Molecular monolayers as interacting rolling balls: crystals, liquid and vapor

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[1] References: B. Kim and V. Putkaradze, *Ordered and Disordered Dynamics in Monolayers of Rolling Particles*, *Phys. Rev. Lett*, **105**, 244302 (2011); D. D. Holm, V. Putkaradze and C. Tronci *Kinetic theory of interacting rolling particles*, submitted (2011).

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Motivation: Dynamics of water monolayers

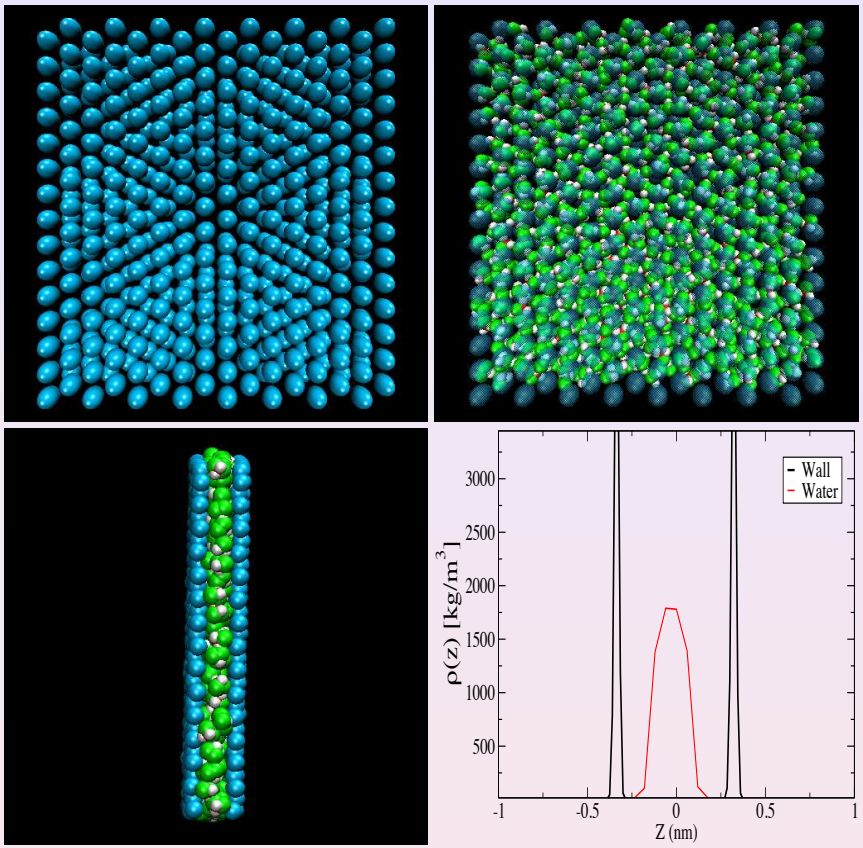


Figure: Water molecules in confined geometry: From P. Kumar, 2010

Motion of molecules is a complex combination of rotation and rolling due to interactions of molecules between themselves and with the substrate.

Introduction

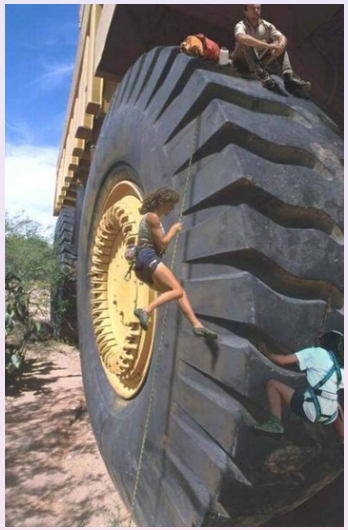
This work

1. Model the molecule/substrate interaction as perfect rolling.
2. Perfect rolling is achieved when the interaction between molecule and substrate is infinitely strong at contact point decaying rapidly away from the contact point.
3. Molecules interact between themselves through long distance interactions (*e.g.*, electrostatic and Lennard-Jones).
4. Thus, we consider the system of interacting asymmetric rolling balls (tippe tops).
5. See N. M. Bou-Rabee, J. E. Marsden, and L. A. Romero, SIAM Review 50, 325 (2008) for the theory of tippe top motion.

Theorem It is not embarrassing to play with tippe tops

Figure: W. Pauli and N. Bohr are playing with a tippe top.

Rolling motion of molecules has been demonstrated in nano-car (nano-truck) design



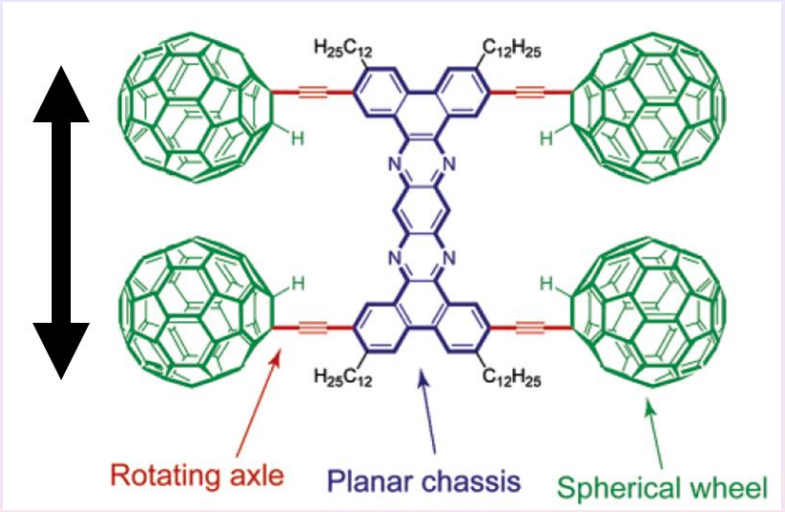
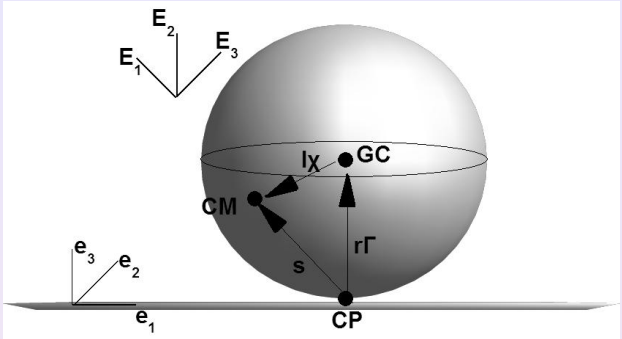


Figure: Big/Nanotruck (Shirai et al, 2006)

Applications: precise delivery of medicine and chemicals, and other fields

Background: rigid ball rolling on a horizontal plane



CM: the center of mass, GC: geometric center of the ball,
$I = \mathrm{diag}(I_1, I_2, I_3)$: moment of inertia,
Ω: angular velocity,
χ: displacement of CM from GC
All variables are in the body frame

Theorem (Chaplygin 1903)

The rolling motion of a ball on horizontal plane can be analytically solvable if $I_1 = I_2$ and $\chi = E_3$, i.e, the mass distribution being cylindrically symmetric.

Rolling as constrained non-holonomic motion

- **Constrained dynamics:**

$$\ddot{x} = f(x, \dot{x}, t)\,, \;\; h(x_i, \dot{x}_j, t) = 0\,.$$

  $h = 0$ is constraint condition imposed on the system.
- **Holonomic constraint:** $h = h(x_i)$. The constraint is imposed on the configurational variables not involving the time-derivatives.
- **Nonholonomic constraint:** $h = h(x_i, \dot{x}_i)$. The constraint involving velocities cannot be integrated into a holonomic constraint. Rolling motion is nonholonomic [2]
- **Rolling motions are in general represented by nonholonomically constrained dynamics.**

[2] See A. Bloch, *Nonholonomic mechanics and control* (2003)

Equation of motion for a rolling ball: Newton's law

- Force and Torque balance is spatial frame
- Rolling constraint
- Problem: Tensor of inertia changes with time

In body frame equations of motion are [3]

$$\left(\frac{d}{dt}+\Omega\times\right)(I\Omega+m\boldsymbol{s}\times(\Omega\times\boldsymbol{s}))=m\gamma\ell\Gamma\times\chi+m\dot{\boldsymbol{s}}\times(\Omega\times\boldsymbol{s})\,,$$

$$\frac{d\Gamma}{dt}=-\Omega\times\Gamma\,.$$

where $s=\ell\chi+r\Gamma$ – vector from CP to CM; Γ is a unit vector pointing up in spatial frame

Rolling condition in body frame: $\mathbf{V}:=\mathbf{v}_{body}=\boldsymbol{\Omega}\times\mathbf{s}$

Lagrange-D'Alembert principle : The constraint force does no work.

[3] D. D. Holm, Geometric Mechanics I

Conservation laws in rolling symmetric ball

- **Conservation laws:** For rolling unbalanced symmetric ball under gravity, $I_1 = I_2$ and $\chi = E_3$ there are following conservation laws
  1. **Energy:**

$$E =< I\Omega, \Omega > + m|\Omega \times \mathbf{s}|^2 + m\Gamma < \mathbf{s}, \Gamma >$$

  2. **Jellett integral:**

$$J =< I\Omega, s >= I_1\Omega_1 s_1 + I_1\Omega_2 s_2 + I_3\Omega_3 s_3 \,,$$

  3. **Chaplygin, or Routh integral:**

$$R = \sqrt{I_1 I_3 + m(I_1 s_1^2 + I_1 s_2^2 + I_3 s_3^2)}\,\Omega_3 \,.$$

- The conservation laws, J and R, allow the equations of motion to be completely integrable, but
- The physical interpretation of J and R by (non-trivial) symmetry arguments [4]

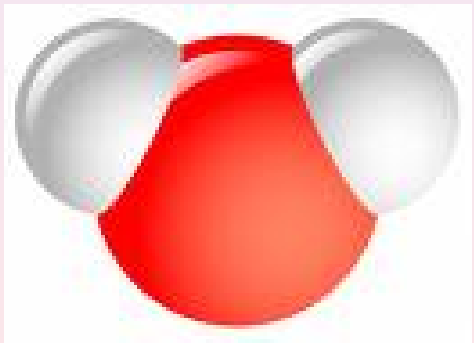
[4] B. Kim, Reg. Chaotic Dyn. **16** (2011)

An ensemble of interacting rolling balls with central (CM) interactions

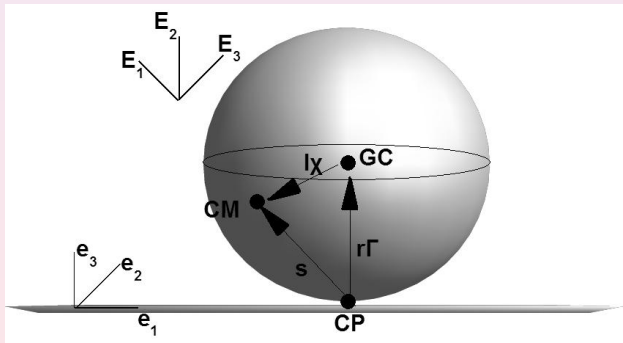
- Interactions are acting only on the center of mass (*e.g*, nucleii in atoms).
- **Conservation laws:** total energy and Jellett integrals J^i for each ball (only for cylindrically symmetric ball under central interactions).
- $J^i =< I^i \mathbf{\Omega}^i, \mathbf{s}^i >$ is conserved under any central force acting on the CM, but is not conserved for *e.g.*, dipole interactions.
- Chaplygin (Routh) integral is not conserved when interaction forces between particles are present.

An ensemble of interacting rolling balls: setup

- **Monolayer of water molecules** on a material surface, e.g. silicon surface.
- Dynamics : sliding translation + rolling
  $\Rightarrow$ extreme case : **purely rolling water molecules.**
  $\Rightarrow$ Rolling water molecules under interaction.
- Interaction : LJ potential (repulsion) + charge dipole potential.



$\Rightarrow$



An ensemble of interacting rolling balls: forces

- LJ potential :

$$U_{i,LJ} = \sum_j 4\epsilon \left[\frac{\sigma^{12}}{r_{ij}^{12}} - \frac{\sigma^6}{r_{ij}^6} \right] ,$$

$$F_{i,LJ} = -\frac{\partial U_{i,LJ}}{\partial r_i} , \tau_{i,LJ} = s_i \times F_{i,LJ}$$

- Dipole-induced electric field E and potential U:
  ϵ_0 : electrical permittivity, p_j: dipole moment of jth ball.

$$E_{i,dipole} = \sum_j \frac{3 < p_j, \hat{r}_{ji} > \hat{r}_{ji} - p_j}{4\pi\epsilon_0 |r_{ij}|^3} ,$$

$$U_{i,dipole} = < p_i, E_i > , \; F_{i,dipole} = -\frac{\partial U_{i,dipole}}{\partial r_i} ,$$

$$\tau_{i,dipole} = s_i \times F_{i,dipole} + p_i \times E_i .$$

An ensemble of interacting rolling balls: equations of motion

- **Equations of motion:**

$$\left(\frac{d}{dt} + \mathbf{\Omega}^i \times\right)\left(I^i \mathbf{\Omega}^i + m\mathbf{s}^i \times (\mathbf{\Omega}^i \times s^i)\right)$$
$$= m\mathbf{\Gamma}\ell^i \mathbf{\Gamma}^i \times \chi^i + m^i \dot{\mathbf{s}}^i \times (\mathbf{\Omega}^i \times \mathbf{s}^i) + \tau^i_{LJ} + \tau^i_{dipole}\,,$$
$$\frac{d\mathbf{\Gamma}^i}{dt} = -\mathbf{\Omega}^i \times \mathbf{\Gamma}^i\,.$$

where $i = 1, 2, 3, ...$

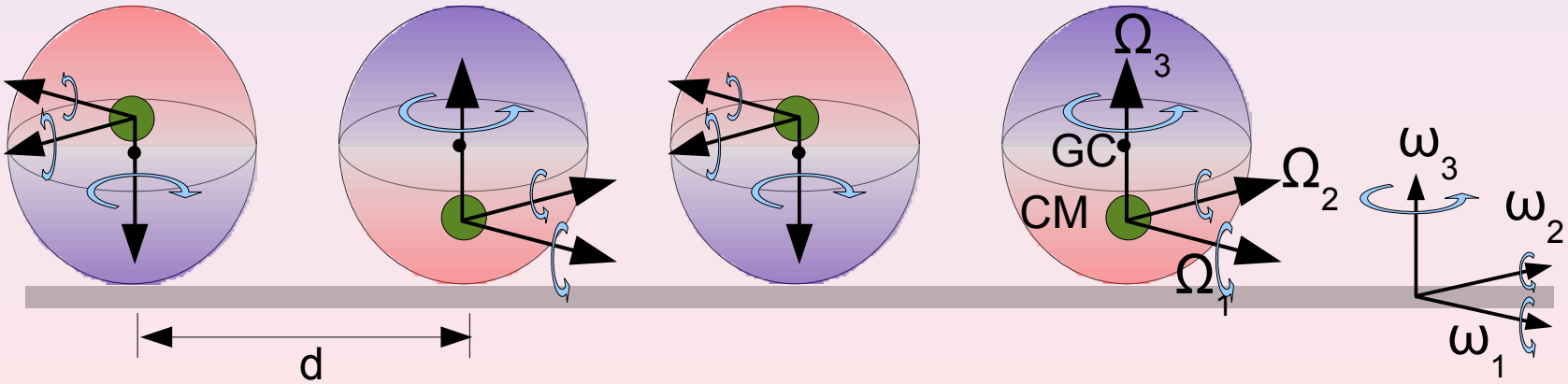
An ensemble of interacting rolling balls: parameters

Parameters for each ball correspond to a water molecule

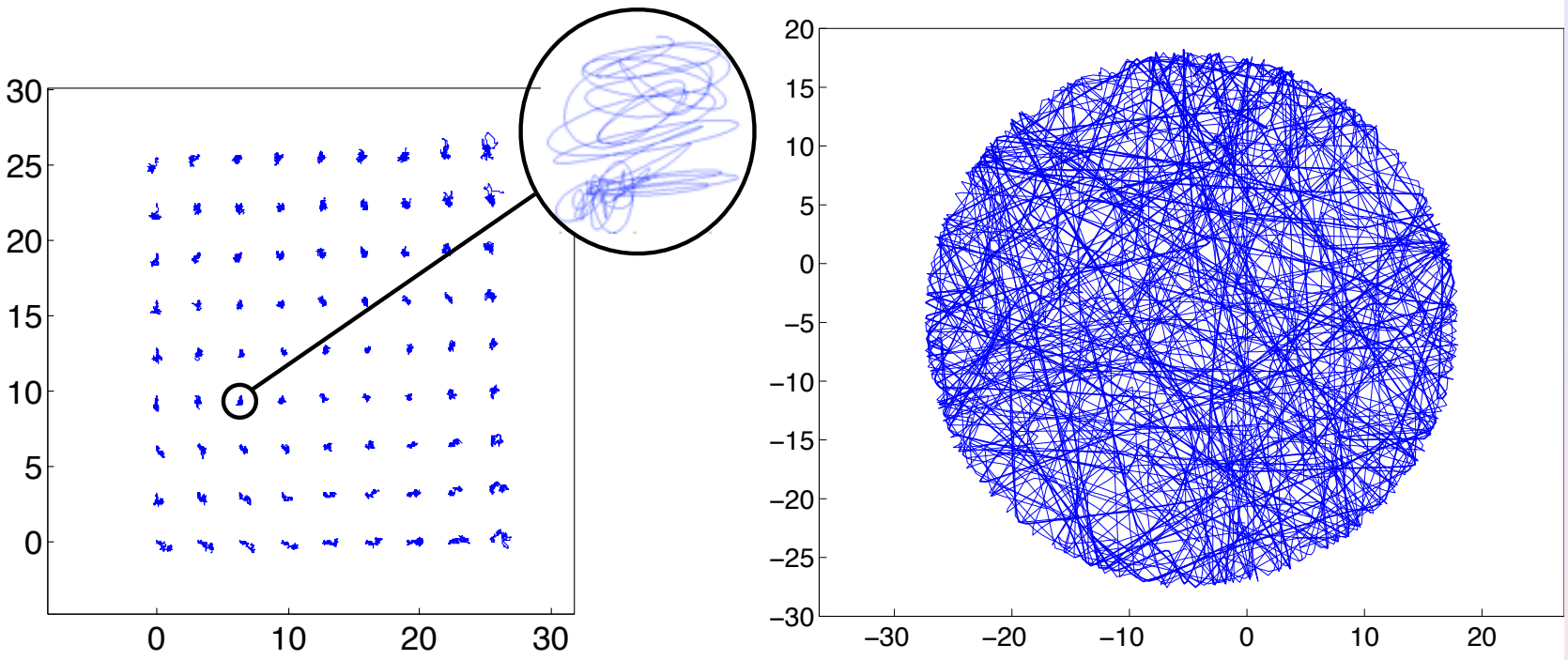
1. Mass $m = 2.991 \cdot 10^{-23}$ g
2. Moments of inertia
   $(I_1, I_2, I_3) = (0.2076, 0.1108, 0.3184) \cdot 10^{-39}$ g·cm^2
3. Radius $r = 1$ Å
4. Displacement of center of mass from the geometric center
   $\ell = 0.068$Å
5. Dipole moment $6.17 \cdot 10^{-30}$ (C $\cdot$ m)
6. Lennard-Jones radius $\sigma = 3.165$ Å and energy
   $\epsilon = 0.650$kJ/mol
7. All energies are in eV.

An ensemble of interacting rolling balls: simulations

- Numerical simulation with 81-100 rolling spherical water molecules near equilibrium lattice.
- Conservation of **total energy** of the whole system : only conservation law of the whole system.
- Stationary states: lattices with balls rolling in the same or alternating direction.



Lattice (ordered) and gas (disordered) states

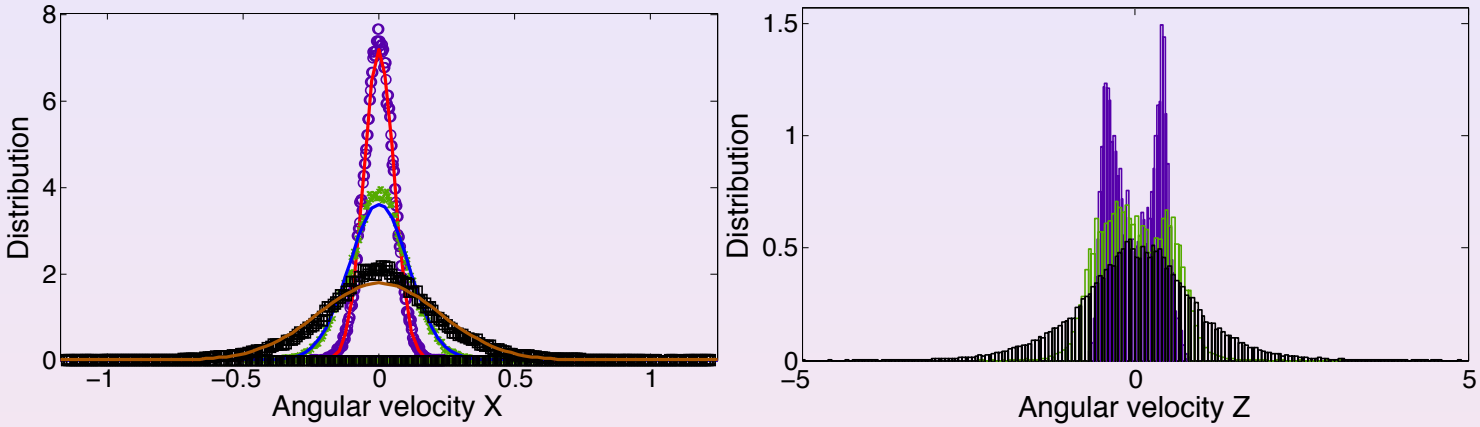


1. Lattice states are nonlinearly stable for small energies, but molecules undergo chaotic motions
2. Statistical physics of ordered and disordered states?
3. Rolling constraint leads to coupling of translational and rotational motion $\Rightarrow$ no equipartition of energy, ergodic property breaks down, *etc.*

Movies!

Problems: no equipartition of energy

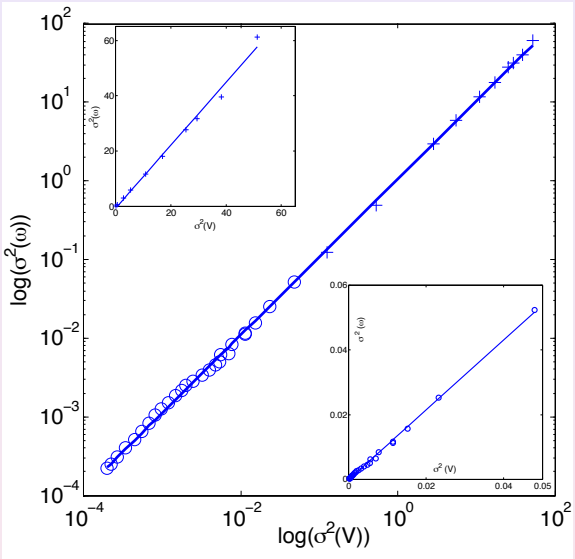
Maxwell distribution in x and y directions only!



1. Distribution in z-direction does not follow any obvious law because of rolling constraint
2. x and y distributions in linear and angular velocities give "temperatures" T_l and T_a
3. Linear and angular "temperatures" are not equal: $T_l \neq T_a$

Linear relationship between ”temperatures”

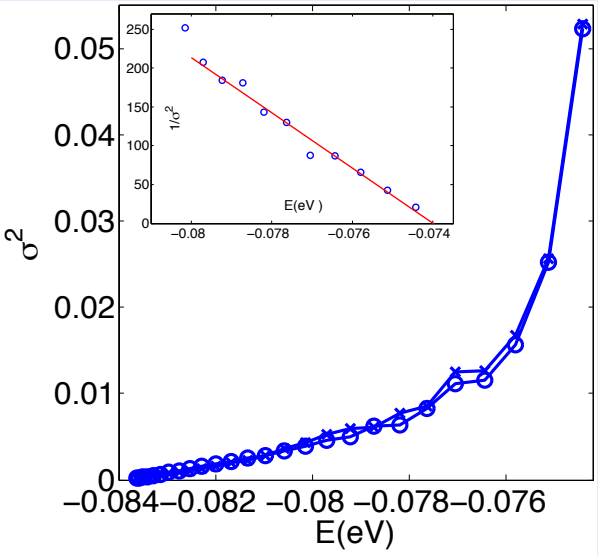
So, is it possible to define a ”temperature”? Maybe



Linear relationship between linear and angular ”temperatures” for all states (lattice and gas).

Equations of state for lattices

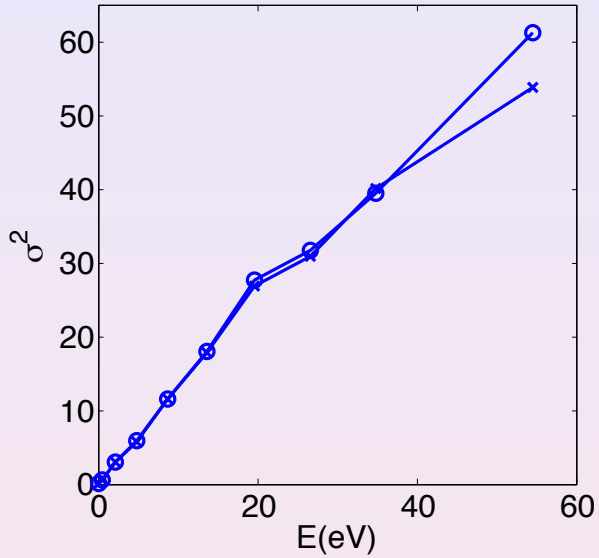
- Define temperature T as the scaled width of linear or angular distribution σ^2.



- When energy increases, lattices are destroyed
- Critical transition at $E_{tot} = E_* \simeq -0.074ev$.
- Equation of state for lattices is

$$T \sim \frac{1}{E_* - E}$$

Equations of state for rolling particle gas



Equation of state is approximately

$$T \sim E$$

Continous modeling through kinetic theory

Describe an evolution equation for density $f(t, \mathbf{x}, \nu, j, \mathbf{n}, \mathbf{v})$ with

$$\nu = \dot{\mathcal{R}}\mathcal{R}^T \quad j = \mathcal{R}I\mathcal{R}^T \quad \mathbf{n} = \mathcal{R}^T\chi \quad \mathbf{v} = \dot{\mathbf{x}} \quad "\boldsymbol{u}_{\mathbf{x}} = \dot{\mathbf{x}}" \quad "\boldsymbol{u}_{\mathcal{R}} = \dot{\mathcal{R}}"$$

$$\frac{\partial f}{\partial t} + \nabla_{\mathbf{x}} \cdot (f u_{\mathbf{x}}) + \nabla_{\mathcal{R}} \cdot (f u_{\mathcal{R}}) + \nabla_{\mathbf{v}} \cdot (f a_{\mathbf{v}}) + \nabla_{\nu} \cdot (f a_{\nu}) = 0$$

How to define accelerations $a_{\mathbf{v}}$ and a_{ν}? One way is to use Euler-Poincaré theory.

The ($SE(3)$-symmetry-reduced) Lagrangian is (with $\|\mathbf{x}\|_j = < j\mathbf{x}, \mathbf{x} >$): [5]

$$\mathcal{L}(\mathbf{x}, \mathbf{v}, \nu, \mathcal{R}, t) = \frac{1}{2} \int f \underbrace{\left(|u_{\mathbf{x}}|^2 + \|\mathcal{R}^T u_{\mathcal{R}}\|_j - U * f - 2\mathcal{R}^T \mathbf{E} \cdot \chi \right.}_{\text{energy part}}$$

$$\underbrace{\left. + |u_{\mathbf{x}} - \mathbf{v}|^2 + \left\| u_{\mathcal{R}}\mathcal{R}^T - \nu \right\|_j^2 \right)}_{\text{constraints defining velocities}} d\mathbf{x} d\mathbf{v} d\nu d\mathcal{R}.$$

[5] See Cendra, Holm, Hoyle, Marsden, J. Math. Phys. 1998

Kinetic equations via Euler-Poincaré

Consider the mapping $\psi := (\psi_{\mathbf{x}}, \psi_{\mathbf{v}}, \psi_{\mathcal{R}}, \psi_{\mathbf{v}_{\mathcal{R}}})$ that takes initial coordinates $(\mathbf{x}_0, \mathbf{v}_0, \mathcal{R}, \mathbf{v}_{\mathcal{R},0})$ to their values at time t. Define

$$X := X\underbrace{(\mathbf{x}, \mathbf{v}, \boldsymbol{\nu}, \mathcal{R})}_{\text{components}} = \dot{\psi} \circ \psi^{-1}\,, \quad \eta := \eta\underbrace{(\mathbf{x}, \mathbf{v}, \boldsymbol{\nu}, \mathcal{R})}_{\text{components}} = \delta\psi \circ \psi^{-1}$$

Use the identity $\delta X = [X, \eta] + \dot{\eta}$:

$$\delta \int \mathcal{L} \mathrm{d}t = \int \left\langle \frac{\delta \mathcal{L}}{\delta X}\,, [X, \eta] + \dot{\eta} \right\rangle = 0 \quad \Rightarrow \quad \frac{\partial}{\partial t}\frac{\delta l}{\delta X} + \mathcal{L}_X \frac{\delta l}{\delta X} - f\nabla \frac{\delta l}{\delta f} = 0$$

$\mathbf{v}$ and $\boldsymbol{\nu}$ components give the constraints:

$$f\,(u_{\mathcal{R}} - \boldsymbol{\nu}\mathcal{R}) = 0\,, \qquad f\,(u_{\mathbf{x}} - \mathbf{v}) = 0$$

Add the non-holonomic variational constraint $\eta_{\mathbf{x}} = \eta_R \mathcal{R}^T \boldsymbol{\sigma}(\mathcal{R})$ to get the dynamic equation closing the system

$$\underbrace{\left(\frac{\partial}{\partial t}\frac{\delta l}{\delta X} + \mathcal{L}_X \frac{\delta l}{\delta X} - f\nabla \frac{\delta l}{\delta f}\right)_{\mathcal{R}} \mathcal{R}^T}_{\text{micropolar terms}} + \underbrace{\left(\frac{\partial}{\partial t}\frac{\delta l}{\delta X} + \mathcal{L}_X \frac{\delta l}{\delta X} - f\nabla \frac{\delta l}{\delta f}\right)_{\mathbf{x}} \boldsymbol{\sigma}^T}_{\text{nonholonomic terms}} = 0$$

Euler-Poincaré equations, continued

Euler-Poincaré dynamic component gives equations for the accelerations $\mathbf{a}_\nu$.
However, there is a problem: the evolution occurs on the nonholonomic distribution

$$\mathbf{v} = \nu \times (-l\mathbf{n} + r\boldsymbol{\Gamma}) := \nu \times \sigma(\mathbf{n})$$

This set is, in general, a distribution and not a manifold, so we cannot do usual calculus (derivatives, tangent bundles, etc)

Workaround: solutions concentrated on constraint distribution

Solution Look at the PDF defined everywhere, but concentrated on the distribution only:

$$f_0(\mathbf{x}_0, \mathbf{v}_0, \nu_0, \mathcal{R}_0) = \phi_0(\mathbf{x}_0, \nu_0, \mathcal{R}_0)\delta(\mathbf{v}_0 - \nu_0 \times \boldsymbol{\sigma}(\mathbf{n}_0))$$

Lemma

Any solution concentrated at the constraint distribution at time $t = 0$ will remain concentrated on the distribution at all later times $t > 0$, i.e.,

$$f(\mathbf{x}, \mathbf{v}, \nu, \mathcal{R}, t) = \phi(\mathbf{x}, \nu, \mathcal{R}, t)\, \delta(\mathbf{v} - \nu \times \boldsymbol{\sigma}(\mathbf{n}))\,.$$

Proof (most straightforward) direct substitution.

Final solution for nonholonomic kinetic theory

Evolution equation for ϕ (for technical reasons, change $\mathcal{R}$ to the microinertia tensor $j = \mathcal{R} i \mathcal{R}^{\mathsf{T}}$):

$$\frac{\partial \varphi}{\partial t} + \boldsymbol{\nu} \times \boldsymbol{\sigma} \cdot \frac{\partial \varphi}{\partial \mathbf{x}} + \boldsymbol{\nu} \times \mathbf{n} \cdot \frac{\partial \varphi}{\partial \mathbf{n}} + \left\langle [\widehat{\boldsymbol{\nu}}, j], \frac{\partial \varphi}{\partial j} \right\rangle + \frac{\partial}{\partial \boldsymbol{\nu}} \cdot (\varphi \, a_{\boldsymbol{\nu}}) = 0 .$$

with $a_{\boldsymbol{\nu}}(\mathbf{x}, \mathbf{v}, \boldsymbol{\nu}, \mathbf{n}, j) = (j + \widehat{\sigma}\widehat{\sigma})^{-1} (j\boldsymbol{\nu} \times \boldsymbol{\nu} + \hat{\mathbf{z}} \times \mathbf{n} - \mathbf{n} \times \partial_{\mathbf{n}} \mathcal{U} * \varphi + \boldsymbol{\sigma} \times (\boldsymbol{\nu} \times \boldsymbol{\nu} \times \mathbf{n}) + \boldsymbol{\sigma} \times \partial_{\mathbf{x}} \mathcal{U} * \varphi)$

Lemma

Kinetic equation admits single-particle solutions of the form

$$\phi = \delta(\mathbf{x} - \mathbf{X}(t)) \delta(\boldsymbol{\nu} - \mathcal{V}(t)) \delta(\mathbf{n} - \mathbf{N}(t))$$

with $\mathbf{X}(t)$, $\mathcal{V}(t)$, $\mathbf{N}(t)$ *satisfying the single particle solutions for the individual ball and the rolling constraint* $\dot{\mathbf{X}}(t) = \mathcal{V} \times \boldsymbol{\sigma}(\mathbf{N})$.

Proof Substitute & compare.

Continous modeling: conservation laws

Fluid approach: conservation laws for momentum+energy.
Does not work here because momentum is not conserved.
Can we formulate any conservation laws? Yes!

Theorem (Existence of exact conservation laws)

Suppose $q(\mathcal{R}, \nu, \mathbf{n})$ is a conserved quantity for the motion of individual ball, i.e. $\frac{dq}{dt} = 0$ when $\mathcal{R}, \nu, \mathbf{n}$ satisfy the equations for individual particles. Define the kinetic density of Q:

$$Q(t, \mathbf{x}) = \int q(\mathcal{R}, \nu, \mathbf{n}) \phi(t, \mathbf{x}, \mathcal{R}, \nu, \mathbf{n}) d\nu d\omega d\mathcal{R} .$$

Then, $Q(\mathbf{x}, t)$ satisfies the conservation law

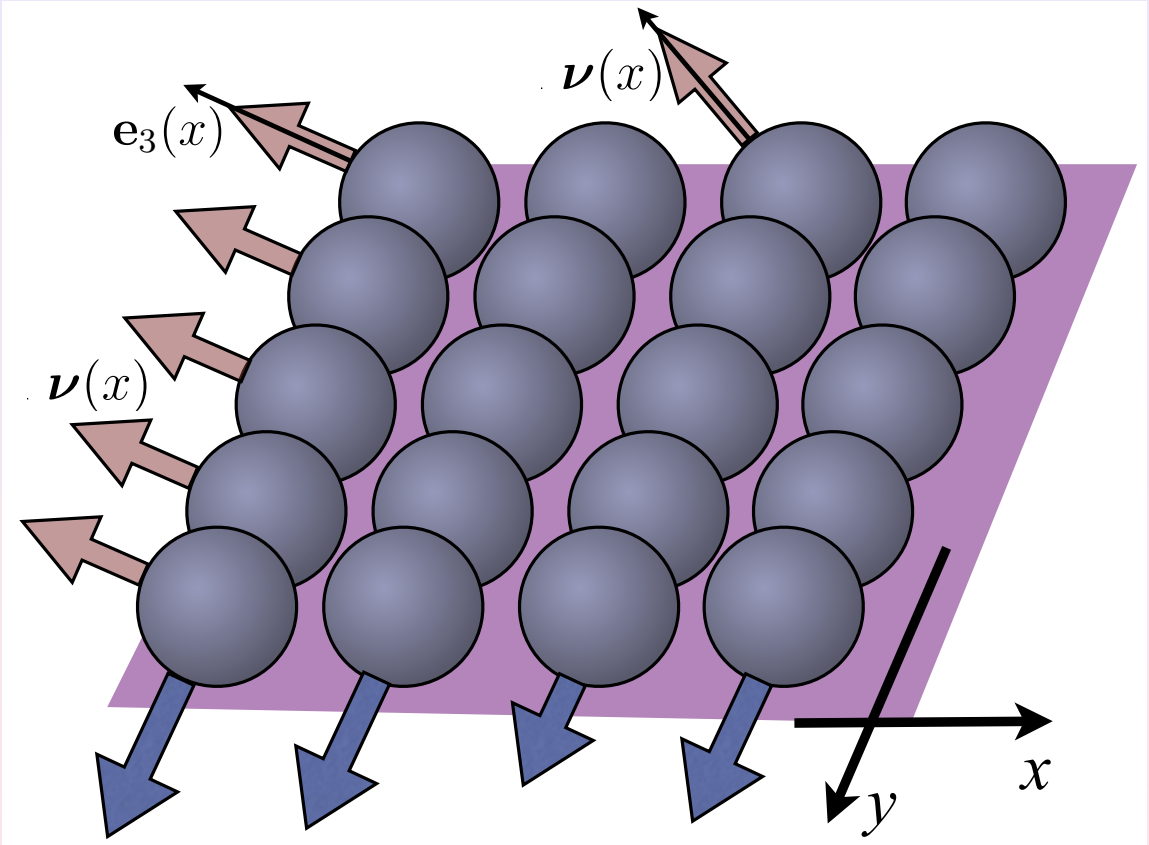
$$\frac{\partial Q}{\partial t} = -div_{\mathbf{x}} \int \nu \times \sigma(\mathbf{n}) q \phi d\mathcal{R} d\nu d\mathbf{n} .$$

Three conservation laws for non-interacting particles: energy, Jellet and Chaplygin densities.

Exact solution of kinetic equation: ”Poiuseulle” flow

$$\varphi(t,\mathbf{x},\nu,\mathbf{n},j) := \varphi_0(x)\delta\big(\mathbf{v}-\mathbf{v}_0(x)\big)\delta\big(\mathbf{n}-\mathbf{n}_0(x)\big)\delta\big(\nu-\nu_0(x)\big)\delta(j-\mathrm{i})\,.$$

Axis of rotation for each ball is aligned with $\mathbf{e}_3$, and $I_1 = I_2$.



Non-uniqueness: For a given potential, there exists a one-parameter family of solutions.

Hydrodynamic models based on cold fluid closure

Take moments of the kinetic equations; close them using the cold fluid ansatz

$$\varphi(\mathbf{x}, \nu, \mathbf{n}, j, t) = \rho(\mathbf{x}, t)\, \delta(\nu - \boldsymbol{\omega}(\mathbf{x}, t))\, \delta(\mathbf{n} - \boldsymbol{n}(\mathbf{x}, t))\, \delta(j - \mathcal{J}(\mathbf{x}, t))\,.$$

Fluid equations are (no exact reduction!)

$$\begin{aligned}
&\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho\, \boldsymbol{\omega} \times \boldsymbol{\sigma}(\boldsymbol{n})) = 0 \\
&\frac{\partial \boldsymbol{\omega}}{\partial t} + (\boldsymbol{\omega} \times \boldsymbol{\sigma}(\boldsymbol{n}) \cdot \nabla)\boldsymbol{\omega} = \boldsymbol{a} \\
&\frac{\partial \boldsymbol{n}}{\partial t} + (\boldsymbol{\omega} \times \boldsymbol{\sigma}(\boldsymbol{n}) \cdot \nabla)\mathbf{n} = \boldsymbol{\omega} \times \boldsymbol{n} \\
&\frac{\partial \mathcal{J}}{\partial t} + (\boldsymbol{\omega} \times \boldsymbol{\sigma}(\boldsymbol{n}) \cdot \nabla)\mathcal{J} = [\widehat{\boldsymbol{\omega}}, \mathcal{J}]
\end{aligned}$$

Possible experimental verification I

Experimental evidence of rolling:

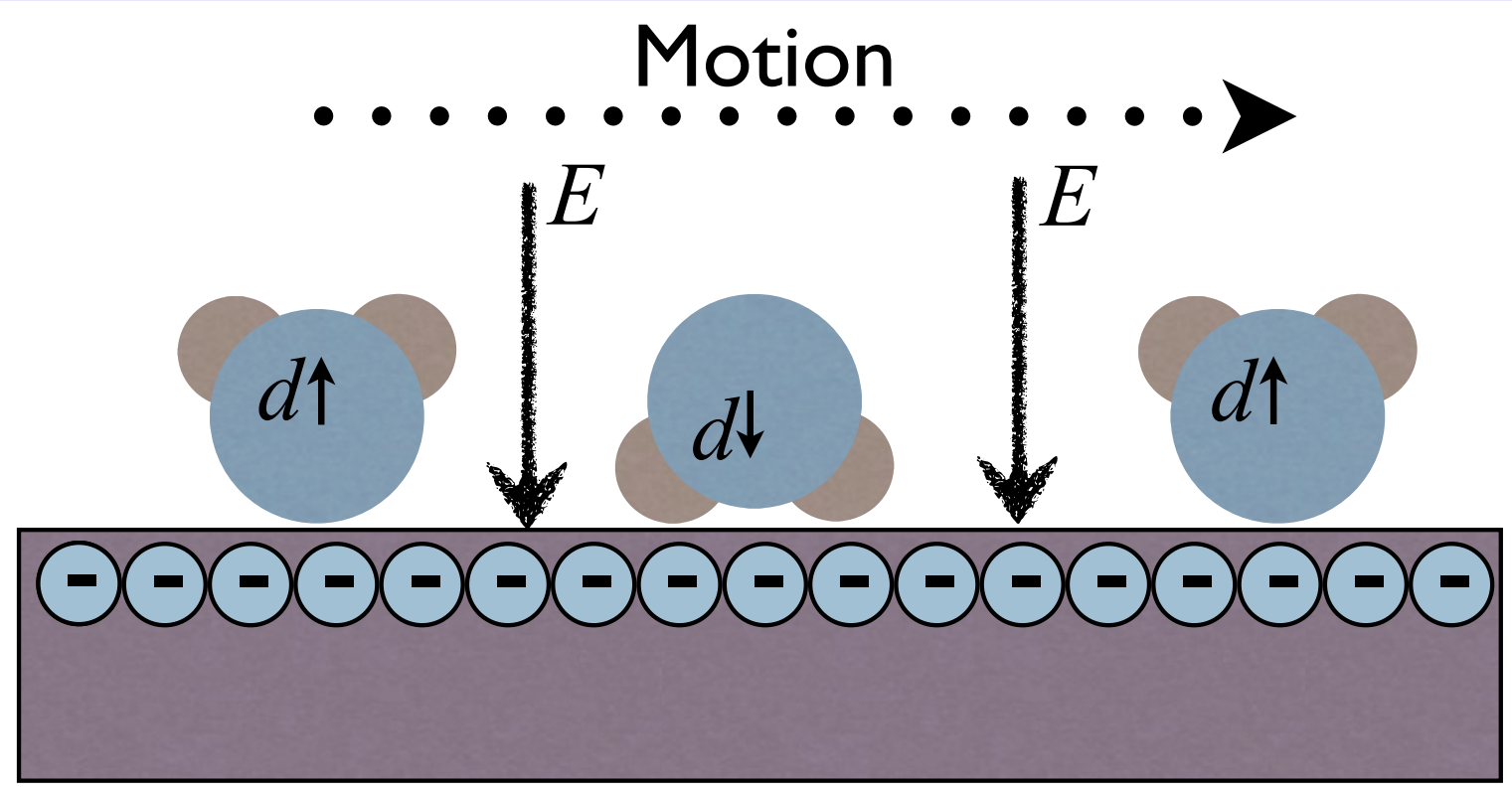
Wave propagation through a lattice (no spinning in base state). Assume an infinite square lattice, and disturbances $\sim e^{-i\omega t+ik_x x+ik_y y}$, with (k_x, k_y) being the wave vector; then

$$\begin{aligned}\left\{\frac{m}{K}(1+\zeta_1)\omega^2-2+2\cos(k_x a)\cos(k_y a)\right\}\times\\ \left\{\frac{m}{K}(1+\zeta_2)\omega^2-2+2\cos(k_x a)\cos(k_y a)\right\}\\ -8\sin^2(k_x a)\sin^2(k_y a)=0\,,\end{aligned}\tag{1}$$

where $\zeta_i = I_i/\left(m(r+\ell)^2\right)$, $K = d^2V_{LJ}/dr^2$ is the spring constant of the *LJ* potential and a is the periodicity of the square lattice.

Absence of rolling is given by $\zeta_i = 0$ which is $10\div 20$ % difference.

Possible experimental verification II



- Surfaces (*e.g.* silica) are charged $\Rightarrow$ rolling involves areas with increased potential energy.
- These areas may be forbidden in classical sense.
- Predict diffusion of water molecules with classical and quantum mechanics.

Conclusions and future work

- Rolling systems show a surprising richness of behavior – gas, fluid and solid states.
- There is no equipartition between linear and angular degrees of freedom
- There is a robust linear relationship between linear/angular temperatures
- Nonholonomic kinetic theory is made possible by considering PDF concentrated on distributions and Euler-Poincare theory.
- Cold fluid closure for continuous equations.
- Future work: Connections to experiments, other constraints *etc.*