

Ordered and Disordered Dynamics in Monolayers of Rolling Particles

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We consider the ordered and disordered dynamics for monolayers of rolling self-interacting particles modeling water molecules. The rolling constraint represents a simplified model of a strong, but rapidly decaying bond with the surface. We show the existence and nonlinear stability of ordered lattice states, as well as disturbance propagation through and chaotic vibrations of these states. We study the dynamics of disordered gas states and show that there is a surprising and universal linear connection between distributions of angular and linear velocity, allowing definition of temperature.

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Introduction.—Molecular monolayers are playing an ever-increasing role in technology as they allow manipulation of contact properties of materials in a precise and controlled manner [1–3]. Previous theoretical work on molecular monolayers has concentrated on either static studies of monolayer structures [1,4] or molecular dynamics simulations where each molecule is moving under the forces and torques from surrounding molecules and the substrate [2,3,5,6]. The direct molecular simulations employed in these papers were quite successful in explaining various properties of liquid water, e.g., formation of contact angle [2] or anomalous properties for nanoconfined water [5,6]. That confinement of water molecules was achieved by constraining the bulk of water to a very narrow (nm) layer by the rigid surface on both sides. On the other hand, experimental data demonstrate the presence of water monolayer on a Si surface under normal conditions, due to the strong bond between the water molecules and the substrate [4,7]. The nature of such a bond is not well understood, so it is difficult to account for in the atomistic molecular simulations.

The purpose of this Letter is to suggest a simple yet physical way to model such a contact bond as a rolling constraint on the molecules. Physically, that leads to the fact that while the molecule itself is moving, its point of contact with the substrate is stationary. This invokes the analogy with a classical problem of rolling body on the surface with perfect friction, appearing when the bond molecule-substrate is infinitely strong at contact point, but decays rapidly away from substrate. In reality, if that bond is large but finite, the motion will be a combination of sliding and rotating. However, the theory of sliding and rolling is not yet well developed [8,9], and so we will restrict ourselves to the simplest possible realization of a perfect friction. Thus, we consider the dynamics of a monolayer of molecules that are self-interacting by the long-range interactions (Lennard-Jones and electrostatic), while the influence of the boundary is limited to restricting the motion to the perfect rolling dynamics. While the rolling dynamics may seem too idealized, it has actually been

observed in the context of functional nanostructures [10]. More complex models of molecule-substrate interaction will result in extra force on the ball, but such interactions will not be considered here.

The study of rolling motion of rigid bodies has a long history in the context of classical mechanics [9,11,12], but the study of collective motion of rolling particles has not been undertaken. The nonholonomic rolling constraint is a major obstacle to constructing statistical mechanics for these systems [13–16]. This Letter is devoted to defining ordered and disordered states, akin to the standard solid and gas or liquid, and computing statistical physics concepts for such systems. We also show the way rolling affects propagation of phonons through a lattice.

Setup of the dynamics.—The rolling particles are simulated as identical spherical rigid bodies of radius r all having the same mass m and the moments of inertia tensors. The center of mass (c.m.) is assumed to be at a position different from the geometric center, as illustrated on Fig. 1. The notation used in this Letter is as follows: Γ_i is the unit vector pointing to the geometric center (GC), Ω is the angular velocity in the ball's coordinate frame, and s_i is the vector pointing to c.m. The equations of motion for an individual ball come from the well-known Chaplygin's equations [9,17]. Under certain symmetry conditions, Chaplygin's ball is completely integrable and has three integrals of motion: one is total energy that is the easily understandable physical quantity. The other two constants of motion are Routh and Jellet integrals that are harder to

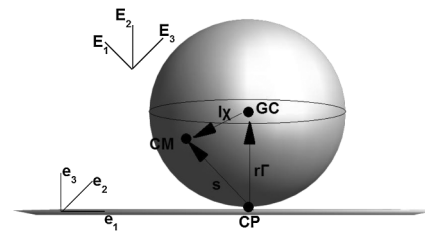


FIG. 1. Schematic of an offset rolling ball dynamics.

explain in terms of elementary physics [18]. The equations of motion for the i th ball are

$$\left(\frac{d}{dt} + \boldsymbol{\Omega}^i \times\right) (I^i \boldsymbol{\Omega}^i + m \mathbf{s}^i \times (\boldsymbol{\Omega}^i \times \mathbf{s}^i)) - m^i \mathbf{s}^i \times (\boldsymbol{\Omega}^i \times \mathbf{s}^i) = \mathbf{s}^i \times \mathbf{F}^i + \mathbf{T}^i, \quad (1)$$

$$\frac{d\boldsymbol{\Gamma}^i}{dt} = -\boldsymbol{\Omega}^i \times \boldsymbol{\Gamma}^i. \quad (2)$$

Here, I^i are the eigenvalues of the tensor of inertia and \mathbf{F}^i and \mathbf{T}^i are the total force and torque acting on the i th particle. These forces and torques include the interparticle interactions. The rolling constraint for velocity of the center of mass \mathbf{V}^i , written as $\mathbf{V}^i = \boldsymbol{\Omega}^i \times \mathbf{s}^i$, cannot be reduced to an equation between configuration variables only, and is thus nonholonomic [11]. Neither linear nor angular momenta are conserved for individual particles or for the whole system. The total energy of the system, however, is conserved. A Hamiltonian approach to this system would be useful, both from the point of view of deriving statistical physics as well as quantization. Recently, an explicit Hamiltonian approach was derived for the nonholonomic Chaplygin sleigh [19]; however, it is not obvious to us how to extend this method for our case.

The intermolecular interactions cause the interchange of linear and angular momentum as well as energy between particles. In our simulations, the Lennard-Jones (LJ) V_{LJ} and the dipole V_d potentials are considered. The dipole \mathbf{p}_i is positioned at the center of mass on each spherical particle. The interactions are given by

$$V_{\text{LJ}} = 4\epsilon \sum_{i \neq j} \left(\frac{\sigma^{12}}{r_{ij}^{12}} - \frac{\sigma^6}{r_{ij}^6} \right), \quad (3)$$

$$V_d = \frac{1}{8\pi\epsilon} \sum_{i \neq j} \mathbf{p}_i \cdot \left(\frac{3(\mathbf{p}_j \cdot \hat{\mathbf{r}}_{ij}) \hat{\mathbf{r}}_{ij} - \mathbf{p}_j}{r_{ij}^3} \right). \quad (4)$$

To be concrete, in the computations of collective dynamics for rolling particles, we use the parameters and interactions relevant to water molecule monolayers by choosing the mass $m = 2.991 \times 10^{-23}$ g, moments of inertia $(I_1, I_2, I_3) = (0.2076, 0.1108, 0.3184) \times 10^{-39}$ g · cm², radius $r = 1$ Å, displacement of center of mass from the geometric center $\ell = 0.068$ Å, dipole moment 6.17×10^{-30} (c.m.), LJ radius $\sigma = 3.165$ Å, and energy $\epsilon = 0.650$ kJ/mol. These values correspond to the parameters of a water molecule [20]. For convenience, we choose the angular velocity scale $\tilde{\omega} = 10^{13}$ rad/s. The rolling constraint then introduces the scaling of velocity to be $\tilde{v} = r\tilde{\omega} = 10$ cm/s. Given a different set of parameters, the details of our computations will be different, but the methods and results outlined here hold for other molecules as well. For the set of parameters considered here, neither Routh nor Jellet integrals for each ball are conserved.

Stationary states: a crystalline lattice.—The existence of stationary states for the system of rolling particles depends on the presence and orientation of the dipole moment. Suppose for now that the dipole moment is absent, and the only interaction between the molecules is Lennard-Jones. Suppose also for the moment that the particles are not moving, and are aligned so both geometric center and center of mass are along $\boldsymbol{\Gamma}$, the unit vector pointing upward from the contact point. It is easy to see then that there is an equilibrium configuration so that the centers of mass are arranged at a distance close to σ , the equilibrium distance of LJ potential. For the case of two and three particles, there is an equilibrium configuration where the particles are arranged at exactly the distance σ from each other. If each of these particles is spun with angular velocity $\boldsymbol{\Omega}_i = (0, 0, \Omega_i)$ pointing upwards, in the absence of nonlocal interaction this will be a neutrally stable state for each particle, although friction forces may destabilize such equilibria, similar to the “tippe top” dynamics [21]. Because LJ forces are exactly at balance, for all Ω_i this will be an equilibrium state. In the presence of the dipole moment, finite lattices cease to be equilibrium configurations. However, if the dipole moment \mathbf{p}_i points exactly along the line from GC to c.m. (which is the case for the particles considered here), an infinite regular lattice, possessing high symmetry (like a triangular or square lattice) will still be an equilibrium state. Then, \mathbf{p}_i can either be arranged in the same directions or be alternating. However, the states with the \mathbf{p}_i all pointing in one direction are unstable both linearly and nonlinearly. Thus, in what follows we concentrate on the states with the alternating \mathbf{p}_i as shown on Fig. 2.

The question about the stability of these states immediately arises. While a detailed investigation of the stability is a complex issue beyond the scope of this Letter, a simple physical explanation can be made showing that these states are linearly unstable. Suppose for simplicity that all rotation rates are the same, $\boldsymbol{\Omega}_i = \boldsymbol{\Omega}_0$. A small perturbation in the spinning stationary state will result to a precession of each particle, which according to the rolling constraint will happen at the same rate as the rotation frequency. The distance between particles will also change with the same frequency, and through the LJ interaction (3) both particles will experience parametric resonance. A similar argument applies to different rotation rates, and more particles in a

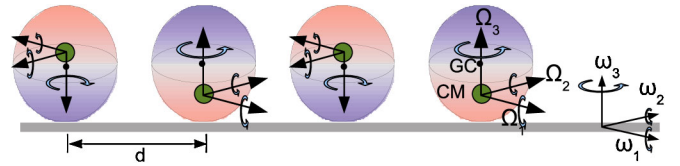


FIG. 2 (color online). Schematic representation of stationary states. The balls are arranged in a lattice with the c.m. at force equilibria. The alternating vertical rotation vector from one ball to the next passes through c.m. for each ball.

lattice. However, these states are nonlinearly stable at least for some of the configurations and initial conditions we have investigated, corresponding to low energies. In Fig. 3, left, we show the centers of 81 rolling balls in a rectangular lattice, over a long simulation time. While each particle remains close to its equilibrium position, the individual trajectories (blowup on Fig. 3) are chaotic and are strongly reminiscent of thermal vibrations in lattices.

Lattice dispersion relation.—In order to suggest a possible experimental verification of rolling motion, we measure the propagation of disturbances through the lattice. The derivation of dispersion relation for a lattice of spinning particles in a general case is difficult, as it involves linearization about oscillating base states. Here, we present the dispersion analysis of the states shown on Fig. 2, with all $\Omega_i = 0$. Assuming an infinite square lattice as described above, we arrive to the following dispersion relation for the propagation of disturbances of the form $e^{-i\omega t + ik_x x + ik_y y}$, (k_x, k_y) being the wave vector:

$$\left\{ \frac{m}{K} (1 + \zeta_1) \omega^2 - 4 + 2 \cos(k_x a) (1 + \cos(k_y a)) \right\} \\ \times \left\{ \frac{m}{K} (1 + \zeta_2) \omega^2 - 4 + 2 \cos(k_y a) (1 + \cos(k_x a)) \right\} \\ - 4 \sin^2(k_x a) \sin^2(k_y a) = 0, \quad (5)$$

where $\zeta_i = I_i / (m(r + \ell)^2)$, $K = d^2 V_{LJ} / dr^2$ is the spring constant of the LJ potential and a is the periodicity of the square lattice. Note that (5) differs from the standard dispersion relation for a square lattice of springs only by the dimensionless coefficients ζ_i , incorporating the effects of rolling. For our values of parameters, $\zeta_i \approx 0.1-0.2$. Thus, the rolling constraint affects the speed of sound by about 10%–20%, which should be a measurable difference.

Disordered states: statistical analysis.—For large initial energies, the lattices become unstable, and in the absence of external boundaries the particles scatter to infinity. Thus, for large energies, we perform simulations in a round potential well with sharp walls, forcing the particles to

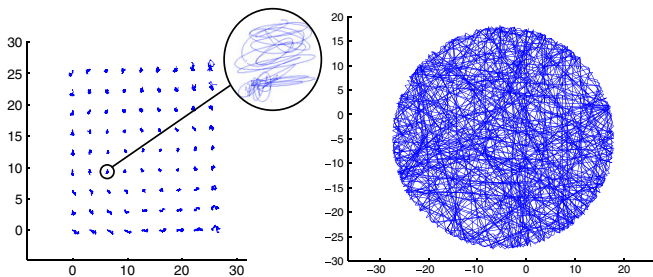


FIG. 3 (color online). Left: trajectory of the center of rolling particles in lattice model, with the blowup showing the trajectory of an individual particle. The finite lattice is not an exact stationary state, so the vibrations are most apparent at the edges. Right: trajectories of a gas state in a circular container.

remain within a circle. An example of such simulation with 16 particles is shown in Fig. 3, right.

The first step towards considering this system as a statistical physics model is to investigate the distribution of linear and angular velocities. For an ideal gas in 3D, the Maxwell-Boltzmann distribution for velocities is

$$f_v(\mathbf{v}) = \left(\frac{m}{2\pi kT} \right)^{3/2} \exp\left(-\frac{m\mathbf{v}^2}{2kT} \right), \quad (6)$$

and similar for the rotational degrees of freedom. The implicit assumption in (6) is that the distribution of velocities in each direction is normal with the same width defines the temperature T of the system. However, in the system of rolling particles there is no reason for (6) to work: first, the rotational and translational components are coupled through the rolling constraint and second, even though the rolling motion is along the plane, each ball undergoes three-dimensional motion.

Figure 4 shows several examples of the distribution for horizontal and vertical angular velocities for several values of total energy of the system. On the left side of this figure, we plot the distribution of ω_x , which is identical to the distribution of ω_y . These distributions are always very close to normal, which are shown with solid curves. The right side of this figure shows distributions of ω_z for the same values of the energy, and it is apparent that this distribution is not normal. The distributions of v_x , v_y , and v_z show the same tendencies. It is important to note, however, that the variances (in proper units) of normally distributed angular and linear velocities are *not* the same, and thus there is no straightforward definition of temperature for this system. We shall also note that due to the non-normal nature of the distribution in the z component and the nonholonomic coupling between angular and linear velocities, the kinetic energy distribution does not follow Maxwell-Boltzmann law. In addition, the kinetic energies of rotational and translational motion are not equal (even in a statistical sense), so the equipartition of energy in our system does not hold.

Temperature as scaled variance.—Clearly, the rolling constraint prevents a straightforward statistical physics description of the rolling particle systems. Nevertheless, there is a surprising relation that connects σ^2 obtained from the angular (σ_ω^2) and linear (σ_v^2) velocities. We

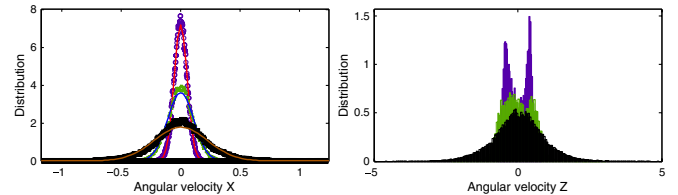


FIG. 4 (color online). Distributions of ω_x (left) and ω_z (right) for different energies of the lattice of rocking and rolling molecules. Solid curves represent fits to normal distributions.

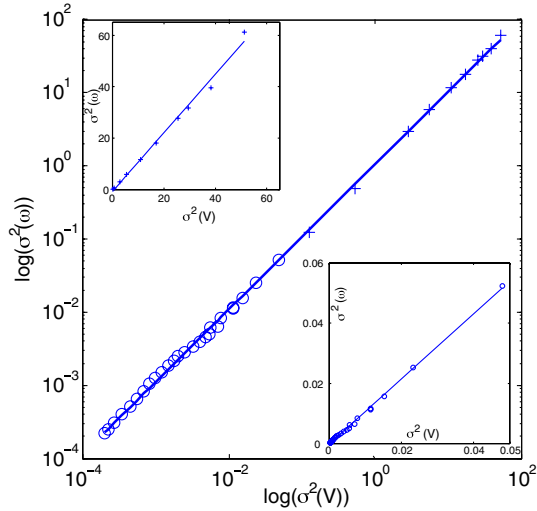


FIG. 5 (color online). Linear relationship between variances of the horizontal linear and angular velocities σ_v^2 and σ_ω^2 for lattice states (circles) and gas states (crosses). Linear fit to both sets of data is also shown as insets.

observed that for all values in our numerical experiments, there is a surprising well-behaved linear relationship $\sigma_\omega^2 = k\sigma_v^2$, with the coefficient $k \approx 1.08$ depending only on the parameters on the system (geometry of the ball, center of mass position, etc.) but not on anything else. That relationship is valid for both lattice and gas states, as shown in Fig. 5. We note that there is no *a priori* reason for such relationship to exist, but the surprising robustness of this law leads us to believe that it could be taken as one of the postulates in future development of statistical mechanics for nonholonomic gas.

Using this linear relation we can define the temperature as the variance of either horizontal linear or angular velocity, or a linear combination of those. All these definitions lead to the same results up to a scaling factor. Thus, on Fig. 6, we plot the scaled variances σ^2 (which are proportional to temperature T) vs total energy of the system E . For the gas states (right) we observe $E \sim \sigma^2 \sim T$, as in

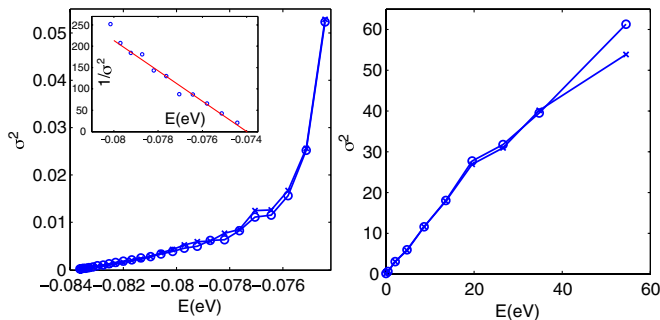


FIG. 6 (color online). Variances vs energy in the lattice state (left) and gas state (right), based on the horizontal velocities. Circles: σ_ω^2 distribution; crosses: σ_v^2 distribution multiplied by $k = 1.08$. Left inset: $1/\sigma^2$ vs E .

ideal gas. Note that since in simulations we use real balls interacting with LJ potential, a more detailed study should show the effects of the finite size of the particles, but our simulations do not allow a reliable investigation of these effects. Figure 6, left shows that a singularity in variance as the lattice states become unstable and cease to exist for small negative energies. The exact nature of the destruction of lattice states is as yet unclear, but the divergence of the variance $\sigma^2 \sim (E_0 - E)^{-1}$ (shown in the inset) indicates the presence of a phase transition.

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