Time and Length Scales in Condensed Matter

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The dance of the atoms
The scientific number system

- Yotta $1'000'000'000'000'000'000'000'000$ $10^{24}$
- Zetta $1'000'000'000'000'000'000'000'000$ $10^{21}$
- Exa $1'000'000'000'000'000'000'000$ $10^{18}$
- Peta $1'000'000'000'000'000$ $10^{15}$
- Tera $1'000'000'000'000$ $10^{12}$
- Giga $1'000'000'000$ $10^9$
- Mega $1'000'000$ $10^6$
- Kilo $1'000$ $10^3$
- One $1$ $10^0$
- Milli $0.001$ $10^{-3}$
- Micro $0.000'001$ $10^{-6}$
- Nano $0.000'000'001$ $10^{-9}$
- Pico $0.000'000'000'001$ $10^{-12}$
- Femto $0.000'000'000'000'001$ $10^{-15}$
- Atto $0.000'000'000'000'000'001$ $10^{-18}$
- Zepto $0.000'000'000'000'000'000'001$ $10^{-21}$
- Yocto $0.000'000'000'000'000'000'000'001$ $10^{-24}$

Powers of 10

- $A = 10^a$ ; $B = 10^b$
- $A \times B = 10^{(a+b)}$
- $A/B = 10^{(a-b)}$
- $\sqrt{A} = 10^{(a/2)}$
How big is an atom?

Iron bar:
L = 30 cm, B = 2 cm \(\Rightarrow\) V = 10^{-4} \text{ m}^3
M = 1 kg

Iron atom:
26 protons + 26 electrons + 30 neutrons
\(\Rightarrow\) m = 10^{-25} \text{ kg}

Number of atoms in the bar:
N = M/m = 10^{25}

Volume per atom:
v = V/N = 10^{-29} \text{ m}^3 = d \times d \times d

Atomic size d:
d = v^{1/3} = 2 \times 10^{-10} \text{ m}

d = 0.2 \text{ nm} \text{ (nanometer)}

How can we see atoms?

Long waves not influenced by thin rod.
\(\Rightarrow\) \(\lambda \leq d\)

\(\lambda = 0.2 \text{ nm}\)

\(\Rightarrow\) X-rays
Aside: "seeing" atoms with diffraction

Bragg's Law (1912):
\[ \lambda = 2d \sin \theta \]

Note: \[ \lambda < 2d \]
How fast do atoms move?

Oscillation period of the bar:
\[ T_{\text{bar}} = 0.12 \text{ ms} \] (proportional to L)

Oscillation period of a molecule:
\[ T_{\text{molecule}} = T_{\text{bar}} \times \frac{d}{L} = 8 \times 10^{-14} \text{ s} \]
\[ T_{\text{molecule}} = 80 \text{ fs} \] (femtoseconds)

L = 0.3 m \quad d = 0.2 \text{ nm}

We want to freeze the motion.

X-ray pulse length < 20 fs

\[ \frac{1}{\tau_{\text{bar}}} = \frac{v_{\text{sound}}}{2L} = \frac{5000 \text{ m/s}}{2 \times 0.3 \text{ m}} \]
Fermi energy and Schrödinger pressure

Free-electron gas (Sommerfeld 1927)

Density of states (in 3d):

\[ D(E) = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \sqrt{E} \]

Fermi energy:

\[ E_F = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{V}\right)^{2/3} \]

Total energy:

\[ E_{tot} = \int_0^{E_F} E \, D(E) \, dE = \frac{3}{5} N E_F \]

Schrödinger pressure:

\[ P_S = -\frac{dE_{tot}}{dV} = \frac{2}{5} \frac{N}{V} E_F \]

Copper:

\[ \frac{N}{V} = 8.5 \times 10^{28} \text{ m}^{-3} \]
\[ E_F = 7.0 \text{ eV} \]
\[ P_S = 38 \text{ GPa} \]
Electron and atom velocities

\[ V_{\text{electron}} \approx V_{\text{Fermi}} = \sqrt{\frac{2E_F}{m}} \]
\[ V_{\text{atom}} \approx V_{\text{sound}} = \sqrt{\frac{K}{\rho_M}} \approx \sqrt{\frac{P_s}{\rho_M}} \]

Copper:
\[ \frac{N}{V} = 8.5 \times 10^{28} \text{ m}^{-3} \]
\[ E_F = 7.0 \text{ eV} \]
\[ \Rightarrow V_{\text{electron}} = 1.6 \times 10^6 \text{ m/s} \]
\[ P_s = 38 \text{ GPa} \]
\[ \rho_M = 9.0 \times 10^3 \text{ kg m}^{-3} \]
\[ \Rightarrow V_{\text{atom}} \approx 2100 \text{ m/s} \left( \exp: V_{\text{sound}} = 4600 \text{ m/s} \approx 5 \text{ nm/ps} \right) \]

Note: Effective electron mass determined by band structure:
\[ m^* = \hbar^2 \left( \frac{\partial^2 E_k}{\partial k^2} \right)^{-1} \]

InSb:
\[ m^*/m = 0.014 \]

URu$_2$Si$_2$:
\[ m^*/m \approx 100 \]

Born-Oppenheimer approximation
Talk overview

1. Introduction

2. Background concepts

3. Examples of time and length scales

4. Fluctuations

5. Our most critical time scale

6. A biology movie
2. Some background concepts ...

Pump-probe experiment:
How fast do we leave and regain equilibrium?

Out-of-equilibrium dynamics of classical and quantum complex systems

Dynamique hors équilibre de systèmes complexes classiques et quantiques

Leticia F. Cugliandolo

LF Cugliandolo, CR Physique (2013)
Equilibrium dynamics

- **Conservative dynamical system**
  - classical variables (e.g., \( \dot{r}, \dot{p} \)) follow deterministic trajectories in phase space.

- **Grand-canonical ensemble**
  - subsystem interacts with fluctuating bath (Langevin dynamics)
  - exchange of energy and particles

- **Ergodic hypothesis**
  - all accessible states populated with equal probability

- **Deterministic chaos**
  - system with non-linear interactions
  - sustained erratic behavior
  - sensitive to initial conditions

- **Coherent collective behavior**
  - resulting from strong interactions
  - spatio-temporal patterns

- **Bifurcation point**
  - qualitative change in trajectories (e.g., phase transitions: order parameter \( M \) zero \( \rightarrow \) non-zero)
  - first-order (e.g., boiling H\(_2\)O)
    - \( M(T) \) jumps discontinuously
    - phase coexistence
    - \( \frac{\partial G}{\partial T} \rightarrow \infty \)
  - second-order (e.g., Curie temperature)
    - \( M(T) \) continuous
    - \( \frac{\partial^2 G}{\partial T^2} \rightarrow \infty \)
    - spontaneous symmetry breaking
Disorder

- **Disordered impurities / defects**
  - *quenched*: slower relaxation for impurities than host
  - *annealed*: similar relaxation times for impurities and host
  - *weak quenched disorder*
    - phases unchanged
    - changed dynamics near phase transition (critical exponents)
    - some discontinuities smoothed out

- **Strong disorder** (e.g., spin-glasses)
  - competing interactions cause *frustration*

- **Structural glasses**
  - e.g., granular media (jamming), colloidal suspensions, quickly-cooled silica or polymer melts, type-II SC vortices
  - more later ...
Non-equilibrium dynamics

- **Close to equilibrium**
  - **Onsager theory**: linear relation between extensive currents (energy, mass) and intensive gradients (temperature, pressure)

- **Far from equilibrium**
  - **Brownian motion**: equilibrated velocity, but not position
  - **Interface dynamics**: (crack propagation, fluid invasion of porous media, aggregation, crystal growth)
    - initially thin interface (thermal effects dominate) roughens to a thick interface (structural disorder dominates)
    - ageing, memory, avalanches, stochastic creep
  - near phase transition (**critical dynamics**)
    - correlation length diverges (fractal clusters)
    - relaxation time diverges (critical slowing down)

- **Across a phase transition**
  - **first-order**
    - nucleation of **bubbles** of stable phase, which grow at thermally-activated rate
  - **second-order** (symmetry breaking)
    - **domain** patchwork of different symmetries
    - evolution of **self-similar** structures
Entropic barriers

- **Mesoscale Non-equilibrium Thermodynamics (MNET)**
  - extends non-equilibrium thermodynamics (Onsager) to molecular level
  - inherently non-linear interactions
  - small fluctuations play a big role
  - analyze:
    - nucleation and growth
    - active biological transport
    - ...
  - treat *entropic barriers*

Critical dynamics

Correlation function:

\[ G(\vec{\rho}, \tau) = \langle n(\vec{r} + \vec{\rho}, t + \tau) n(\vec{r}, t) \rangle_{\vec{r}, t} \]

Correlation length \((l_c)\) and time \((\tau_c)\):

\( l_c \) and \( \tau_c \) diverge at \( T = T_c \) according to

\[ \frac{1}{(T - T_c)^{\gamma}} \]

\( \gamma \) = critical exponent

Scattering function (directly measurable):

\[ S(\hat{k}, \omega) = \int d\hat{k} \int d\omega \ G(\vec{\rho}, \tau) e^{i(\hat{k} \cdot \hat{\rho} - \omega \tau)} \]
**Diffusion**

Fick's law of diffusion:  
\[ J_x = -D \frac{dn}{dx} \]

\( D \) [m\(^2\)/s] = diffusion constant

Interact with a fluctuating bath (Langevin equation)  
\[ \rightarrow \] random walk (Brownian motion)

\[ \int \mathcal{W}(x, t) \propto e^{-x^2/2\sigma(t)^2} \]
\[ \sigma(t) = \sqrt{Dt} \]
\[ \langle t \rangle = \text{diffusion length} \]

Scattering function:  
\[ S(k, \omega) \propto \frac{1}{1 + \omega^2 \tau_c^2} \]
\[ \tau_c = \frac{1}{Dk^2} \]

**Scattering function:**

\( D \)-values (RT):
- air: 10\(^{-5}\) m\(^2\)/s
- water: 10\(^{-9}\)
- lipids: 10\(^{-11}\)
- proteins: 10\(^{-13}\)
- H in Fe: 10\(^{-13}\)
- Al in Cu: 10\(^{-26}\)

**Stokes-Einstein:**
\[ D = \frac{k_B T}{6\pi \eta r} \]

Na, Cs diffusion in clay:  
\[ D \approx 10^{-13} \text{ m}^2/\text{s} \]

S Churakov, Sci Env Tech (2013)
The mysterious glass transition

Cool a glassy liquid $\Rightarrow$ viscosity increases with Arrhenius law:

$T < T_A$: $\Delta E$ grows with decreasing $T$
implies increasing large cooperative motions (which motions?)

$T = T_0$: $\Delta E$ becomes infinite
"broken ergodicity"
glassy configuration stuck forever near one state
specific heat measurements $\Rightarrow$ entropy = 0 at or near $T_0$
(significance?)

$\Rightarrow$ not simply a gradual slowing down as $T \rightarrow T_0$

Questions:

- phase transition at $T_0$?
- long- or short-range (jamming) interactions important?
- which configurations are accessible and what are transition rates?
(hard to study because of long time scale)

Facit: neither close-to nor far-from equilibrium
requires new physics
perhaps related to biology (always out of equilibrium)

\[
S = \frac{0}{\Delta E} \sim \frac{1}{T - T_0} \quad \eta \propto e^{\Delta E/k_B T}
\]

Langevin dynamics and the FDT

A particle of mass $M$ moves with velocity $v(t)$, sees viscous damping $\gamma$ and feels a randomly-fluctuating force $A(t)$:

$$\dot{v}(t) + \gamma v(t) = A(t)$$  \textit{Langevin equation of motion}

Solution for $t >> 1/\gamma$:

$$v(t) = \int_0^t e^{\gamma(t'-t)} A(t') dt'$$

Assume: $A(t)$ has zero mean ($\langle A(t) \rangle = 0$) and $t$-indep variance ($\langle A(t) A(t') \rangle = A^2 \delta(t-t')$). The steady-state variance of the velocity is then:

$$\langle v^2(t) \rangle = e^{2\gamma t} \int_0^t dt' \int_0^{t'} dt'' e^{\gamma(t'-t'') \langle A(t') A(t'') \rangle}$$

$$= \frac{A^2}{2\gamma} (1 - e^{2\gamma t}) \rightarrow \frac{A^2}{2\gamma}$$

From equipartition: $\frac{1}{2} M \langle v^2 \rangle = \frac{k_B T}{2}$, which implies $\gamma = \frac{M}{2k_B T} A^2$.

This fundamental relation between viscous and random forces is a special case of the Fluctuation Dissipation Theorem.
3. Examples of time and length scales
Water: structure and fluctuations

Nano-structure of water determined by hierarchical hydrogen-bonded clusters

Critical points:
- gas-liquid: 374° C, 218 bar
- low-ρ (low-T) – high-ρ (high-T) ice:

Fluctuations:
- at a wide range of frequencies (~glass)
- at low T: slower, but larger amplitude

Interaction with proteins:
- 7 Å thick hydration shell
- residence time of H₂O molecule: 1-40 ps

"fractal ice"

Zakharov, Biophys (2012)

Scattering studies of supercooled H₂O at LCLS

Sellberg, Nature (2014)
Water: time scales after irradiation

Ionizing Radiation ➔ Ground state

~0 fs Excitation ➔ Preexisting trap?

~? fs Proton Transfer ➔ electron attachment

10-1000 fs Hydration ➔ Solvation

<300 fs ➔ ~1 ps

dissociation ➔ recombination ➔ deexcitation

O H OH H₂

Solvated Electron

Chemistry: time scales

- Dissociation and geminate recombination
- Solvation dynamics
- Non-geminate recombination
- Diffusional rotation

- C=C
  - Internal conversion
  - Vibrational cooling
  - Intersystem crossing

- Vibrational cooling
  - S = 1
  - S = 0

- Internal conversion
  - S = 0
  - S = 0

- Time [s]
  - $10^{-15}$
  - $10^{-12}$
  - $10^{-9}$
  - $10^{-6}$
Iron tris-bipyridine: spin cross-over

$[\text{Fe}^{++}(\text{bpy})_3]^{2+}$

Heterogeneous catalysis: processes
Correlated electrons: degrees of freedom

Metal-to-Insulator Transition

High Temperature Superconductivity

Colossal Magneto-Resistance

Chimera
Correlated electrons: fluctuations

Facit: correlated-electron materials have "electronic liquid-crystal" properties.
Correlated electrons: time scales

1T-TaS$_2$

Ultrafast metal-insulator transition in 1T-TaS$_2$: Peierls or Mott-Hubbard?

Different time-scales

MIT time scale from pump-probe PES: < 100 fs ➔ Mott-Hubbard

L Perfetti, NJP (2008)
Magnetism: time and length scales

- superparamagnetism
- single molecule magnet
- domain wall
- spin diffusion
- exchange interaction between spins
- spin-orbit
- optomagnetism
- spin-transfer torque
- magnetic writing
- macroscopic wall motion
- spin-waves
- correlation
- Fe 3d

\[ \Delta E \Delta t = \frac{\hbar}{2} = 0.33 \text{ eV fs} \]
Ultrafast demagnetization

1996: Beaurepaire's discovery (using Magneto-Optic Kerr Effect MOKE)

An intense laser pulse demagnetizes Ni within 200 fs.

Interpretation: "3-temperature model" (ignores angular momentum)

Unresolved question: where does the angular momentum go?
Magnetic vortex switching

R Hertel, Jülich, (2008)
Materials modeling: time and length scales

BD Wirth, J Nuc Mat (2004)
Radiation defect cascade

nanocrystalline Ni
5 keV knock-on event
SIA: self-interstitial atom
RCS: replacement collision sequence

Biology: time and length scales

- **Glucose**
- C-C bond
- Hemoglobin
- Ribosome
- Virus
- Mitochondria
- Bacteria
- Erythrocyte

Time scales:
- $10^{-15}$
- $10^{-12}$
- $10^{-9}$
- $10^{-6}$
- $10^{-3}$

Length scales:
- $10^{-6}$

Processes:
- Bond vibration
- Trans-membrane electron transfer
- Photodissoc. of CO from heme
- Methyl rotation
- Side-chain rotamers
- Trans-cis photoisomerization
- Loop motion
- Fast de-caging
- Large domain motions

[http://w3.dbb.su.se/~barth]
Protein folding: energy landscapes

Levinthal golf course

Lehninger, Principles of Biochemistry (2008)

KA Dill, Nat Str Bio (1997)


Lehninger, Principles of Biochemistry (2008)
"Protein quake": time scales

Cytochrome: heme-ligand bond breaking

Myoglobin: photo-detachment of CO


(time-resolved Laue diffraction)

Bacteriorhodopsin: time scales

retinal: I → J
(500 fs)

4. Fluctuations in time and space

- power-law distributions
- 1/f noise
- self-similarity
  - quasicrystals and Penrose tiling
  - fractals
  - aggregation
- self-organized criticality
Power-law fluctuations

Sandpile avalanches

Creep rate

Spin glass: power-law relaxation

n-spin echo experiments near $T_{\text{glass}}$ in Au$_{0.86}$Fe$_{0.14}$

Cadek, Mat Sci Eng (2002)


Pappas, PRB (2003)
1/f noise in art and music

Jackson Pollack paintings
Eyes in the Heat (1946)

Musical pitch variations
Voss+Clarke, Nature (1975)

What is special about 1/f?
- balance surprise and monotony
Which is more pleasing?

1/f^0
"white"

1/f^2
"Brown"

1/f^1
"self-similar"

M Gardner + RF Voss, Sci Am (1978)
1/f in condensed matter

Barkhausen magnetization jumps

Resistor voltage

Simulated protein energy fluctuations

Pellegrini, PRB (1983)

Durin, J Mag Mag Mat (1996)

Requirement: escape from a distribution of traps

Bizzarri, Phys Lett (1997)
Self-similarity

1/f noise is self-similar

⇒ familiarity in art and music

"fractal"
Crystals and quasicrystals

The 14 Bravais lattices

Only 2, 3, 4 and 6-fold axes possible

Ho-Mg-Zn

Al-Mn

Schechtman, PRL (1984)
Penrose tiling

2 tiles with (local?) matching rules \(\rightarrow\) aperiodic tiling ... but with diffracting planes ...

\[
\tau = \frac{1 + \sqrt{5}}{2}
\]

... self-similarity (inflation) ...  
... and "Penrose recurrence".
Fractals

Mandelbrot, Freeman (1977)

How long is the coast of England?

\[ L(s) \propto s^{1-D} \]

Fractal dimension \( D = 1.25 \)

Koch island \( D = 1.25 \)

Menger sponge \( D = 2.73 \)
Diffusion-limited aggregation

Soot particles in flight
X-ray scattering (at LCLS XFEL)

\[ I(q) \propto q^{-D} \]

\[ D = 2.3 \pm 0.3 \]

Self-organized criticality

Self-Organized Criticality: An Explanation of 1/f Noise

Per Bak, Chao Tang, and Kurt Wiesenfeld
Physics Department, Brookhaven National Laboratory, Upton, New York 11973
(Received 13 March 1987)

We show that dynamical systems with spatial degrees of freedom naturally evolve into a self-organized critical point. Flicker noise, or 1/f noise, can be identified with the dynamics of the critical state. This picture also yields insight into the origin of fractal objects.

Frictional sliding-block "earthquake" model:

Continue to push:
- critical situation reached (SOC)
- power-law probability distribution of quakes
- 1/f noise spectrum
- fractal distribution of local strains
5. **Climate dilemma**: time scale = 36 years

If we continue status quo:

- **Global energy consumption**:
  - 2000: 13.5 TW
  - 2050: 27 TW
  - 2100: 40 TW

- **CO₂ emission**:
  - 2000: 6.6 Gtons/yr
  - 2050: 11 Gtons/yr
  - 2100: 700 ppm

- **Atmospheric CO₂**:
  - Limit for $\otimes T = +2^\circ$ (450 ppm)
Needed: 10 TW C-free energy by 2050

Options:

1) Nuclear fission
   - 1 GW plant/1.6 days for next 45 years
   - exhaust $^{235}$U in 10 yrs

2) CO$_2$ capture / storage
   - store 1 x Lake Superior / yr; leakage < 1%/yr

3) Solar
   - 10 TW at 10% \(\Rightarrow\) need 350 x 350 km$^2$
   a) PV
      - must reduce cost by factor 15
      - pumped storage for US:
        - 5000 Hoover Dams / day
   b) Solar thermal – worth considering
   c) Biomass
      - conversion efficiency <1%
      - use all arable land not used now for food
   d) Liquid solar fuels (e.g., methanol)
      - Understand photocatalysis
        at atomic time and length scales!

Lewis + Nocera, PNAS (2006)
Crookes' address

British Academy of Science, Fall 1898, Bristol, England:

- "All civilized nations stand in deadly peril".
- Lack of fixed nitrogen fertilizer to feed growing population.
- Not taken seriously then by majority of Englishmen.
- 30 years later, Haber-Bosch process discovered and industrially developed.
- Now feeds 1/3 of global population.

Th Hager, "The Alchemy of Air" (2008)
Photosynthesis

**Natural photosynthesis:**
- ca 1% efficient
- UV damage ➔ plants must replace all photosensitive molecules every 30 min!!

**Artificial photosynthesis:**
- needs sophisticated molecular engineering
- important step: electron (and hole) transfer

Benniston, Mat Today (2008)
Marcus theory: electron transfer

- RA Marcus, Nobel Prize (Chemistry, 1992)
- Quantify electron transfer from donor (D) acceptor (A) in a polar solvent.
- Define "nuclear coordinate" corresponding to solvent polarization.
- Assume parabolic potentials.
- Barrier height $b$ vs electron affinity difference $\Delta$.

\[ b = \frac{(\Delta + \Lambda)^2}{4\Delta} \]

Inverted regime at large $-\Delta$: essential to inhibit back-reactions in photosynthesis.

Marcus, J Chem Phys (1956)
Liquid solar fuels

Goal: $3H_2 + CO_2 \rightarrow CH_3OH + H_2O$

Requires:
- extracting $CO_2$ from atmosphere (absorb on KOH, <$100 / ton)
- electro-hydrolysis to split water (use photovoltaics)
- catalytic hydrogenation of $CO_2$ to produce methanol

Possible catalyst: $Mo_6S_8$ clusters

ClimeWorks, ETH/EMPA

The methanol economy

G Olah, J Org Chem (2009)
**Metal-organic frameworks (MOF)**

Advantages:
- Flexible chemistry
- Highly porous
- Combines heterogeneous and homogeneous catalysis

Disadvantage:
- Poor stability

BP's dream: heterostructure MOF
"REDOX junction"

YG Li, Chem Comm (2007)

MX Yang, Inorg Chem Comm (2011)
6. The life of the cell

time-lapse factor: \( \sim 10^6 \)

Harvard Biovisions (2009)
Thank you for your attention.