | c_j) \), \( Q_j \in O(3) \), \( c_j \in \mathbb{R}^3 \)

\[
\frac{d}{dt} Q_j = Q_j W_j \quad \text{(no sum), where} \quad W_j = -W_j^T
\]

The permitted time-dependence,

\[
\frac{d^2}{dt^2} \left( Q_j y_k + c_j \right) = Q_j \frac{d^2 y_k(t)}{dt^2}
\]

that is,

\[
\ddot{c}_j = -Q_j (W_j^2 y_k + \dot{W}_j y_k + 2W_j \dot{y}_k)
\]

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

\[
\ddot{c}_j = 0 \quad \text{and} \quad W_j = 0
\]

That is, \( Q_j \in O(3) \) must be constant and \( c_j = a_j t + b_j \) must be an affine function of \( t \)
Simplest case - translation group

\[ G_T = \{(I|\nu^1e_1 + \nu^2e_2 + \nu^3e_3): \nu^1, \nu^2, \nu^3 \in \mathbb{Z}\} \]

Discrete translation group

\[ y_{\nu,k}(t), \quad \nu \in \mathbb{Z}^3, \quad k = 1, \ldots, M, \quad t > 0 \]

All of the atoms

\[ y_k(t) = y_{(0,0,0),k}(t), \quad k = 1, \ldots, M \]

Simulated atoms

\[ y_{\mu,k}(t) = g_\mu(y_k(t)) = y_k(t) + \mu^i e_i + \mu^i tA e_i = y_k(t) + (I + tA)(\mu^i e_i) \]

Permitted time-dependence
Naïve passage to continuum level

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

\( \mathbf{x} \sim \mu^i \mathbf{e}_i \) for some \( \mu \in \mathbb{Z}^3 \) up to an error of molecular dimensions

\( \mathbf{y}_k(t) \sim 0 \) up to an error of molecular dimensions

\[ \mathbf{y}(\mathbf{x}, t) = (\mathbf{I} + t\mathbf{A})\mathbf{x} \quad \text{“affine motion”} \]

Recall, for “simple materials”

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

\[ \mathbf{F}_t(\mathbf{y}, \tau) = (\mathbf{I} + \tau\mathbf{A})(\mathbf{I} + t\mathbf{A})^{-1} \]

This describes a viscous flow if and only if \( \mathbf{A} = \mathbf{a} \otimes \mathbf{b}, \mathbf{a} \cdot \mathbf{b} = 0 \),
in which case \( \mathbf{F}_t(\mathbf{y}, \tau) = \mathbf{I} + (\tau - t)\mathbf{a} \otimes \mathbf{b} \).
However, even if rank \( \mathbf{A} > 1 \), we have

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

because

\[ \rho(\mathbf{v}_t + \nabla \mathbf{v} \mathbf{v}) = \rho(-\mathbf{A}(\mathbf{I} + At)^{-1}\mathbf{A}(\mathbf{I} + At)^{-1}y + \mathbf{A}(\mathbf{I} + At)^{-1}\mathbf{A}(\mathbf{I} + At)^{-1}y) = 0 \]
Some viscometric flows, i.e., cone and plate flow, seem to have no analog at atomic level. My personal view: failure of full time-dependent frame-indifference in molecular dynamics

The definition of “viscometric flows” misses some affine motions having all the good properties of viscometric flows
Key question: how representative are these solutions?

- Attracting in some sense?
- If one takes more and more simulated atoms (and a fixed group), with certain averages of initial conditions prescribed, the behavior is statistically like the large body/large time limit of a suitable boundary value problem (?).

Another way to explore this issue: look at other theories of physics intermediate between MD and continuum

**Maxwell-Boltzmann Equation**

\[ f : \mathbb{R} \times \mathbb{R}^3 \times \mathbb{R}^3 \rightarrow \mathbb{R}^\geq \]

\[
\frac{\partial f}{\partial t} + \mathbf{v} \cdot \frac{\partial f}{\partial \mathbf{y}} = \int_{\mathbb{R}^3} \int_{\mathcal{S}} (f' f' - f f) |\mathbf{v}_{*} - \mathbf{v}| dS d\mathbf{v}_{*}
\]

**Maxwell-Boltzmann equation**

\[
\begin{align*}
\mathbf{v} &= \mathbf{v}_{*} - ((\mathbf{v}_{*} - \mathbf{v}) \cdot \mathbf{e}) \mathbf{e} \\
\mathbf{v}' &= \mathbf{v} + ((\mathbf{v}_{*} - \mathbf{v}) \cdot \mathbf{e}) \mathbf{e} \\
\end{align*}
\]

\[
\begin{align*}
f' &= f(t, \mathbf{y}, \mathbf{v}) \\
f &= f(t, \mathbf{y}, \mathbf{v})
\end{align*}
\]
OMD solutions have their own “statistics”

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

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

$$f(t, y, v + A(I + tA)^{-1}y) = f(t, 0, v)$$
This yields an exact reduction of the Maxwell-Boltzmann equation

\[ f(t, y, v) = f(t, 0, v - A(I + tA)^{-1}y) \]

\[ = g(t, v - A(I + tA)^{-1}y), \quad v \in \mathbb{R}^3, \quad y \in \mathbb{R}^3, \quad t > 0 \]

\( g(t, w) \) satisfies

\[ \frac{\partial g}{\partial t} - \frac{\partial g}{\partial w} \cdot A(I + tA)^{-1}w = \int_{\mathbb{R}^3} \int_S (g'_*g' - g_*g)|w_* - w| dSdw_* \]

Apparently includes all known exact solutions of the M-B equation for special molecular force laws

(A further reduction is possible that leads to a ODE operator on the left hand side at the expense of slightly complicating the right hand side)
H theorem

\[ H(t, y) = \int_{\mathbb{R}^3} f \log f \, dv = \int_{\mathbb{R}^3} g \log g \, dw \]

\[ \frac{\partial H}{\partial t} + \text{tr}(A(I + tA)^{-1})H \leq 0 \]

Prototypical molecular density corresponding to these flows…

\[ g(t, w) \]

\[ \varepsilon(t) \rightarrow 0 \]
**Principle of Material Frame Indifference**

change of frame

\[ y^* = R(t)y + c(t) \]

where \( R : [0, \infty) \rightarrow SO(3) \) and \( c : [0, \infty) \rightarrow \mathbb{R}^3 \)

\[ y^*(t, x) = R(t)y(t, x) + c(t) \]

Cauchy stress

\[ \sigma^* = R(t)\sigma R(t)^T \]

\[ \sigma(t, x) = f_{t,x}(y) \], where \( f_{t,x} \) for each \( t > 0, x \in \Omega \) is a functional defined on a space of histories \( y(z, s), z \in \Omega, s < t \).

PMFI:

\[ \sigma^*(t, x) = f_{t,x}(y^*) \quad \text{if and only if} \quad \sigma(t, x) = f_{t,x}(y) \]

where \( \sigma^* \) and \( y^* \) are related to \( \sigma \) and \( y \) by the above
Suggested modification of PMFI

Add:

The equations of motion are identically satisfied for the family of affine motions \( y(t, x) = (I + tA)x, \ x \in \Omega. \)

(In Eulerian form, the suggested principle asserts that velocity fields of the form \( \mathbf{v}(t, \mathbf{y}) = A(I + tA)^{-1}\mathbf{y} \) satisfy identically the equations of motion for every linear transformation \( A \))

(homogeneous materials only)

- Satisfied by every successful constitutive equation of which I am aware
- Have to look “on the fringes of legitimate theory”
Some interesting examples

**LES equations**

$$\overline{v}_t + \nabla \overline{v} \cdot \overline{v} = -\nabla P + \nu \Delta \overline{v} - \nabla \cdot \tau, \quad \nabla \cdot \overline{v} = 0,$$

where $P$ is the average kinematic pressure, $\nu$ is the kinematic viscosity, the overbar denotes spatial filtering,

$$\overline{u}(t, y) = \int_{\mathbb{R}^3} g(y - y') u(t, y') \, dy'$$

and

$$\tau = \overline{v} \otimes \overline{v} - \overline{v} \otimes \overline{v}$$

satisfied!

**Langevin equation**

$$X_{\nu,k}, \nu \in \mathbb{Z}^3, \ k = 1, \ldots, M \text{ each with effective mass } m \text{ in a simple shearing flow with velocity } \mathbf{v}(X) = \dot{\gamma} X_2 e_1, \ \dot{\gamma} = \text{const.}, \text{ and } \mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3 \text{ is an orthonormal basis.}$$

The beads interact according to a potential energy

$$\varphi(\ldots, X_{\nu_1,1}, \ldots X_{\nu_1,M}, X_{\nu_2,1}, \ldots, X_{\nu_2,M}, \ldots)$$

whose derivative is assumed to be frame-indifferent and permutation invariant.
Langevin, continued

\[
X_k = X_{(0,0,0),k}, \quad k = 1, \ldots, M \quad \text{simulated atoms}
\]

\[
X_{\nu,k}(t) = X_k(t) + (I + tA)\nu^i e_i \quad \text{all atoms}
\]

\[
m\ddot{X}_k = \frac{\partial \varphi}{\partial X_{(0,0,0),k}} - \gamma m (\dot{X}_k - \dot{\gamma} (X_k \cdot e_2) e_1) + R_k
\]

\[
\langle R(t) \rangle = 0, \quad \langle R(t) \cdot R(t') \rangle = 2\gamma k_B T m \delta(t - t')
\]

All other atoms also satisfy the Langevin equation with the same noise!

Suggested way of writing the Langevin equation for general affine motions:

\[
m\ddot{X}_{\nu,k} = \frac{\partial \varphi}{\partial X_{\nu,k}} - \gamma m (\dot{X}_{\nu,k} - A(I + tA)^{-1}X_{\nu,k})) + R_k
\]
Other groups besides the translation group
(joint work with Traian Dumitrica)
Objective MD study of a carbon nanotube under torsion

- Three-body Tersoff potentials for carbon
- Twist was controlled by controlling the group parameters (interesting open question: what generalized forces answer to variations of group parameters?)
- The groups chosen were various subgroups of the following group (with no translational subgroup) listed earlier:

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

1. \( h = (R_\theta |e + (R_\theta - I)x_0) \), \( R_\theta e = e, \ |e| = 1, \ x_0 \cdot e = 0, \ e, x_0 \in \mathbb{R}^3, \ \tau \neq 0, \) and \( \theta \) is an irrational multiple of \( 2\pi \).

2. \( g = (R_{\nu \psi} |(R_{\nu \psi} - I)x_0) \), \( R_{\nu \psi} e = e, \) is a proper rotation with angle \( \psi = 2\pi/n \), \( n \in \mathbb{Z}, \ n \neq 0. \)

No time-dependence of the group elements was introduced.
Objective MD: study of buckling of C nanotube under torsion

(12, 12) CNT

3 deg/Angstrom twist
Effect of different choices of the fundamental domain
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?
The most interesting cases pending...

- Subperiodic groups (as in this case of C-nanotubes) but with time-dependent group elements
- There are fascinating nontrivial cases of this type
- Best described as “flowing nanostructures”
- Do these flows at atomic level have the same fundamental significance for the measurement of material properties as viscometric flows and the bending and twisting of beams do for continuum theory?