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«You cannot be serious, men!» Can the Andersen-Parrinello & Rahman MD serve as a serious scale-bridging tool?

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PART I

1. Pre-Andersen MD

What is MD

- MD is a method "... for studying classical *statistical mechan ics* of well-defined systems through a <u>numerical solution of</u> <u>Newton's equations.</u>"
- Conventionally, birth of MD ≡ Fermi-Pasta-Ulam numerical experiment (1955) (background ensemble ≡ microcanonical ensemble {N, E, Ω}).
- "... <u>MD simulations</u> ... are in a sense <u>computer experiments</u> which open new avenues in investigations of the microscopic origin of material phenomena."

What is MD after

- MD was first proposed to simulate the behavior of fluid materials, under the assumption that "...time averages of properties of the simulated fluid are equal to microcanonical ensemble averages of the same properties."
- "Upon increasing external pressure crystals usually undergo structural phase transitions. Often, the final structure is unknown and simulations can be very useful in identifying possible candidates."

What are the main limitations of MD

- Writes A. (end of 1979): "A MD calculation can simulate the motion of only a *small number of particles* (typically, between 50 and 1000). A physical system with this number of particles is *more like a droplet than a bulk fluid*, and *its properties would be strongly affected by its surface* ... to eliminate ... surface [effects] ..., periodic boundary conditions are ordinarily used."
- P&R say (1981): "...periodic boundary conditions ... are obtained by periodically repeating a unit cell of volume Ω containing the N particles by suitable translations. ... every particle can be thought of as being at the 'center'. In other words, ... the summation over J in [the Newton equations] extends over the infinite system generated by the periodic boundary conditions."

What are the equations of Pre-Andersen MD

r_I ≡ *current position vector* of *I*-th molecule in a *simulation cell* of *fixed volume* Ω;

• Lagrangian: $L = \hat{K}(\dot{r}_1, \dots, \dot{r}_N) - \hat{V}(r_I, \dots, r_N)$, where

kinetic energy
$$K = \frac{1}{2} \sum_{I} m_{I} \dot{r}_{I} \cdot \dot{r}_{I},$$

Intermolecular potential $V = \frac{1}{2} \sum_{I} \sum_{J} \Phi(r_{IJ}), \quad r_{IJ} := |r_{I} - r_{J}|;$

• motion equations:
$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{r}_I} \right) - \frac{\partial L}{\partial r_I} = 0$$
 ($I = 1, ..., N$), i.e.,

$$m_I \ddot{r}_I = -\sum_{J \neq I} \frac{1}{r_{IJ}} \Phi'(r_{IJ})(r_I - r_J) \quad (I = 1, ..., N)$$

NB. Recall quote from P&R 1981 about summation over J !!

Molecular Dynamics & Continuum Mechanics

- MD is a method "... for studying classical *statistical mechanics* of well-defined systems through a <u>numerical solution of</u> <u>Newton's equations.</u>"
- CM is a *field theory* aiming to posit initial/boundary-value problems for such fields as displacement, velocity, and stress.
- MD simulations concern a basic cell \mathscr{X} of <u>attomole size</u> and have a duration \mathscr{T} of <u>nanosecond order</u>, with time step one femtosecond

(1 attomole = $10^{-18} \times 6.0221 \times 10^{23} \simeq$ one million of molecules; 1 nanosecond = one billionth of a second; femto = 10^{-15})

At the CM scale, the MD space-time regions $\mathscr{X} \times \mathscr{T}$ are to be regarded as (point, instant) pairs (x, t). To establish any link between MD and CM, scale-bridging criteria must be posited.

2. Andersen–Parrinello & Rahman MD

Basic References

- H.C. Andersen, J. Chem. Phys. 72 (4), 2384 (1980).
- M. Parrinello and A. Rahman,
 - Phys. Rev. Lett. 45, 1196 (1980)
 - Polymorphic transitions in single crystals: A new molecular dynamics method. J. Appl. Phys. 52, 7182 (12) (1981).

Main Idea(s)

"We (Laio & Parrinello, 2002)

- use the edges of the simulation cell as collective variables
- and [we] define a *metadynamics* that drives the system away from the local minimum towards a new crystal structure.

...We illustrate the power of the method by studying the <u>pressure-induced</u> diamond to simple hexagonal <u>phase transition</u> in a model of silicon."

Geometry of Simulation Cell

A molecule's *current* and *referential position vectors*:

$$\boldsymbol{r}_{I} = \zeta_{I}^{i} \boldsymbol{h}_{i}$$
 and $\boldsymbol{s}_{I} = \zeta_{I}^{i} \boldsymbol{g}_{i}$ $(I = 1, \dots, N)$

- ζ_I^i *i*-th convected coordinate of I^{th} molecule
- *N* number of molecules in simulation cell
- g_i, h_i referential and current covariant base vectors
 - i.e., referential and current lattice vectors
- $F = h_i \otimes g^i$ deformation gradient at (macrolocation of) simulation cell
- *gⁱ* <u>contravariant base vectors</u> (lattice cell needs not be a right parallelepiped)
- Hence, $r_I = F s_I$, the Cauchy-Born scale-bridging criterion.

3. Exact and Uncompromising MD vs. A-P&R MD

Central Kinematic Assumption

• both molecules and simulation cell fluctuate:

$$r_I = F s_I \quad \Rightarrow \quad \dot{r}_I = \dot{F} s_I + F \dot{s}_I$$

Kinetic Energies

Given that

$$\dot{r}_I = \dot{F} s_I + F \dot{s}_I,$$

• exact kinetic energy:

$$\begin{split} \boldsymbol{K} &\coloneqq \frac{1}{2} \sum_{I} m_{I} \dot{\boldsymbol{r}}_{I} \cdot \dot{\boldsymbol{r}}_{I} = \boldsymbol{F}^{T} \boldsymbol{F} \cdot \frac{1}{2} \sum_{I} m_{I} \dot{\boldsymbol{s}}_{I} \otimes \dot{\boldsymbol{s}}_{I} \\ &+ \dot{\boldsymbol{F}}^{T} \dot{\boldsymbol{F}} \cdot \frac{1}{2} \sum_{I} m_{I} \boldsymbol{s}_{I} \otimes \boldsymbol{s}_{I} + \dot{\boldsymbol{F}}^{T} \boldsymbol{F} \cdot \sum_{I} m_{I} \boldsymbol{s}_{I} \otimes \dot{\boldsymbol{s}}_{I}. \end{split}$$

• P&R kinetic energy:

$$K_{PR} = \boldsymbol{F}^T \boldsymbol{F} \cdot \frac{1}{2} \sum_{I} m_I \dot{\boldsymbol{s}}_I \otimes \dot{\boldsymbol{s}}_I + \frac{1}{2} I |\dot{\boldsymbol{F}}|^2,$$

with I > 0 an adjustable parameter (dim(I) = mass × length²).

More on Kinetic Energies

For $I := \sum m_I s_I \otimes s_I \equiv$ referential inertia tensor,

$$2(\mathbf{K} - \mathbf{K}_{PR}) = \underbrace{\dot{\mathbf{F}}^T \dot{\mathbf{F}} \cdot (\mathbf{I} - \mathbf{I} \mathbf{1}_{ref})}_{(1)} + \underbrace{\dot{\mathbf{F}}^T \mathbf{F} \cdot \dot{\mathbf{I}}}_{(2)} + \underbrace{\dot{\mathbf{F}}^T \mathbf{F} \cdot \mathbf{Skw} \left(\sum_{I} m_I s_I \otimes \dot{s}_I\right)}_{(3)}$$

• Say P&R about the Lagrangian they associate with *K*_{PR}:

"Whether such a Lagrangian is derivable from first principles is a question for further study; its validity can be judged, as of now, by the equations of motion and the statistical ensembles that it generates."

Q.1 – When is it that *K* reduces to K_{PR} ?

Assumptions one can think of

- **a.** $I = I \mathbf{1}_{ref} \implies K K_{PR} = (2) + (3)$
- **b.** I = const. \Rightarrow $K K_{PR} = 1 + 3$
- **c.** $\dot{F}^T F \in Sym \implies K K_{PR} = 1 + 2$
- a. strictly speaking, appropriate almost only for *fluids*; as to
 b., note that < *I* >= 0
- a. and b. are kinematical constraints on molecule fluctuations
- c. is a kinematical constraint on cell fluctuations, equivalent to symmetry of macroscopic velocity gradient:

cell fluctuation motion should be irrotational (have null spin)

a., b. and c. together yield the P&R kinetic energy!

Q.2 – Is there an uncompromising choice of a kinetic energy of A–P & R type?

Recall that

- **a.** $I = I \mathbf{1}_{ref} \implies K K_{PR} = 2 + 3$
- **b.** I = const. \Rightarrow $K K_{PR} = 1 + 3$
- **c.** $\dot{F}^T F \in Sym \implies K K_{PR} = 1 + 2$

Note that

b. and **c.** together yield the desired **P**&**R**-type kinetic energy:

$$\left| \frac{\tilde{K}}{2} = \frac{1}{2} F^T F \cdot \sum_{I} m_I \dot{s}_I \otimes \dot{s}_I + \frac{1}{2} \dot{F}^T \dot{F} \cdot I \right|$$
$$\left(\frac{K_{PR}}{2} = \frac{1}{2} F^T F \cdot \sum_{I} m_I \dot{s}_I \otimes \dot{s}_I + \frac{1}{2} I |\dot{F}|^2 \right)$$

Q.3 – Why no MD practitioners ever worried about conceptual foundations of A–P & R MD?

A. (offered by G. Ciccotti) – Because A–P&R MD is regarded as a trick to generate the desired statistics. Q.4 – What are the uses of the (exact or) uncompromising versions of A–P & R MD?

Serious Work Program

with A. Di Carlo, M. Ribezzi Crivellari,

M. Paoluzzi, L.R. Zastrow, M. Minozzi, ...

- 1st Goal. (Cell microdynamics, fast)
 Find out whether kinetic couplings (2) and (3), neglected in trademark A–P & R MD, do affect *cell fluctuations*.
- 2nd Goal. (Cell macrodynamics, slow)

By an array of interacting A–P & R-like cells simulated in parallel, each of which is regarded as a material element (\equiv an infinitesimal chunk of a simple continuous body), construct *atomistically-informed approximations to a continuum*.

PART II

4. Constitutive Bridging: a Conceptual Use of MD, à la A–P&R or not

A typical energy landscape



- colors suggest level curves of stored-energy map $F \mapsto \hat{\sigma}(F)$
- a path through a saddle point connecting two local minima ≡ a dynamics allowing to clear the energy barrier between two phases

This picture can be looked at

- with the eyes of a solid-state physicist interested in structural phase transitions of crystalline solids, such as austenite/martensite phase changes
- with the eyes of a continuum mechanist/analyst, whose interests are in a mathematical study of sensible initial/boundaryvalue problems in elasticity

A lot to gain for the solid-state physicist, who works at the microscopic scale and uses MD

- to gather info about energy landscapes: set of local minima, shape & height of energy barriers, ...
- to find out whether there is an evolutionary process connecting two given local minima, be it
 - $\frac{artificial}{force}$, introducing a pseudo-time and a pseudo-driving $\frac{1}{force}$ (i.e., a metadynamics)
 - <u>real</u> & <u>multiscale</u> in both space and time, running on-the-fly computations based on a coupled atomistic-continuum approach

Not much to gain for the mechanist/analyst, who works <u>at the macroscopic scale</u> and aims to put on a firm footing such issues as ...

... J. Ball's assumptions on stored-energy map

we recall that J. M. BALL's [1] existence results concerning minimizers of the functional (1.2) are obtained when $\hat{\sigma}$ is *polyconvex*, *polycoercive*, and consistent with the growth condition:

(A)
$$\hat{\sigma}(F) \to +\infty$$
 as det $F \to 0+$

Precisely, $\hat{\sigma}$ is polyconvex if there is a convex function

(1.6)
$$(X, Y, \delta) \mapsto \sigma(X, Y, \delta)$$

over $\operatorname{Lin} \times \operatorname{Lin} \times \mathbb{R}$ such that, for each $F \in \operatorname{Lin}^+$,

(1.7)
$$\sigma(F, F^*, \det F) = \hat{\sigma}(F).$$

 $\hat{\sigma}$ is polycoercive if there are constants p, q, r, \varkappa , and λ , with

$$(\mathbf{B}^{++})_1 \qquad p \ge 2, \quad q \ge \frac{p}{p-1}, \quad r > 1,$$

such that, for all $F \in Lin^+$,

 $(\mathbf{B}^{++})_2 \qquad \hat{\sigma}(F) \ge \varkappa \{ \|F\|^p + \|F^*\|^q + (\det F)^r \} + \lambda, \quad \varkappa > 0$

Note that

- any talking about Finite Elasticity requires that the properties of a class of energy functionals are specified;
- any Molecular Dynamics run requires that a specific intermolecular potential is chosen.

Micro/Macro Constitutive Consistency Issues

- given an intermolecular potential, to find a consistent class of energy functionals;
- given a class of energy functionals, to find all consistent intermolecular potentials.

5. More about

uncompromising vs. A-P&R MD

Lagrangian Version of A-P&R MD

• Lagrangian:

$$\begin{pmatrix} L \\ L_{PR} \end{pmatrix} = \begin{cases} \hat{K}(\boldsymbol{s}_{I}, \dot{\boldsymbol{s}}_{I}; \boldsymbol{F}, \dot{\boldsymbol{F}}) \\ \hat{K}_{PR}(\dot{\boldsymbol{s}}_{I}; \boldsymbol{F}, \dot{\boldsymbol{F}}) \end{cases} - \frac{1}{2} \sum_{I} \sum_{J} \Phi(r_{IJ}) + \boldsymbol{\Omega}_{ref} \boldsymbol{S} \cdot \boldsymbol{F},$$

where $r_{IJ} := |F(s_I - s_J)|$ and S = external referential stress = observable applied stress.

• motion equations:

$$\begin{cases} \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{s}_{I}} \right) - \frac{\partial L}{\partial s_{I}} = 0, \quad (I = 1, \dots, N) \\ \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{F}} \right) - \frac{\partial L}{\partial F} = \Omega_{ref} S. \end{cases}$$

• iso-enthalpy, iso-stress ensemble $\{N, H \equiv \text{enthalpy}, S\}$:

$$\begin{cases} H \\ H_{PR} \end{cases} = \begin{cases} \hat{K}(\boldsymbol{s}_{I}, \dot{\boldsymbol{s}}_{I}; \boldsymbol{F}, \dot{\boldsymbol{F}}) \\ \hat{K}_{PR}(\dot{\boldsymbol{s}}_{I}; \boldsymbol{F}, \dot{\boldsymbol{F}}) \end{cases} + \frac{1}{2} \sum_{I} \sum_{J} \Phi(r_{IJ}) - \Omega_{ref} \boldsymbol{S} \cdot \boldsymbol{F} .$$

Uncompromising A-P&R Motion Equations

• motion equations:

$$m_I(\ddot{Fs}_I) + F \sum_{J>I} \frac{1}{r_{IJ}} \Phi'(r_{IJ})(s_I - s_J) = 0 \quad (I = 1, ..., N),$$

$$\sum_{I} m_{I}(\ddot{Fs_{I}}) \otimes s_{I} + F\Big(\sum_{I}\sum_{J>I}rac{1}{r_{IJ}} \Phi'(r_{IJ})(s_{I}-s_{J}) \otimes (s_{I}-s_{J})\Big) - \Omega_{ref}S = 0.$$

• a relevant consequence:

$$\underline{\boldsymbol{S}^{int}} = \boldsymbol{S}, \quad \boldsymbol{S}^{int} := \left(\sum_{I} \sum_{J>I} \frac{1}{r_{IJ}} \Phi'(r_{IJ})(r_{I} - r_{J}) \otimes (r_{I} - r_{J})\right) \boldsymbol{F}^{-T}$$

the internal stress S^{int} is a motion constant.

A–P&R Motion Equations

• motion equations: for $C := F^T F$,

$$m_I(\ddot{s}_I + C^{-1}\dot{C}\dot{s}_I) + \sum_{J>I} \frac{1}{r_{IJ}} \Phi'(r_{IJ})(s_I - s_J) = 0 \quad (I = 1, ..., N),$$

$$I\ddot{\boldsymbol{F}}=\Omega_{cur}(\boldsymbol{T}-\boldsymbol{P})\boldsymbol{F}^{-T},$$

where $T := (\det F)SF^T \equiv external current stress,$

$$\mathbf{P} := (\det \mathbf{F})^{-1} \Big(\sum_{I} \sum_{J>I} \frac{1}{r_{IJ}} \Phi'(r_{IJ})(\mathbf{r}_{I} - \mathbf{r}_{J}) \otimes (\mathbf{r}_{I} - \mathbf{r}_{J}) - \sum_{I} m_{I} \mathbf{v}_{I} \otimes \mathbf{v}_{I} \Big)$$

with $v_I = F \dot{s}_I$, and **P** the so-called *virial stress*.

• The difference (T - P) drives the fluctuation motion:

"The basic idea ... is to allow the tensor h [our F], which characterizes the molecular dynamic cell, to vary in time as a result of the difference between the varying internal microscopic stress tensor [our P] and the constant external stress tensor σ [our T]." (Ray&Rahman, 1984)

6. Micro/Macro Consistency

More on the Cauchy-Born Rule

- The C-B rule is the standard recipe for *computing the storedenergy mapping corresponding to a given atomistic potential*. For a recent review of its uses, see
 - J. Ericksen, Math. Mech. Solids 13, 199 (2008)
- For a validation of the C-B rule at zero temperature, see
 - W. E and P. Ming, Arch. Rational Mech. Anal. 183, 241 (2007)

From the Introduction: "We prove, under certain sharp stability conditions, that the correct nonlinear elasticity model is given by the classical Cauchy-Born rule in the sense that the elastically deformed states of the atomistic model are closely approximated by solutions of the continuum model with stored energy functionals obtained from the Cauchy-Born rule."

Zero-Temperature MD

 no-fluctuation equations (all the same, no matter whether starting from exact, uncompromising or trademark A–P&R motion equations):

(*)
$$\sum_{J>I} \frac{1}{r_{IJ}} \Phi'(r_{IJ})(s_I - s_J) = 0$$
 $(I = 1, ..., N),$

(force balance for I-th molecule);

$$(**) \quad \sum_{I} \sum_{J>I} \frac{1}{r_{IJ}} \Phi'(r_{IJ})(s_I - s_J) \otimes (s_I - s_J) \coloneqq \widetilde{\boldsymbol{S}}^{int} = \widetilde{\boldsymbol{S}} := \boldsymbol{F}^{-1} \boldsymbol{S}$$

(micro/macro stress balance).

Induced Micro/Macro Consistency Condition

• Given the constitutive equation for an elastic material:

$$\widetilde{\boldsymbol{S}} = \partial_C \hat{\sigma}(\boldsymbol{C}), \quad \boldsymbol{C} = \boldsymbol{F}^T \boldsymbol{F},$$

the *'microscopic' molecule potential* Φ and the *'macroscopic' stored-energy mapping* $\hat{\sigma}$ should satisfy:

$$\sum_{I}\sum_{J>I}\frac{1}{r_{IJ}}\Phi'(r_{IJ})(s_{I}-s_{J})\otimes(s_{I}-s_{J})=\partial_{C}\hat{\sigma}(\boldsymbol{F}^{T}\boldsymbol{F}),\quad\forall \boldsymbol{F}.$$

- One may ask, e.g.,
 - what $\hat{\sigma}$'s are consistent with one or another Φ ?
 - what is a candidate *elasticity tensor*?

What the relationships between, say,

• Ciarlet-Geymonat's elastic energy density

 $\hat{\boldsymbol{\sigma}}_{CG}(\boldsymbol{F}) = \alpha_1 |\boldsymbol{F}|^2 + \alpha_2 |\boldsymbol{F}^*|^2 + \varphi(\det \boldsymbol{F}), \ \varphi(\delta) = \alpha_3 \delta^2 - \alpha_4 \log \delta \ (\alpha_i > 0)$

and

• Lennard-Jones potential

$$\Phi^{LJ}(r) = V_0\left(\left(\frac{r_0}{r}\right)^{12} - s_0\left(\frac{r_0}{r}\right)^6\right)$$

Morse potential

$$\Phi^{M}(r) = f_{C}(r) \left(\exp\left(-2\frac{r}{r_{0}}\right) - \exp\left(-\frac{r}{r_{0}}\right) \right)$$

????

What if we set

• the macroscopic elasticity tensor

$$\mathbb{A} := \partial_F \big(F \partial_C \Psi(C) \big)$$

equal to the corresponding microscopic construct:

$$\partial_F (F \partial_C \Psi(C)) = (\mathbb{A} =) \sum_{I=1}^N \sum_{J>I}^N (s_I - s_J) \otimes (s_I - s_J) \otimes \partial_F \left(\frac{1}{r_{IJ}} \frac{\partial \Phi}{\partial r_{IJ}}\right)$$

????

Basta, per oggi.

E grazie per la vostra attenzione!

Appendix. What metadynamics makes sense to explore energy landscapes

A Typical Energy Landscape



- colors suggest level curves of stored-energy map $F \mapsto \hat{\sigma}(F)$
- a path through a saddle point connecting two local minima ≡ a dynamics allowing to clear the energy barrier between two phases

A Metadynamics Trick to Escape Energy Minima



Fig. 1. Time evolution of the sum of a one-dimensional model potential $V(\sigma)$ and the accumulating Gaussian terms of Eq. **2**. The dynamic evolution (thin lines) is labeled by the number of dynamical iterations (Eq. **1**). The starting potential (thick line) has three minima and the dynamics is initiated in the second minimum.

• from A. Laio & M. Parrinello, Escaping free-energy minima, PNAS 99 (2002)

Recall assumption advanced to reduce the uncompromising-totrademark gap in A–P&R Lagrangians:

the simulation cell's fluctuation motion be irrotational.

Accordingly,

irrotationality of cell fluctuations

should be incorporated in whatever *metadynamics* one runs. Interestingly, in the literature

this measure is always taken,

often approximately and/or in disguise!