Molecular Simulation, a new computational frontier of Theoretical Physics: a historical reconstruction.

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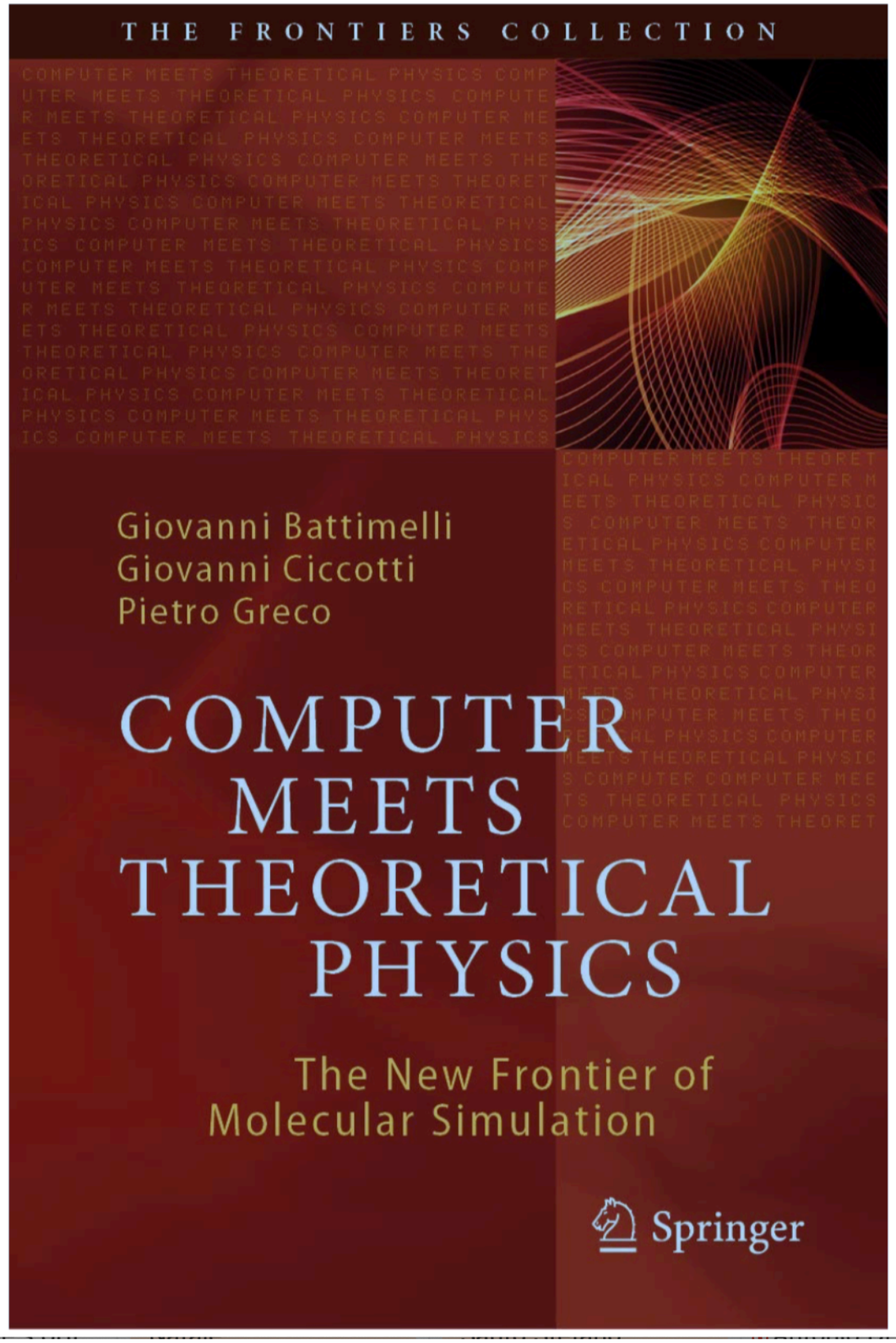
The antecedent

A book (2020) on the history and epistemology of Molecular Simulation (= Molecular Dynamics [+ Monte Carlo] in Condensed Matter, i.e. Computational Statistical Mechanics - no high energy)

THE BOOK, ITS CONTENTS, ITS MEANING [1]



THE BOOK, ITS CONTENTS, ITS MEANING [2]

Contents

The Summary: what I am trying to convey

1. Molecular Simulation ([MS] what is it ?) as a part of Theoretical Physics (= noetic reconstruction of the material world) and the computer as realization of its dream.

2. Evolution and meaning of MS

3. Why MS, almost 70 years old has not found yet its historian, epistemologists ?

Molecular Dynamics [1]

Newton's Dynamics:

$$m_N \ddot{R} = -\nabla E_0(R)$$

- ✦ a classical system of point particles (the nuclei) interacting via an effective interaction potential $E_0(R)$,
- ✦ $E_0(R)$ can be obtained ab initio (AIMD) or by some suitable fitting procedure $\longrightarrow$ phenomenological model, e.g. with a Pairwise Additive Potential [PAP], $V(R) = \sum_{i<j} v(R_{ij})$
- ✦ if PAP, the equations of motion are numerically integrable for a number of particles finite but large enough to study, by statistical approach, the thermal properties of matter

MOLECULAR DYNAMICS [2]

Equilibrium (classical) Statistical Mechanics (1)

- a closed system evolving in time under time-independent forces will reach a STATIONARY state

- the microscopic properties are ‘irrelevant’ while the statistical (or macroscopic) are stable and interesting (THERMODYNAMICS).

They can be computed by time or ensemble averages.

MOLECULAR DYNAMICS [3]

Equilibrium (classical) Statistical Mechanics (2)

Boltzmann

Observable

$$O = \overline{\hat{O}(R,P)} \equiv \lim_{\tau\to\infty} \frac{1}{\tau}\int_0^\tau dt\, \hat{O}(R(t),P(t))$$

$$= \frac{1}{\mathcal{N}}\sum_{i=1}^{\mathcal{N}} \hat{O}\left(R(ih),P(ih)\right) = \sum_{l\in \text{visited states}} \left[\frac{n_l}{\mathcal{N}}\right]\hat{O}_l$$

$$\simeq \int dRdP\, \rho(R,P)\hat{O}(R,P) = \langle O\rangle$$

ν_l probability of state l

Ensemble or probability density

Gibbs

- properties coming from an observable ➔ **mechanical** (e.g., pressure)
- properties coming from ν_l or ρ, i.e. probability ➔ **thermal** (e.g., free energy)

MOLECULAR DYNAMICS [4]

Computationally:

$N \sim 32 \div 10^6\,(10^9), \quad n = \dfrac{N}{V}$

$\text{Boundary Conditions} : \underline{\text{Periodic (PBC)}}$ for thermodynamic limit: min(S/V) effect

Initial Conditions: positions, regular lattice; velocities, Maxwellian

V_N , *simple:* pairwise additive $\left(\sum_{i<j} v_{ij} \, ; \mathcal{O}(N^2) \right)$; short range (MIC)

extensions: $\longrightarrow$ long range (Coulomb) by Ewald sums

$\longrightarrow$ *n*-body potentials $\mathcal{O}(N^m)$ but glue potential $V_N(\alpha)$ with $\alpha = \sum_{i<j} \varphi_{ij}$

$\longrightarrow$ stiff intramolecular potentials:

$\begin{cases} \text{Constraints:} \quad \sigma(R) = 0\,; \quad m\ddot{R} = F - \lambda \nabla \sigma \ : \text{SHAKE} \\ \text{Multiple Time-Step (Martyna, Tuckerman, Berne) : RESPA} \end{cases}$

Integration Algorithms: robust, time reversible, symplectic, e.g. velocity Verlet

Various ensembles (thermostats, barostats …):

extended variables simulations (Andersen, Nosé, Hoover,…

WHY IS MOLECULAR SIMULATION THEORETICAL PHYSICS? [1]

The fundamental law

In principle, the behavior of a piece of matter in ordinary conditions comes out of *t*-dependent Schroedinger Equation and Quantum Statistical Mechanics with

[Relativistic Quantum Field Theory not needed for that!]

$$\mathcal{H}(r,R;p,P) = K_N(P) + K_e(p) + \underbrace{V(r,R)}_{H_e(r,p|R)}$$

Coulomb

$$i\hbar\frac{\partial\widetilde{\Psi}(r,R,t)}{\partial t} = \mathcal{H}\widetilde{\Psi}(r,R,t) \;\Leftrightarrow\; \mathcal{H}\Psi_n = E_n\Psi_n$$

Not Soluble by Brute Force

WHY IS MOLECULAR SIMULATION THEORETICAL PHYSICS? [2]

Born-Oppenheimer approximation

since $m_N \gg m_e$

$$H_e(r, p\,|R)\Phi_s(r\,|R) = E_s(R)\Phi_s(r\,|R)$$

and $|\nabla_R \Phi_s| \ll |\nabla_r \Phi_s|$

$$\Psi(r, R; t) = \sum_s \chi_s(R; t)\Phi_s(r|R) \simeq \chi_0(R; t)\Phi_0(r|R)$$

i.e. the (often valid) **adiabatic approximation**

where $\chi_0(R; t)$ is given by

WHY IS MOLECULAR SIMULATION THEORETICAL PHYSICS? [3]

$$\imath\hbar\frac{\partial}{\partial t}\chi_0(R;t) = \mathcal{H}_N(R,P)\chi_0(R;t)$$
$$\equiv \left[K_N(P) + E_0(R)\right]\chi_0(R;t)$$

the strict adiabatic approximation
(no electronic jumps allowed)

the dynamics of the nuclei, apparently independent from the electrons, is driven by $E_0(R)$ as interaction potential (an adjustable mean field, no more Coulomb!)

Why is Molecular Simulation Theoretical Physics? [4]

when $\begin{cases} \text{nuclei are heavy enough} \\ \text{temperature is high enough so that} \end{cases}$

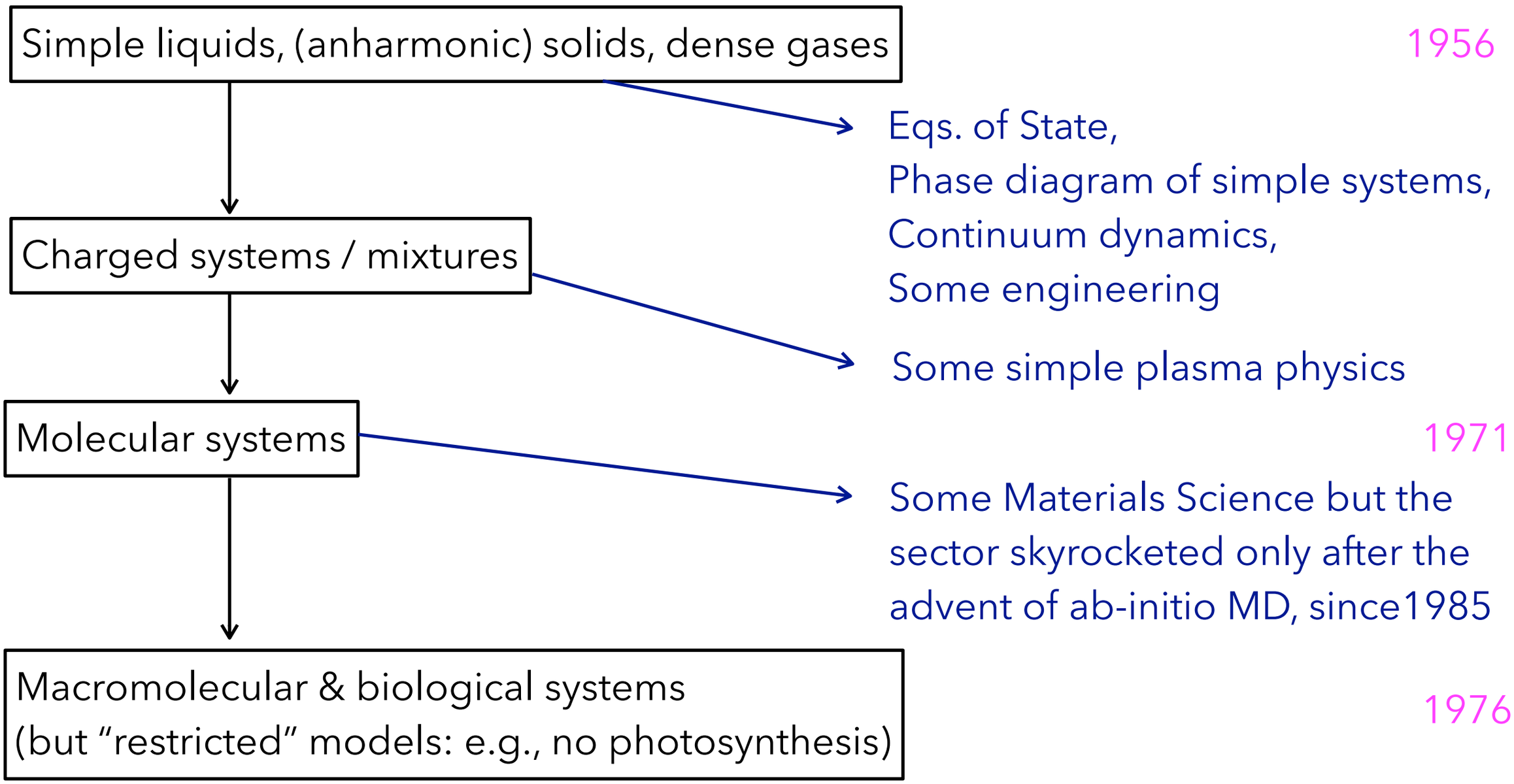
$$\Lambda = \frac{h}{\sqrt{2\pi m_N k_B T}} \ll \text{internuclear distance } r$$

Dynamics, no more quantum, is, as seen before, Newton:

$$m_N \ddot{R} = -\nabla E_0(R)$$

MACHINE OF DREAMS: THE BEGINNING

» How it all started



Evolution of Molecular Simulation: The Extensions [1]

Domesticating some more concepts and tools from Theoretical Physics

» Extend time and/or length scales → Theoretical treatment of metastability; Mathematical theory of large deviations; Rigorous coarse-graining (e.g. from Mori-Zwanzig)

Getting the Quantum World (0) (Ground state; Finite-Temperature equilibrium Statistical Mechanics) → Hartree-Fock, DFT, Ab-initio MD

→ Path Integrals (and, for bosons, symmetrisation) and polymer isomorphism

NB the essential tools remain **Metropolis MC** or **MD**
ALTHOUGH playing new, more abstract, roles

Evolution of Molecular Simulation: The Extensions [2]

Concepts TO BE domesticated

Getting the Quantum World (1): Quantum dynamics →

- Semiclassical Limit (some success)
- Quantum classical approaches for non-adiabatics dynamics (far from really successful)
- Full Quantum Dynamics (in its infancy due to the improper mathematical formulation of Feynman path-integrals)

The still unthinkable →

Solve the relativistic quantum statistical dynamics of a plasma

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Evolution of Molecular Simulation: Where is it Aiming?

Understand/Design/Control

- Real Materials
- Soft Matter
- Pharmaceuticals/drugs
- Biological processes
  (the not so hidden dream: Theoretical Physics firing Medical Doctors!)
- Plasma/thermonuclear fusion

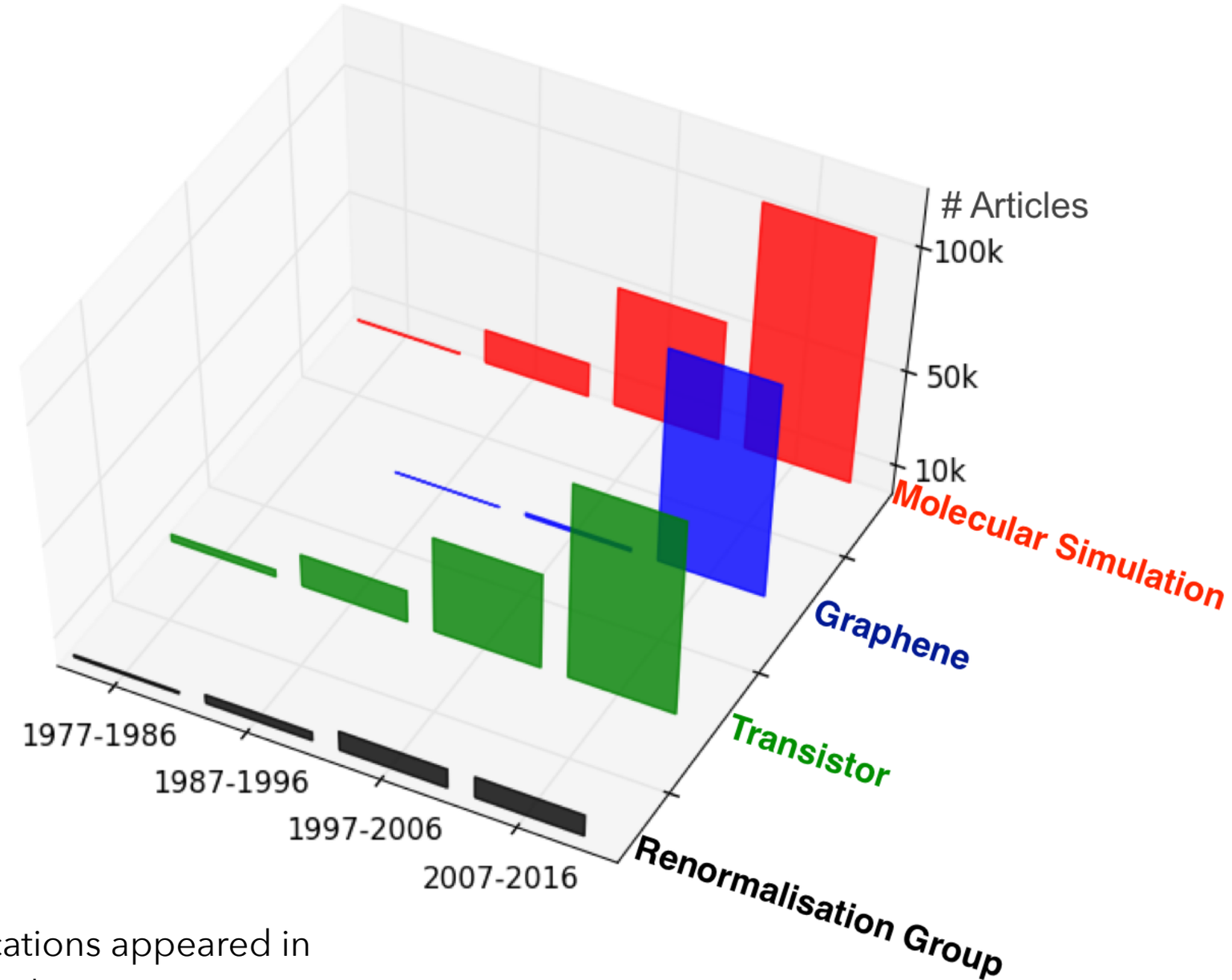
NB to maintain the pace of the progress it seems that Biologists, Chemists and Physicists no longer suffice. Applied Mathematicians have entered the field to help formulating, with mathematical rigor, concepts and algorithms coming from probability/stochastic processes, numerical analysis, etc

Development and Meaning: An Interesting Fact

1.Molecular Simulation in the new era

Just as an example:

	RG	Transistor	Graphene	Mol Simul
1977-1986	1051	3050	-	456
1987-1996	3916	13931	136	14049
1997-2006	8632	41150	1416	49762
2007-2016	9565	83559	89759	101622



The growth of the number of publications appeared in the last four decades in the subjects shown

Preliminary Conclusions

1. **Why** so much **history and epistemology** of **relativity** and **quantum mechanics** and so little about **theoretical computer simulation**?
2. **Why no history and no epistemology of MS?**

Intrinsic "reasons":

adiabatic nature of the paradigmatic shift

Sociological "reasons":

professional profiles of contributors
(Chemists are not "intellectuals", Physicists are …)

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CONCLUSIONS

1. **There has been an important PARADIGM SHIFT** (let me avoid the doubtful concept of scientific revolution but …) **in Theoretical Physics ~70 years ago but has passed unnoticed**

2. **I discussed MS but the same has happened in Astrophysics and Quantum Lattice Chromodynamics**

3. **It is time to call the attention of good historians to this important essentially unexplored field before all its founding fathers disappear**