**Non-equilibrium phase behavior and friction of confined
molecular films under shear: A Non-equilibrium Molecular
Dynamics study**

Sz. Maćkowiak*

Institute of Physics, Poznań University of Technology,

Piotrowo 3, 60-965 Poznań, Poland.

D.M. Heyes[†] and D. Dini[‡]

Department of Mechanical Engineering,

Imperial College London, Exhibition Road,

London, SW7 2AZ, United Kingdom.

A.C. Brańka[§]

Institute of Molecular Physics, Polish Academy of Sciences,

M. Smoluchowskiego 17, 60-179 Poznań, Poland.

(Dated: October 5, 2016)

Abstract

The phase behavior of a confined liquid at high pressure and shear rate, such as is found in elastohydrodynamic lubrication, can influence the traction characteristics in machine operation. Generic aspects of this behavior are investigated here using Non-equilibrium Molecular Dynamics (NEMD) simulations of confined Lennard-Jones (LJ) films under load with a recently proposed wall-driven shearing method without wall atom tethering [Gattinoni, Maćkowiak, Heyes, Brańka and Dini, Phys. Rev. E 90, 043302 (2014)]. The focus is on thick films in which the nonequilibrium phases formed in the confined region impact on the traction properties. The nonequilibrium phase and tribological diagrams are mapped out in detail as a function of load, wall sliding speed and atomic scale surface roughness, which is shown can have a significant effect. The transition between these phases is typically not sharp as the external conditions are varied. The magnitude of the friction coefficient depends strongly on the nonequilibrium phase adopted by the confined region of molecules, and in general does not follow the classical friction relations between macroscopic bodies, *e.g.*, the frictional force can decrease with increasing load in the Plug-Slip (PS) region of the phase diagram owing to structural changes induced in the confined film. The friction coefficient can be extremely low (~ 0.01) in the PS region as a result of incommensurate alignment between a (100) face-centered cubic wall plane and reconstructed (111) layers of the confined region near the wall. It is possible to exploit hysteresis to retain low friction PS states well into the Central Localization high wall speed region of the phase diagram. Stick-Slip behavior due to periodic in-plane melting of layers in the confined region and subsequent annealing is observed at low wall speeds and moderate external loads. At intermediate wall speeds and pressure values (at least) the friction coefficient decreases with increasing well depth of the LJ potential between the wall atoms, but increases when the attractive part of the potential between wall atoms and confined molecules is made larger.

I. INTRODUCTION

Although friction is one of the most important practical physical phenomena its molecular origins are still only partially understood.^{1–4} Friction is an extremely complex physical process, and its origin can vary from system to system. This is in part because the contact topology, molecular interactions and mechanisms of energy dissipation can vary with material and physical conditions, such as whether the contact is dry or lubricated by an intervening liquid or solid. For two dry macroscopic surfaces in contact, if F_N is the average normal load and F_f the average steady state tangential force needed to slide one of the surfaces, the friction coefficient is defined by $\mu = F_f/F_N$. Amontons and Coulomb (and even earlier by Leonardo Da Vinci, as recently discovered,⁵) showed that μ is independent of (apparent) contact area and sliding speed for macroscopic bodies, which has been found more recently to be because contact is between surface asperities.^{6,7}

Controlling friction between contacts acting on a much smaller lengthscale has become a pressing issue in a number of fields involving miniaturized mechanical components.⁸ Experiments carried out on atomistically flat surfaces have shown that on this scale the friction laws can be quite different to the classical ones of Coulomb and Amontons.^{9,10} Notably, the friction coefficient increases with relative sliding speed,¹¹ and there can be periodic variations of the sliding force arising from the traversal of the two crystalline surfaces over each other. The generic features of this behavior can be explained by the Frenkel-Kontorova-Tomlinson model.^{12–14} Coupling between the lattice dynamics and the phonons of the two surfaces dominates the observed behavior.¹⁵ Modelling friction has been able to help clarify the origins of these effects on the nanoscale and mesoscale.^{16–18}

In particular, these trends have been confirmed by Non-equilibrium Molecular Dynamics (NEMD) calculations carried out in the last few decades, which have also shown that the relative orientation of the two surfaces can have a marked effect on μ . In fact, if the relative orientation of the two surfaces causes the ratio of the lattice spacing in a given sliding direction to be an irrational number, the friction coefficient will be zero. This ‘superlubricity’ can be suppressed if an adsorbed molecule ‘pins’ the two surfaces together dynamically.^{19,20}

When there is a molecularly thin third material acting as a lubricant between the two sliding surfaces, experiment, and NEMD simulations have shown that the instantaneous friction coefficient can vary with time in a repetitive way for relatively low sliding speeds. This ‘Stick-Slip’ behavior has been attributed to a recurrent solidification and shear-induced melting of the confined material during the sliding process.^{21–23} The precise details of these physical changes are not well characterised, and could well vary from system to system.^{24,25} NEMD simulations of Lei and Leng,¹⁸ on monatomic molecules indicated that the ordering-disordering transition takes place within the layers parallel to the wall, and that the stick-slip events originate from relative sliding of adjacent layers, and the layer next to the wall with the wall. They also concur with Klein’s phenomenological model that the energy dissipation occurs during the slip part of the cycle, and not just at the point of melting of the stick state.²⁶ The results from the present study, presented in Sec. III, agree with Ref.¹⁸ in that we found that melting occurs within individual layers (i.e., in-plane or ‘2D’ melting) rather than of the whole sample. Gattinoni *et al.*²⁷ showed by NEMD computations that stick-slip behavior can also occur as a result of periodic elastic deformation of the wall region next to the confined material, **the stored energy which then is released** in a ‘slip’ stage (*i.e.*, ‘true’ stick-slip).

In some tribological applications the pressures applied in the contact zone can be several GPa so that any confined film can be in a solid or semi-solid state as a result of this.^{28,29} Friction arising from a solid lubricant has been modeled using NEMD.³⁰ NEMD simulations have revealed a rich non-equilibrium steady state phase diagram of the confined system,^{31,32} which under pressure and high shear rates can transform into a non-flowing plug with slip at the walls. This we have called the ‘Plug Slip’ (PS) state. It has been found that several layers of molecules can be essentially immobilised (‘epitaxially bound’) next to the walls.³³

NEMD investigations of the impact of applied pressure and shear rate on the confined film states have been reported previously by us.^{27,31,32} Boundary-driven simulations mimicking a typical traction drive experimental arrangement were carried out with thermostatted sliding walls as a means of initiating and sustaining shear flow. The calculations showed that an immobilised plug can adopt various structural arrangements and orientations with respect to the walls. The relation between, μ and the crystal structure of the plug and interface plug-wall region was not investigated in these previous studies, which is redressed here. The relationship between the friction coefficient and the physical state of the intervening film has been reported by us in Refs.^{27,31,32}.

New NEMD equations of motion and analysis tools are used here. There is a more detailed discussion of thermostatting procedures for a confined system in a slit geometry. While the study of more complex molecule experimental systems is obviously of practical interest such an approach should use methods where some level of understanding has already been developed. This is best performed before the parametric space becomes too large. The computational procedural issues associated with the generic type of

system we investigate involving a confined system, non-equilibrium states, and external loading is far from being solved, even at the level of the simplest of models. The simple mono-atomic system considered here (condensed phase argon) is suitable to address these issues. The Lennard-Jones potential used in the simulations was originally developed to represent simple molecules like argon, but here should best be viewed as acting as a coarse-grained model of a larger molecular system.

The purpose of this work is to explore in greater detail the non-equilibrium phase behavior of confined liquids under conditions of high pressure and shear rate. These conditions may be found in MEMS devices or elastohydrodynamic contacts.^{27,31,32} Some of the previously observed NEMD steady states have been detected experimentally. For example, Plug-Slip,^{34,35} and Central Localization,³⁶ steady states have been detected using a novel methodology based on phosphorescence imaging. [Martinie and Vergne,³⁷](#) also gave evidence that the LJ shear localised states are present in real lubricants under traction experiment conditions despite the simplicity of the computer model. These non-equilibrium phase transformations affect the lubrication performance by in general decreasing the traction coefficient below values expected for Couette flow acting across the system. This is because of slipping effects between the molecular layers and where the shearing does take place the shear rates are larger than the average and therefore the lubricant in that region will exhibit enhanced shear thinning.

The focus in this work is on the traction behavior of thick liquid films rather than the frictional properties of thin films containing just a few molecules typical of Atomic Force Microscope (AFM) and boundary lubrication experimental and modelling studies. Different factors and physical processes are important in these two limits. Although

we refer to μ as the friction coefficient as is common in tribology, the term ‘traction coefficient’ which is applied in the lubrication field would perhaps be more appropriate. Our previous studies, using specifically written codes and LAMMPS,³⁸ for various system sizes and model construction (*e.g.*, tethered and non-tethered wall atoms) established some features of these non-equilibrium steady states. This work reveals a number of new trends, such as a considerable history dependence in certain regimes in the steady state structure map, and anomalous friction coefficient behavior.

In Sec. II technical aspects of the NEMD model are presented, supplemented with relevant derivations in the Appendix. Results and discussion are presented in Sec. III. Conclusions are made in Sec. IV.

II. THEORY AND METHODOLOGY

A. System geometry and confining method

A schematic diagram of the confined system geometry used in the NEMD simulations is shown in Fig. 1. Regions A and C represent the solid walls, and region B is the confined part of the system, which can be a liquid, a solid or a nonequilibrium steady state, or may be a mixture of the two phases.

FIG. 1: The model NEMD system composed of a confined region between two solid walls. The upper and lower zones A and C (red on-line) represent the walls composed of atoms, while zone B is the confined part B (green atoms on-line). An external pressure, P_N is applied to the system in the z direction (shown as a red vertical arrow). The wall sliding speed in the x direction, v_0 , is shown for both walls by blue arrows. L is the distance in the z direction between centers of mass of both walls, and S is the square cross sectional area of the system. The system is periodically repeated in the x - and y -directions.

Wall construction

The shear stresses on the wall atoms could result in its break up. In order to obviate this some previous NEMD simulations have been carried out using a tethering potential to constrain the wall atoms to vibrate about their average lattice sites.^{31,39–41} One of

consequences of tethering, as derived and discussed in the Appendix, is the nonconservation of the total momentum (TM). This is because the tethering acts as an external force on the whole system. The analytic form of the tethering potential if too stiff can also lead to algorithmic stability problems and a failure to generate the canonical distribution, even at equilibrium. Also there is an arbitrariness in the choice of the form of the tethering potential which could introduce unrealistic features in the wall phonon spectrum. In addition, with change of density the spring constants should change but, again, there is no rigorous expression to specify this. Other NEMD studies have instead made stress-resilient walls by introducing a stronger binding energy between the wall atoms than between the confined molecules (and the cross terms).^{18,32} In our calculations the walls are built without any artificial springs attached to the atoms but with a stronger binding energy between the wall atoms than between the confined molecules. The possible limitations of tethering are thereby removed.

Shear imposition

The imposition of shear in NEMD is still not a trivial problem, even for Couette flow of bulk liquids.⁴² In the case of sample confinement by walls the only physically reasonable mechanism is to induce shear flow through the relative sliding of the boundary walls. Many of the past literature studies have considered cases which mimic an Atomic Force measurement (AFM) or some other curved element which slides over a flat surface,^{17,43} and in the boundary lubrication regime where there are just a few molecules confined between the sliding surfaces. In those cases the Prandl-Tomlinson model (PT) is often directly exploited to formulate the model and interpret the results. The top surface member is deemed to be pulled by a spring connected to a hypothetical stage moving at constant velocity.^{43,44} The present work considers instead two atomistically flat walls

which move with the same constant speed but in opposite directions. The walls are separated here by about 20 molecular layers, not just a few ‘lubricant’ molecules as might be the case in boundary lubrication. Thus, the present model has more in common with Couette flow in micro- or nanoelectromechanical systems (MEMS or NEMS)⁴⁵ than an Atomic Force Microscope (AFM) experiment. For example, pressure does not change the number of atoms per unit area in contact in the present model.

The shearing of region B by the sliding of the walls can be performed where the wall velocities are 0 and $2v(t)$ along one cartesian direction. Alternatively if the average wall velocities are equal and opposite, and the wall masses are the same, the simulation can be performed in an immobilised frame of reference connected with the center of mass. The total momentum of the system is conserved if the forces acting on the walls are equal and opposite, which is the procedure adopted here, and by Khare in a previous NEMD simulation of sheared bead-spring polymers under confinement.⁴⁶ Instead of fixing wall atoms to lattice sites which acts as an external force constraint, the conservation of the total linear momentum is used to facilitate the maintenance of the wall’s lattice structure.

External load imposition

The application of an average external load (‘barostat’) to the confined system needs to be carried out in a way which mimics experiment with minimal intrusion on the confined region dynamics. Different barostats have been proposed and used in the literature for the slit geometry which we have reviewed and discussed in Ref.³², Bulk-modified barostats,⁴⁷ have the problem that they uniformly scale the coordinates of the molecules which is inappropriate for a confined system where there are (naturally) density inhomogeneities. Also the instantaneous pressure of the system is not well-defined using

the virial route as the system’s volume is not well defined. In addition, a suitable value of the barostat feedback time constant, τ , which determines the system-barostat coupling is needed in the bulk barostats. This must not influence the calculated physical properties to any great extent. With such, ‘global’ barostats,^{44,48–50} the extra τ term is added to improve the ability to control the imposed load and eliminate possible instabilities caused by the barostat. Our equations to enforce an applied normal pressure overcome some of the above mentioned difficulties, as no instantaneous pressure, P_{inst} , needs to be calculated to drive the system. The normal pressure is applied through a constant external force to each wall atom and the ‘damping’ is provided by the constant b in the equations of motion (see below). This procedure is found to be sufficiently robust.

Interatomic interactions

The interaction potential used in the simulations was,

$$U(r) = 4a_1\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - a_2 \left(\frac{\sigma}{r} \right)^6 \right] \quad (1)$$

where ϵ is the reference potential (*i.e.*, $a_1 = a_2 = 1$) well depth and σ is the molecular diameter. The reduced units used for the presented quantities are based on a_1 and a_2 (both positive here) being set to unity. The value of a_1 between the wall atoms was set to 10 and it was 1 between the atoms in the confined region. The cross interactions between atoms in the walls and those in the confined region had the value, $a_1 = 1$, and $a_2 = 1$ was used as the default value, unless stated. The stiffness of the wall, and as a consequence the extent of dynamical coupling between the walls and the confined region, was tuned via a_1 . The parameter, a_2 , controls the affinity of the confined molecules with the walls, which increases with a_2 . This is often referred to as the ‘wetting’ parameter, as when a_2 increases the contact angle of a droplet of region B molecules next to a wall decreases.

Thermostatting

When the shear rate is applied to the system, it is important to remove heat to reach a steady state in the least intrusive way. A stochastic or Langevin thermostat has been used but its consequences have not been fully established, especially away from equilibrium,⁵¹ where the thermodynamic temperature is not defined. The definition of temperature for nonequilibrium systems is still an open problem. The thermodynamic expression for the temperature is in fact linked to the definition of the entropy, which, for nonequilibrium steady states is still under debate. Despite these reservations the kinetic temperature definition is a widely used operational choice.

The issue of thermostatting a confined fluid system as part of a dynamical system has been studied a number of times.^{51–53} Thermostatting the wall atoms rather than the confined sample is the most physically realistic option. The implementation of bulk system thermostats without modification may lead to spurious particle dynamics. A good example is the Nosé-Hoover thermostat which requires conservation of total linear momentum and a zero initial value.

For wall-confined systems we propose a solution to this problem. The wall-based thermostatting method can still conserve total linear momentum, which is proved in the Appendix for the Velocity Scaling (VS) method with a TM correction, and also for an extended Nosé-Hoover (NH) thermostat for an equilibrium system, *e.g.* in the absence of shearing. Even when the system is sheared the total (linear) momentum is conserved because the instantaneous shear forces on the two walls are equal and opposite.

In fact, we have used both tethered and non-tethered walls to implement boundary driven

shear under applied pressure, and in practice they apparently give (at least in broad detail) hardly distinguishable non-equilibrium phase diagrams.^{31,32} Realistic results can therefore be achieved using several ways of coupling the system to the outside world. The advantage of the present approach is that it is a well defined deterministic dynamical system which acts without recourse to tethered walls.

B. Shearing method equations of motion

The shearing method (‘shearostat’),³² used here applies a wall force which is proportional to the difference between the current relative velocity between the two walls and its target value, $2v_0$. For equal wall masses each wall necessarily translates with an equal and opposite mean value tending to v_0 , to conserve zero total momentum. The top and bottom walls do not have the same instantaneous average velocities because of the interaction with the confined part of the system. However, as the driving forces acting on each wall are equal and opposite at every time step, the total system momentum is conserved throughout the simulation. Therefore the center of mass is fixed. In the equations of motion only the relative velocity between the two walls is included specifically in the equations of motion.

The use of the relative velocity between the walls in the chosen equations of motion can be understood from Petravic’s discussion on the origin of friction in a finite volume.⁵⁴ It was shown that the equilibrium fluctuation expression for the friction coefficient of a massive particle in a liquid of finite volume decays to zero. The frictional force on the pushed particle goes to zero as the liquid just gets dragged along with it. It was argued that as the frictional force is proportional to the relative liquid-particle velocity, both particle and the finite liquid volume need to have infinite mass for the frictional force on

the massive particle to be finite at all times.

Consider a large particle of finite mass, m , moving through a viscous medium of infinite volume (or equivalently, mass). In this case, the frictional force will eventually decay in proportion to the particle's velocity at time t , or $v(t)$. The relation between the total force acting on it, $F_T(t)$, and the particle acceleration is, $a(t) = dv(t)/dt = F_T(t)/m$, where $F_T(t)$ is the sum of the driving, $F_d(t)$, and frictional, F_f , forces. Take the friction force to be proportional to the relative velocity between the particle and the host liquid, *i.e.*, $F_f(t) = -\eta v(t)$, where the friction coefficient, η , is a constant. If there is no driving force, the particle acceleration reduces to $a(t) = -v(t)\eta/m$, and the particle's velocity decays with time. It was shown in Ref.⁵⁴ that to maintain a constant velocity (*i.e.*, $v(t) \rightarrow v_0$, or equivalently $a(t) \rightarrow 0$) the particle mass needs to tend to infinity. In fact, this end result can also be achieved if the total force acting on the particle tends to zero, *i.e.*, if $F_T(t) \rightarrow 0$, which means that a constant average velocity can be achieved by applying a driving force which satisfies, $F_d(t) \rightarrow -F_f(t)$. Thus, instead of having two infinite masses moving relative to each other to determine the finite friction force, an average velocity of the finite mass particles (which in our case is a wall) can be maintained by exploiting Newton's first law, and balancing the finite friction force by a driving force. This is the foundation of the equations of motion for the shearing walls used here. The details are given below.

The NEMD equations of motion used in the simulations and according to the Fig. 1 are,³²

for region A,

$$\begin{aligned}\dot{\underline{r}}_i^A &= \underline{p}_i^A/m_i^A, \\ \dot{\underline{p}}_i^A &= \underline{F}_i^{AA} + \underline{F}_i^{AB} + \left\{ \underline{F}_i^{exA} + b \left(\frac{\mathbb{P}_A^z}{M_A} - \frac{\mathbb{P}_C^z}{M_C} \right) \hat{\underline{z}} \right\} + \left\{ \gamma \left(\left| \frac{\mathbb{P}_A^x}{M_A} - \frac{\mathbb{P}_C^x}{M_C} \right| - 2v_0 \right) \hat{\underline{x}} \right\},\end{aligned}\quad (2)$$

for region B,

$$\begin{aligned}\dot{\underline{r}}_k^B &= \underline{p}_k^B/m_k^B, \\ \dot{\underline{p}}_k^B &= \underline{F}_k^{BA} + \underline{F}_k^{BB} + \underline{F}_k^{BC},\end{aligned}\quad (3)$$

and for region C,

$$\begin{aligned}\dot{\underline{r}}_l^C &= \underline{p}_l^C/m_l^C, \\ \dot{\underline{p}}_l^C &= \underline{F}_l^{CC} + \underline{F}_l^{CB} + \left\{ \underline{F}_l^{exC} - b \left(\frac{\mathbb{P}_A^z}{M_A} - \frac{\mathbb{P}_C^z}{M_C} \right) \hat{\underline{z}} \right\} - \left\{ \gamma \left(\left| \frac{\mathbb{P}_A^x}{M_A} - \frac{\mathbb{P}_C^x}{M_C} \right| - 2v_0 \right) \hat{\underline{x}} \right\},\end{aligned}\quad (4)$$

where $\underline{p}_i, \underline{p}_k$ and $\underline{p}_l$ are the atom momenta, $\mathbb{P}_A^x, \mathbb{P}_C^x, \mathbb{P}_A^z, \mathbb{P}_C^z$ are the total instantaneous momenta of walls, A and C in the x and z directions, respectively. The forces, $\underline{F}_i^{AA}, \underline{F}_k^{BB}$ and $\underline{F}_l^{CC}$ denote the pair forces between atoms within regions, A, B and C. The quantities, $\underline{F}_i^{AB}$ and $\underline{F}_l^{CB}$, denote the cross forces between atoms in the denoted regions. The atom indices range from $i = 1, \dots, N_A$, in region A, and $l = 1, \dots, N_C$ in region C. The term, $(\mathbb{P}_A^z/M_A - \mathbb{P}_C^z/M_C)$ is the relative wall speed in the z direction, and $\underline{F}_i^{exA,C} \pm b(\mathbb{P}_A^z/M_A - \mathbb{P}_C^z/M_C)\hat{\underline{z}}$ is the force responsible for maintaining the target pressure (*i.e.*, the ‘barostat’ term). The relation between the normal pressure P_N and external force in the z direction is $\underline{F}_i^{exA} = -(P_N S/N_A)\hat{\underline{z}}$, and $\underline{F}_i^{exC} = (P_N S/N_C)\hat{\underline{z}}$ for the two walls. The extent of coupling between the system and the barostat is controlled through the constant, b .

In Eqs. (2) and (4), the term, $|\mathbb{P}_A^x/M_A - \mathbb{P}_C^x/M_C|$ is the relative wall speed in the x direction, and, $\pm\gamma(|\mathbb{P}_A^x/M_A - \mathbb{P}_C^x/M_C| - 2v_0)\hat{\underline{x}}$ is the applied shear force, which we refer to as the ‘shearostat’ or the driving force, $\underline{F}_d(t)$ term. The target macroscopic or

nominal shear rate in the confined region of thickness h is $2v_0/h$, where, h , is typically a function of applied pressure, v_0 , and time under barostatted conditions. The extent of coupling between the system and the shearostat driving term is governed by the magnitude of, γ . In Ref.³² it was shown that the driving force causes the walls to move with an average velocity, v_0 , for a range of γ -parameter values, and in this study the parameter γ was set to 200.

III. RESULTS AND DISCUSSION

The nonequilibrium phase and frictional behavior of the confined molecular system under external pressure and shearing is mapped out here. The confined system was periodic in the x (streamwise) and y (spanwise) directions and bounded by the walls in the z direction. The Lennard-Jones (LJ) potential was used for the pair interactions between the atoms, with parameters corresponding to argon of, $\epsilon/k_B = 120$ K and $\sigma = 0.340$ nm, and a force truncation distance equal to 2.5σ . The results are given, unless stated, in reduced units of σ for length, and $(m\sigma^2/k_BT)^{1/2}$ for time, where k_B is the Boltzmann's constant. Energy is in units of ϵ and the atomic mass, m , is the unit of mass. The applied pressure and sliding speed are also given in SI units where explicitly indicated. The MD calculations were performed with the walls at a constant reduced temperature, $T^* = k_BT/\epsilon = 1$ using the velocity scaling thermostat applied only to the wall atoms. The equations of motion were integrated with the Verlet leapfrog algorithm⁵⁵ using a time step of 0.005. The system consisted of $N = N_A + N_B + N_C$ atoms in total, where $N_A = N_C = 576$ are for the walls, and $N_B = 1440$ for the confined region B (see the slab geometry annotation on Fig. 1). Region B was started from a face-centered cubic (FCC) solid made from 18 layers of $[6 \times 6]$ four-atom cells in the xy plane, with the $[100]$ axis

along the x direction. The walls took the form of either, (a) a non-crystalline solid or (b) four FCC(100) layers of $[6 \times 6]$ four-atom cells, which are commensurate with the initial FCC structure in region B. Thus, two different types of ABC slab were studied, one with crystalline walls, denoted as the ‘FF’ structure, and one with noncrystalline and atomistically rough walls referred to as the ‘RR’ structure. The calculations were performed on a (v_0, P_N) grid of more than 400 state points composed of 21 uniformly distributed external pressure, P_N , values in the range, $0 - 2000$ MPa, and 21 evenly spaced target speeds, v_0 , in the range $0 - 200$ m/s. For each (v_0, P_N) value, a production simulation of 2×10^5 time steps which corresponds to 1000 reduced time units (2.5 ns) was carried out, each after an equilibration simulation of the same length.

The time average friction coefficient was calculated from, $\langle F_x \rangle / F_N$, where F_x and F_N were estimated from the stress tensor components calculated according to the Method of Planes.³⁹ The frictional force allows for a more direct comparison with classical macroscopic laws of friction. The friction coefficient being a unitless scalar quantity enables a better comparison with the behavior of other materials and processes to be made.

A. Non-equilibrium states and FF wall tribological properties

Different confined region steady state structures were seen to appear as a function of v_0, P_N . The large number of (v_0, P_N) -points considered enabled the tentative steady state phase diagram presented in Refs.²⁷ and³¹ to be established in greater detail. The enhanced resolution reveals new types of particle arrangements and more precisely determined physical state boundaries. This includes some newly observed regions which

were not discovered in our previous NEMD studies. The physical and structural states produced were identified using velocity, temperature and density profiles, the measured friction coefficient and assembly atom configuration snapshots. Four different classes of steady state were identified from the simulations, namely, Liquid (L), Central Localized (CL), Stick-Slip (SK-SL) and Plug-Slip (PS) states, which are discussed under their respective headings below.

Liquid (L)

Examples of the liquid state are shown in Fig. 2. In this state a molecule can explore

FIG. 2: Projections of the instantaneous particle coordinates on the xz plane of three state points in the ‘Liquid’ (L) steady state region of the phase diagram. The specific (v_0, P_N) pair values are given on the figure. The solid wall particles in the bottom and top parts of the figure are shown in red online, and the confined particles in the middle are green. The arrows on the two walls indicate the direction of the applied target sliding speed, v_0 . Alongside are shown the corresponding time average density, $\rho(z)$, velocity, $v(z)$, and temperature, $T(z)$ profiles.

any point in the confined region given enough time. The (normalized) velocity profile, $v(z)$ across the region between the walls is approximately linear in z (corresponding to the classical Couette flow), apart from near the walls. The temperature profile, $T(z)$, is parabolic while the density profile, $\rho(z)$, is flat in the middle of the confined region, apart from oscillations near the wall, which is well known to occur for liquids in

general near solid walls (*e.g.*, see Refs.^{56,57}). The values of the friction coefficient are relatively low, mostly less than 0.1. The friction coefficient of liquids against a solid wall under ambient conditions is typically very much smaller. For example, assuming stick boundary conditions, $\mu \sim (d\eta/dP)(dv_0/dz)$, where the last term is approximately the shear rate. For example, for *n*-octane,⁵⁸ $(d\eta/dP) \sim 10^{-11}$ s, so even with a very large shear rate of 10^7 s⁻¹, the friction coefficient would still only be, $\sim 10^{-4}$. Therefore for the liquid in molecularly thin gaps the friction coefficient can still be much larger than for the bulk liquid against a wall.

On the (v_0, P_N) diagram this steady state liquid forms for relatively low values of pressure, which depends on v_0 and to a good approximation complies with the condition, $P_N < 173 + 4.16v_0$. The non-equilibrium liquid state can exist at pressures and temperatures outside the normal equilibrium range. It will have, however, certain structural and dynamical differences from a ‘normal’ liquid, for example, in being anisotropic on the molecular scale due to the shearing action, and in sustaining a time averaged non-zero shear stress (and therefore continuous heat production) which is not the case for equilibrium liquids.⁵⁹

The film solidifies at high pressure, but this is not a prerequisite for a molecularly thin film to behave in this way. For example molecular dynamics simulations on dodecane,²⁵ have shown that even near atmospheric pressures films 6-7 molecules thick can solidify.

Central Localization (CL)

This type of steady state dynamical structure forms when the applied external pressure is sufficient to order the region B molecules next to the walls so that they are in registry with the wall atoms, but with a fluid region in the central part of the confined film.

FIG. 3: As for Fig. 2 except the state points shown are in the Central Localization (CL) steady physical state region.

This is illustrated in Fig. 3 for selected nonequilibrium state points. The width of the central melted part increases with wall velocity. Compared to the liquid state, L, the velocity profile in the central region exhibits a greater slope than what would be the Couette average ($2v_0/h$), as the confined atoms next to the walls are hardly flowing. The temperature profile is parabolic in the central part where the system is melted. In the solid part of the confined region the temperature profile is essentially linear between the walls and the melted region, which is typical of a solid between a heat source and sink.⁶⁰ The density profiles help to confirm the formation of a crystal arrangement of the particles near the walls. In this state the friction coefficient, $\langle\mu\rangle$, is larger than in the liquid state, being typically in the range, $0.1 - 0.25$.

Stick-Slip (SK-SL)

Representative snapshots of Stick-Slip configurations for $P_N = 600$ MPa and $v_0 = 2$ m/s are shown in Fig. 4 together with the associated time average steady state velocity, temperature and density profiles. In this region of the state phase diagram the wall frictional force fluctuates strongly with time and it has an approximate underlying periodicity, as illustrated in Fig. 4. The average friction coefficient is relatively high, with a value in the range $\langle\mu\rangle \simeq 0.25 - 0.50$. This behavior occurs for relatively low sliding speeds in the

FIG. 4: As for Figs. 2 and 3 except three typical Stick-Slip steady states are shown. Note that the applied pressure and wall speed are lower than for the CL states of the previous figure.

range, $0 < v_0 < 30$ m/s and in an external pressure range of, $400 < P_N < 800$ MPa. This type of behavior has been observed using SFA and frictional force experiments for many chemical systems.^{61–64} Although it is widely known as ‘Stick-Slip’ behavior, its specific origin for confined films, as discussed in the Introduction, has not been definitively established. Most studies of SK-SL are for thin films near the boundary lubrication regime. In contrast our studies are for thicker films, like those of Khare.⁴⁶

These simulations reveal that in the SK-SL state the sample undergoes regular periodic changes from an FCC solid to the sliding structure in which particles form melted or partially melted layers. The size, amount and location of the layers changes with time, which produces characteristic density profiles. Because of the repeated structural changes this process generates much heat (like latent heat of melting) which is reflected in the high friction coefficient values observed. Figure 5 shows that the resistance to sliding increases in the solid part of the cycle and decreases in the melted state. This is in fact a more chaotic process than is often portrayed schematically in the literature, however, because the location and cycle time depends on a solid nucleation event taking place.

Figure 5(a) shows from top to bottom the time-dependence of the potential energy U , temperature of the central region, T , instantaneous friction coefficient, μ , and system

FIG. 5: Panel (a): From top to bottom lines represent the time-dependence of the instantaneous potential energy $U(t)$ (the green line), temperature $T(t)$ (the blue line), friction coefficient $\mu(t)$ (the black line), and distance between the centers of mass of the two walls $L(t)$ (the red line) in the Stick-Slip part of the state diagram. The state point has the values, $P_N = 600$ MPa, and $v_0 = 2$ m/s, which is the same as for the right frame of Fig. 4. The left and right panels present snapshots of the system when stick and slip respectively occur, which is indicated by arrows towards specific times on the central frame. Panel (b): The position ($x(t)$, $y(t)$, $z(t)$) of a typical molecule from the central region (the blue, red and green line respectively) during stick-slip and xy plane snapshots of the system before, during and after slip in the 5th and the 7th layer of the system. The green line $z(t)$ suggest that the particle is trapped in the certain layer.

thickness, L . It may be seen that the friction coefficient correlates well with U and L as might be expected. The main temperature rise occurs just after μ and U decrease

rapidly at the end of the stick state. The temperature behavior suggests that most of energy dissipation occurs within the following slip stage, as also shown in Refs.²⁶ and¹⁸. The left and right panels present snapshots of the system when stick and slip respectively occur, which is indicated by arrows towards specific times on the central frame. The stick state is more ordered than the slip state but both are layered. The time dependence of the cartesian coordinates of a typical particle are shown in Fig. 5(b). These can be seen to undergo a series of ‘jumps’ of the x and y coordinates in the layer plane, but do not move between layers (as $z(t)$ is statistically constant on the layer separation scale). This suggest that the stick-slip behavior for the class of system modeled here is an ordering-disordering transition *within each layer*, rather than of the whole confined region becoming disordered. This **persistence** of the layering structure in the stick and slip states was discovered by Lie and Leng,¹⁸ from their NEMD simulations.

Thompson and Robbins,⁴³ in their NEMD simulations found SK-SL behavior in the same wall speed range where it is also seen in this study. Figure 5 is qualitatively very similar in the thickness and μ time dependence to Fig. 2C in Ref.⁴³. The sliding speed used there was $v_0 = 15.8$ m/s, while in our cases we observed stick-slip behavior in range of the sliding speed $0 - 25$ m/s. Even though their system is much smaller than ours (432 LJ atoms as opposed to 2592 atoms here), the period of the stick-slip step is comparable (230 as opposed to 77 reduced time units here). The SK-SL behavior has been observed using SFA, and frictional force experiments have been carried out on many types of lubricant-like molecule (e.g. cyclohexane, octamethylcyclotetrasiloxane, n-octane, n-tetradecane and branched isoparaffin 2-methyloctadecane).^{21,22,63} These are for much smaller applied sliding velocities, v_0 , typically in the range $0.5 - 50$ $\mu\text{m/s}$ which is effectively in the $v_0 \rightarrow 0$ limit from the point of view of our simulations. As typical for

NEMD the employed shearing rates are much larger than experiment, as also pointed out by Lei and Leng,¹⁸ but here they serve to demonstrate that the SK-SL behavior can extend to much larger sliding speeds under specified conditions. We note, in addition, that the sliding speeds we consider in our simulation are in fact realizable in some real systems, for example, elastohydrodynamic lubrication (typically up to *ca.* 4 m/s), and the sliding speed between the disc platter and the head in computer hard drives is in the range 0 – 50 m/s. Note that in this (v_0, P_N) region, the NEMD simulations reveal that the Stick-Slip behaviour observed is a steady state **oscillatory** phenomenon.

Plug-Slip (PS)

FIG. 6: Several examples of Plug-Slip steady states for different normal pressure values and sliding speeds specified on the figure. The time average density, $\rho(z)$, velocity $v(z)$ and temperature $T(z)$ profiles are shown together with the corresponding particle assembly snapshot configurations. The solid plug is indicated by a blue dashed rectangular frame. The ‘Wet’ and ‘Dry’ interfaces are denoted by W and D.

The part of the (v_0, P_N) diagram with parameter ranges, *ca.* $v_0 < 50$ m/s and $P_N > 700$ MPa is characterized by the presence of a solid plug on the inside of the confined region. Representative examples of the PS state are shown in Fig. 6. The orientation and structure of the plug is different from that of the wall. Also, the plug may be attached to one of the walls, when its orientation or (and) structure is different from the wall particle arrangement. This can be concluded from the velocity profile. For example, in

the leftmost frame of Fig. 6 (where $P_N = 1100$ MPa, and $v_0 = 10$ m/s) the plug can be considered to be attached to the top wall because the upper part of the confined region velocity profile has the same velocity as the upper wall.

Two types of shear localized boundary are defined. A boundary is termed ‘dry’ (D) if the velocity profile $v(z)$ undergoes a sharp change over about one molecular diameter (as seen on panel c of Fig. 6). In panel (a) the lower interface is denoted by W (for ‘wet’) as it can be seen that $v(z)$ changes over at least three layers (molecular diameters). The bottom wall moving in the opposite direction is clearly lubricated as it shears monotonically in the lower boundary region. In fact, the interface changes with time and although the snapshot of the plug looks well defined and crystalline, it undergoes intermittent local melting.

It can be difficult to define exactly the structural state of the region between the wall and plug when shearing takes place. This can make the tribological properties and mechanisms more difficult to interpret than in the other generic states. Figure 6(c) clearly shows two dry shearing interfaces, as the velocity profile $v(z)$ undergoes a sharp change several layers into the confined region. The state of the plug between the walls can be defined by its solid crystal symmetry and its orientation relative to the walls. By inspection it was observed that the plug in the PS phase always had a different orientation and (or) symmetry to that of the walls, even though the $v(z)$ profile might suggest that the system is shearing in only one region (as evident in Fig. 6). This aspect of the solid state behavior was also identified in the PS region for very low velocities ($v_0 < 2$) m/s in Ref.²⁷. In that work this occurrence was attributed to dry slippage of the confined solid at one of the walls. As seen here, this is a special case of a more general picture, as the PS interface can be classified as being so-called dry or wet.

Because some of the structures span the simulation cell in the periodic directions there will inevitably be more of a system size dependency for these. The present set of data used 6×6 four-atom unit cells in the periodicity plane. Test simulations with 4×4 and 12×12 gave practically the same phase results as for 6×6 . The 8×8 case showed more sensitivity in the PS phase, however. The plug in our system can adopt various semi-crystalline or polycrystalline states which can have a different periodicity length to the FCC structure of the walls. A greater system size dependence of the PS state on the grounds of particle packing is perhaps to be expected therefore.

FIG. 7: The nonequilibrium phase diagram of the FF type of system displayed on the (v_0, P_N) plane. The regions on the map where the different types of steady state structures form are indicated. The annotation, L, SK-SL, PS and CL refers to the Liquid, Stick-Slip, Plug-Slip and Central-Liquid regions, respectively. The extended TR region indicates gradual transition regions between the various phases going through intermediate structures which are difficult to characterize in simple terms. The square lattice indicates the (v_0, P_N) grid points used in simulations.

FIG. 8: Contour map of the friction coefficient, $\langle \mu \rangle = f(v_0, P_N)$ of the FF system. The friction value scale is given separately in the right hand frame. The boundaries between the persistent nonequilibrium phases shown in Fig. 7 are marked with dotted red lines. The stars indicate points on the P_N, v_0 grid that are used for the lines given on Fig. 9.

The domains of stability of the L, CL, SK-SL, and PS steady states on the (v_0, P_N) diagram are shown in Fig. 7, and the corresponding friction map is given in Fig. 8. In the figure the extended light grey area denoted by ‘TR’ for ‘transitional region’ is where state classification is uncertain from the $v(z)$, $T(z)$, $\rho(z)$ profiles and particle configurations. In general there is a good correlation between the phase and friction map diagrams. The L, CL and SK-SL regions identified on Fig. 7 correspond well to the map of friction coefficient regions where, $\langle\mu\rangle < 0.1$, $0.1 < \langle\mu\rangle < 0.25$ and $\langle\mu\rangle > 0.25$, respectively.

A notable feature of the friction map in Fig. 8 is the non-trivial tribological nature of the PS steady state region, as the friction pattern consists of irregular patches with $\langle\mu\rangle$ varying considerably between very low values typical of the liquid to higher values typical of the CL phase. Analysis of the plug structures revealed that the very low values of $\langle\mu\rangle$ in the PS region occurred when an easily sliding solid layer on the plug surface was oriented parallel to the crystalline wall surface, which is the ‘dry’ case. **The calculation of the PS region was performed several times with different (v_0, P_N) paths and length of equilibration.** Even though the $\langle\mu\rangle = f(v_0, P_N)$ pattern of the PS region in Fig. 8 depends slightly on the history of how each v_0 and P_N value was reached from previous states, the irregular friction map pattern and range of $\langle\mu\rangle$ -values from 0 to 0.25 exhibited remained a characteristic feature of the PS state.

B. Consequences of the wall atom - confined molecule interactions

Figure 9 shows the influences on $\langle\mu\rangle$ from the form of the pair potential between the wall atoms, as controlled through the well depth parameter, a_1 in Eq. (1), and between the wall and confined region atoms adjusted through the wetting parameter, a_2 in Eq. (1).

Additional simulations varying these parameters were carried out along the CL-L path in the pressure range, 500 – 1000 MPa. Figure 9 shows that for a range of sliding

FIG. 9: Dependence of the friction coefficient on the two parameters of the modified LJ potential given in Eq. (1). The simulations were performed for, (a) fixed value of $a_2 = 1$ and various values of a_1 , and (b) a fixed value of $a_1 = 2.5$ and various values of a_2 applied to the cross interactions, U_{AB} and $U_{BC}(r)$. The P_N and v_0 values correspond to a CL to L phase path at $P_N = 500$ MPa. The same trend was obtained for $P_N = 1000$ MPa in L phase. Points where these results were obtained are indicated by stars markers on Fig. 8. The time average friction coefficient, $\langle \mu \rangle$, is plotted as a function of a_1 or a_2 for selected values of sliding speed given on the figure. The various colored lines and symbols indicate different sliding speeds, as specified in the annotation.

speeds between 50 – 100 m/s, the friction coefficient changes almost linearly with a_1 and a_2 . The friction coefficient decreases with increasing a_1 and increases with a_2 . These parameters have a strong effect for the well-compressed and thin liquid region found for

some of the PS, CL, and (high pressure) L cases. The a_1 and a_2 sensitivity is hardly noticeable at low pressure. For phases where the liquid gap is large and the pressure is low no major changes in $\langle\mu\rangle$ were observed when a_1 and a_2 were varied in this range.

The interaction parameters, a_1 and a_2 affect the collision statistics between wall and therefore the translational kinetic energy dissipation in the system. Hence one might expect a_1 and a_2 to influence the value of the friction coefficient. This dependency is especially noticeable at high pressure (e.g. $P_N = 500$ to 1000 MPa) when the wall and confined region atoms are strongly coupled. Their effect is hardly evident for lower values of normal pressure (e.g. $P_N = 100$ MPa) as the parameter effects are more distributed within the rest of the liquid. When a_1 increases, the rigidity of the walls increases and the kinetic energy is removed less efficiently from the sheared region as there is weaker coupling between the wall and confined region dynamics. This causes the friction coefficient to go down with increasing a_1 . When the wetting parameter, a_2 , increases the attraction or adhesion between the wall and confined region atoms increases, hence enhancing their dynamical coupling and therefore friction coefficient. For the range of values of a_1 and a_2 considered in Fig. 9 no significant changes in the steady state phase diagram were observed. However, in general, it should be expected that the potential parameters can influence the phase formed. In fact, this was observed in similar NEMD simulations for a_2 in the $0.1 - 1$ range (*i.e.*, in the dewetting region) considered in Refs.^{27,31}. In the present study the a_2 values considered are in the range, $1 - 10$, to explore the effects of strong attraction between the wall and confined liquid.

C. Film Thickness

Granular systems dilate when flow is initiated from a stationary state.⁶⁵ It might be anticipated that the time average thickness, $\langle L \rangle$, measure of the region B gap would be a signature of its non-equilibrium structural state or phase. This possibility is investigated with the aid of Fig. 10, which shows the v_0 dependence of the gap thickness and the friction coefficient for selected pressure values.

FIG. 10: The average thickness of the system $\langle L \rangle$ in the z direction, and corresponding friction coefficient $\langle \mu \rangle$ as a function of P_N and v_0 in the PS and CL regions. See Fig. 8 for the location of the states on the phase diagram. The blue bold markers indicate the border between abnormal and expected monotonic behavior and where the CL phase starts. The dashed lines are the friction coefficient and the continuous lines are the confined film thickness.

In the CL region the film thickness increases monotonically with v_0 and almost linearly in some cases. The friction coefficient (or equivalently the frictional force as the normal load is constant along the line) decreases with increasing wall speed which is contrary to the experimental trend at low pressure.¹¹ This is possibly because here the gap increases at the same time to an extent at high pressure that the confined region offers less resistance to shear.

In the low wall speed PS region, Fig. 10 shows that the correlation between the film thickness and friction coefficient properties is less evident. In fact the film thickness in places in the (v_0, P_N) plane can decrease with increasing v_0 . Irregular behavior of $\langle\mu\rangle$ in the PS region is reflected in irregular but not always well correlated variations in $\langle L\rangle$. In general the degree of a correlation between $\langle\mu\rangle$ and $\langle L\rangle$ is weak, if at all, in the PS phase region. This is in contrast to observations for the Stick-Slip region where the instantaneous L and μ trends are more closely connected and regular (see Fig. 5).

D. Hysteresis in the system

In this section the sensitivity of the system behavior at a given (v_0, P_N) to the history of previous states is investigated. Additional calculations were performed at a fixed value of P_N and gradually increasing the sliding speed from $v_0 = 0$ to $v_0 = 200$ m/s at the rate of $\delta v_0 = 0.15$ m/s every 10 time steps, up to the final target value. Each value of v_0 was obtained with a precision of $\simeq 10^{-4}$ of the root mean square thermal velocity. The resulting friction map is shown in Fig. 11. On reducing the sliding speed gradually from $v_0 = 200$ to $v_0 = 0$ m/s for each P_N value, the $\langle\mu\rangle$ -map produced is qualitatively similar to that of Fig. 8. Hysteresis is rather weak in the L, CL and SK-SL regions, but can be significant for those states originating in the PS domain.

Figure 11 shows that on increasing the wall speed from a point within the PS region to take the system into the CL region *i.e.*, for $P_N \approx 1500$ MPa, and v_0 between 25 and 75 m/s, the friction behavior is different. The rectangular region marked on the figure highlights the new $\langle\mu\rangle$ behavior, in which the very low friction PS behavior is

FIG. 11: The friction coefficient map of the FF system, which follows the same type of plot in Fig. 8 but is obtained by increasing the velocity of sliding from a very low value and at constant P_N . The bold dash-dot line indicates that significant hysteresis behavior occurs within this region, which is illustrated further in the snapshot configurations given in Fig. 12.

seen to extend far into CL area. The atom assembly snapshot structures associated with the rectangular box region in Fig. 11 are shown in Fig. 12. At $P_N = 1500$ MPa and when the sliding speed is first increased up to $v_0 = 180$ m/s the PS structure can be seen to persist along the top row of frames. The central plug region planes become more aligned with the flow (see the bold dash-dot lined rectangle). This PS state is retained on decreasing v_0 back to $v_0 = 10$ m/s. The atom configurations reveal that this trend can occur if a solid plug in the PS regime has a dry contact with the walls so that an easily sliding contact interface is developed, which can persist to much higher speeds than is typical of that nonequilibrium phase. This structure is stable and long-lived even when the applied sliding speed is changed slightly.

Thus, in these confined sheared systems it may be possible to achieve a particular desired stable tribological state at a given (v_0, P_N) point by following a predetermined pressure

FIG. 12: Particle configurations for $P_N = 1500$ MPa and the marked area in Fig. 11. The top row of frames follows increasing wall speed from left to right. The bottom row of frames indicates a decreasing wall speed from right to left, starting from the last configuration of the top row.

and wall velocity path to get to that point. In particular, to maintain low $\langle\mu\rangle$ values with increasing sliding speed it can be favorable to increase first the pressure to the desired value at low v_0 (preferably in the PS region), and then increase the sliding rate so that the PS state structure persists to much higher v_0 . This effect presumably arises because of a high energy barrier along the (probably) narrow transition path between the PS and CL states. In experimental systems one might expect these trends to appear for molecularly thin films such as is found in boundary lubrication.⁶⁶

The friction force map, $\langle F_f \rangle = f(v_0, P_N)$ shown in Fig. 13, takes the form of a 3D perspective (note that Figs. 8 and 11 show the friction coefficient map). The figure shows that for most of the diagram, that is, in the L, SK-SL and CL regions, there is a monotonic increase in frictional force with pressure. This trend is consistent with Amontons' first law for macroscopic bodies which states that the frictional force is proportional to

FIG. 13: Friction force map $\langle F_f \rangle = f(v_0, P_N)$ of the FF wall type shown in 3D landscape form. The red dotted line in the top left hand corner marks the limit of the irregular friction force behavior area. For further clarification, representative examples of the friction force dependence on the applied load are marked on the figure as red, blue and black lines for three v_0 of 20, 100 and 180 m/s, respectively.

the applied load. However, the $\langle F_f \rangle$ decreases with increasing wall speed which conflicts with Coulomb's Law of Friction^{1,67} which states that the kinetic frictional force is independent of the sliding velocity for macroscopic bodies. More pronounced deviations from macroscopic friction are evident in the PS state region where it can be seen that the friction force is nonmonotonic in load and can even in places decrease with increasing pressure and v_0 . This counterintuitive friction coefficient behavior was also observed in experimental studies of Deng *et al.*,⁶⁸ who demonstrated that an increase in normal force can lead to a decrease in the frictional force. It is reasonable to conclude that this is a consequence of structural changes in the film caused by that change in load which affect the slipperiness of the boundary.

E. Phase and tribology behavior for rough walls (RR)

It is known that the structure and roughness of the wall can have a considerable influence on tribology on both the macroscopic and atomic scales, which can be important in practical applications. There have been experimental and some NEMD studies of this effect (see for example Refs.^{3,69-72}). Roughness can increase or decrease the flow rate and slip length depending on the chemical nature of the wall and liquid (*e.g.*, broadly hydrophobic or hydrophilic in interaction), and the relative size of the wall roughness and its periodicity compared to that of the dimensions of the molecules of the confined system. It is therefore of interest **to explore the effect surface roughness has** on the present system's structural and tribological phase diagram. We confine our attention to relatively modest extents of roughness with low amplitudes and periodicities of order the molecular diameter of the liquid molecule (*i.e.*, not pillared or patterned surfaces typical of MEMS devices).

The above simulation results were obtained using a FCC crystalline wall, which may be considered to be atomically smooth in the present context. The effects of atomic-scale roughness were explored in this study by melting the whole FF system and then freezing it rapidly. This was used as the starting structure for each value of P_N, v_0 . The values of P_N, v_0 were then achieved following the same procedure as for the previously presented FF systems. Each load and speed on the grid the system was brought to the target P_N and v_0 by gradually and simultaneously increasing the normal pressure from the same initial low load pressure, P to P_N and from an initial low speed v to v_0 . The increments of wall pressure were, $\delta P = 42$ Pa and for the wall speed were, $\delta v = 0.15$ m/s every 10 time steps up to the final target value. These increments were chosen in a random order but with fixed magnitude to avoid hysteresis effects between neighboring state values, a

procedure which was considered to be physically in keeping with typical experimental protocols.

The phase diagram was obtained at least three times starting from different initial rough wall configurations. The phase and tribological diagram produced in the three cases was the same within simulation statistics. All three regions illustrated in Fig. 1 were initially noncrystalline. The FF wall structure was ordered and statistically the same for both walls, while in the RR case it was always asymmetric with the atom positions irregularly positioned on an atomic scale in a different way on the two walls. This asymmetry had a significant influence on the formation and nature of the steady states produced, as will be shown below. The interaction between the wall atoms was relatively strong and no mixing or exceptional penetration of the wall boundary atoms into the central region was observed. The surface structure did change by a small amount during sliding and a slight change of roughness probably occurred. The interest here was not in producing a detailed map of the roughness dependence on $\langle\mu\rangle$, but rather in establishing the extent to which a rough wall can change the phase and frictional characteristics.

Figure 14 shows the (v_0, P_N) map of the nonequilibrium states phase diagram obtained for the RR system, which should be compared with Fig. 7, the corresponding plot for the FF system. The various steady-state structures and states were identified from the density, velocity and temperature profiles, and analysis of the snapshot particle configurations. This is the same procedure as used for the FF systems. Figure 14 shows that at low pressures there is the L phase, and a somewhat expanded PS phase at high pressure. There are some differences however, in that the L steady state possesses a more upwardly curved boundary, and the PS region extends towards larger v_0 (*e.g.*, *ca.*

FIG. 14: Diagram of steady state phase structures of the RR system. Three main regions established are, Liquid (L), Plug-Slip (PS), and between them, labeled ‘Mainly AM’, denotes a ‘mixture’ of AM, PS and various unclassified structural states identified from the $\rho(z)$, $v(z)$, $T(z)$ time averaged profiles and atom assembly snapshots. A square lattice indicates the (v_0, P_N) points at which the simulations were performed.

140 m/s at $P_N = 2000$ MPa). There is no Stick-Slip behavior in the RR systems, which suggests that the solid (crystalline) state needs to occupy the whole of the gap for the system to manifest this effect. The RR (v_0, P_N) phase diagram is quite different to the FF case in the main aspect that an Asymmetric Melting (AM) state appears approximately in the region where the CL states appeared for the FF system. This qualitative change was observed in Refs.^{27,31} but for somewhat different system parameters and conditions. New features and a more extensive investigation of the AM state are reported here.

Asymmetric Melting (AM)

Figure 15 gives a molecule assembly snapshot of an AM state which shows the confined region solidifying at the upper surface wall. The confined region molecules organize to conform to one of the wall surfaces which then pulls the rest of the confined system along with it. Initially liquid particles fill the irregularities on the wall surface and a defect

FIG. 15: A particle configuration snapshot of an Asymmetric Melting (AM) steady state for a particular normal pressure value (700 MPa) and sliding speed (70 m/s). The time average density, $\rho(z)$, velocity $v(z)$ and temperature $T(z)$ profiles are shown alongside the particles snapshot configuration. As in Figs. 2, 3, 4, 6, the solid wall particles in the bottom and top parts of the figure are shown in red online and the confined particles in the middle given in green. The horizontal arrows indicate the direction of the applied sliding speed, v_0 .

crystal structure is created. Then, after the formation of a layer several molecules thick of this structure, further growth develops with a more crystalline structure, but with dislocations.

The $v(z)$ profile shows that slip takes place only in the vicinity of the lower wall. The defected crystal surface can grow on either surface, which is consistent with the formation of the AM structure being by a heterogeneous nucleation process. The opposite boundary zone is partially melted, which is where the transition between the macroscopically imposed shear velocity difference between the two walls takes place. Therefore in the AM state there is only one sheared interface. The velocity, $v(z)$, and temperature, $T(z)$, profiles are asymmetric, indicating the physically different solid and liquid regions near the two walls. The precise location of the boundary between the two regions is less well defined, however, and the diffuseness of this solid-liquid interface is a characteristic feature of this nonequilibrium phase. In fact, in the AM region marked on Figure 14 there was quite a large variability in the structures formed, with some looking more PS-like or L-like depending on the P_N, v_0 location. Even in the region

where the CL phase would be expected, sometimes the PS state formed, presumably **because the molecules assembled on the rough walls in a way** that favored the creation of a plug. There was more variability between individual realizations of the system in this part of the P_N, v_0 diagram than for the FF systems. The overall structure eventually formed depended on how the molecules organized initially on the two wall surfaces.

FIG. 16: The friction force map, $\langle F_f \rangle = f(v_0, P_N)$, for the RR walls system shown in 3D landscape form. Several representative lines of the friction force dependence are marked on the figure. The red, blue and black lines are for 20, 100 and 180 m/s wall speeds, respectively. The red dotted line marks out the boundary of the irregular $\langle F_f \rangle$ behavior regime.

Figure 16 presents the RR friction force dependence on normal load and sliding speed as a 3D plot, which broadly corresponds to that shown in Fig. 13 for the FF system. The friction coefficient map of the RR system is quite featureless compared to the FF case. The form of $\langle \mu \rangle = f(v_0, P_N)$ in the L and PS regions is similar to that in Fig. 8, and the ‘AM’ region displays some irregularities. Also the $\langle \mu \rangle$ -values are typically lower and do not exceed 0.25. As for the FF system, Amontons’ first law is not always obeyed,

especially in the PS region. As may be expected, because in the RR system the PS or AM-PS regions dominate more of the P_N and v_0 parameter space, the irregular friction behavior extends over a wider independent variable domain than in the FF system case. Figure 16 also shows examples of $\langle F_f \rangle = f(F_N)$ for three v_0 values which shows that Amonton’s first law is obeyed only in a limited (mainly Liquid) range of v_0 and P_N , which is below the dashed red line. The dashed red line shows the boundary between classical and unusual friction behavior.

Previous NEMD simulations of amorphous versus crystalline walls for confined alkane systems have been performed, which have shown the strong link between the atomic scale roughness and the phase and frictional trends. For example, Jabbarzadeh *et al.*,⁷⁰ showed that amorphous walls can sustain liquid-like states to smaller gap widths than is the case for crystalline walls, with a decrease in the effective yield stress. These calculations showed a significant difference in behavior of dodecane films confined between amorphous surfaces, which at 300 K retained liquid-like behavior down to film thicknesses of at least 1.8 nm. Films confined between crystalline surfaces showed an abrupt transition to a very high viscosity state at a film thickness of 4 nm.

IV. CONCLUSIONS

In this work the friction coefficient, and friction force maps are presented and interpreted in the light of the accompanying non-equilibrium phase diagram. The focus is not so much on the boundary lubrication and AFM type experiments, but more on the fully lubricated thick film limit which is a prototype model closer to elastohydrodynamic lubrication in real experiments.^{37,73} The emphasis is on the nonequilibrium states-friction map relationships. The advantage of NEMD is it provides both the tribology and the associated confined film nonequilibrium phase diagram as a function of the wall sliding speed and applied normal pressure, the two being linked manifestations of the same state. In fact, the present results appear to be the first comprehensive comparison of these links by NEMD for this tribological regime.

Stick-Slip behavior is observed which is shown to be accompanied by a novel recurrent in-plane melting of crystalline layers of the confined sample which form parallel to the wall. The so-called Plug-Slip phase is shown to exhibit particularly anomalous frictional behavior, for example the friction coefficient can decrease with increasing load, which is contrary to Amontons' first law for macroscopic friction. The frictional behavior can be state point history dependent to varying extents depending on the part of nonequilibrium phase diagram considered. For example, it is shown that it is possible by increasing the pressure first and then the wall speed, to 'lock in' to much higher sliding speeds very low friction states which normally appear at low sliding speeds only. It is shown that the phase diagram is sensitive to the level of wall roughness, and perhaps surprisingly the tribological map is more featureless with a rough wall than for a crystalline wall. The high friction coefficient Stick-Slip region appears to disappear for an atomistically rough wall. There have been previous NEMD,⁷⁴ and experimental investigations,⁷⁵ of the

effects of various types of roughness constructed from crystalline ordered or patterned walls, particularly on the slip length, where it has been found that a positive slip length (where the extrapolated flow velocity terminates within the walls) gives a smaller friction coefficient. It appears that the truly atomistic rough wall case considered here, which would be more relevant to glassy walled channels, has not been widely investigated for high pressure and shear rate systems to date.

A general result of these simulations is the widespread departure from a linear velocity profile in a confined material gap between the walls. This can take the form of strain rate localization near the wall or in the central region of the confined sample, a general phenomenology that has been observed for a wide range of liquids, see for example, Refs.^{76–81}. Coexistence and strong coupling exists between a largely unsheared (‘plug’) region and a sheared liquid-like domain. These features are correlated with the nonequilibrium state of self-organisation of the confined molecules into a coexistence of crystal and melted like states. The orientation of crystalline planes of the molecules next to the wall can lead to particularly low values of the friction coefficient.

Large stress fluctuations can occur even within the plug, which gives rise to Stick-Slip or serrated time dependent stress profiles indicating the occurrence of intermittent plastic flow.⁸² In the Central Localization region of the phase diagram, extreme plastic deformation produces a liquid-like layer typically only a few molecules thick, which is consistent with work on metallic glasses under shear.^{77,83,84}

These spherical Lennard-Jones molecules probably accentuate the richness of the tribology and phase diagram because they readily crystallize. Large approximately

spherical organic molecules might show similar trends. Although some of these features may be ‘washed out’ for more flexible less spherical molecules a number of them generated by the Lennard-Jones confined sample, such as non-linear velocity profiles (‘shear banding’) in liquid systems composed of more structured molecules are known to occur for more normal lubricant liquid like systems,^{34–36,85,86} so this feature appears to be generic to the liquid state under these conditions.

V. ACKNOWLEDGMENTS

The work has been supported by the Polish National Science Center grant DEC-2012/05/B/ST3/03255.

references

- * Electronic address: `szymon.mackowiak@put.poznan.pl`
- [†] Electronic address: `d.heyas@imperial.ac.uk`
- [‡] Electronic address: `d.dini@imperial.ac.uk`
- [§] Electronic address: `branka@ifmpan.poznan.pl`
- ¹ B. N. J. Persson, *Sliding Friction, Physical Properties, and Applications*, (Springer, Berlin, 2000).
- ² J. Krim, Surface Science, **500**, 741, (2002).
- ³ B. Bhushan, *Springer Handbook of Nanotechnology*, (Springer, Berlin, 2004).
- ⁴ H. Spikes, and W. Tysoe, Tribol. Lett. **59**, 21 (2015).
- ⁵ I. M. Hutchings, Wear **360-361**, 51 (2016).
- ⁶ J. Gao, W. D. Luedtke, D. Gourdon, M. Ruths, J. N. Israelachvili, and U. Landman, J. Phys. Chem. B **108**, 3410 (2004).
- ⁷ Y. Mo, and K. T. Turner, Nature **457**, 1116 (2009).
- ⁸ E. Gnecco, S. Maier, and E. Meyer, J. Phys. Cond. Matt. **20**, 354004 (2008).
- ⁹ O. M. Braun, and A. G. Naumovets, Surf. Sci. Rep. **60**, 79 (2006).
- ¹⁰ A. Socoliuc, R. Bennewitz, E. Gnecco, and E. Meyer, Phys. Rev. Lett. **92**, 134301 (2004).
- ¹¹ E. Riedo, E. Gnecco, R. Bennewitz, E. Meyer and H. Brune, Phys. Rev. Lett. **91**, 084502 (2003).
- ¹² M. Weiss, and F.-J. Elmer, Phys. Rev. B **53**, 7539 (1996).
- ¹³ M. Weiss, and F.-J. Elmer, Zeit. F. Physik B **104**, 55 (1997).
- ¹⁴ T. Kawaguchi, and H. Matsukawa, Comp. Phys. Comm. **142**, 1001 (2001).
- ¹⁵ N. Omote, T. Maruyama, H. Araki, D. Matsumura, D. Tanaka, M. Kaneko, and K. Hayashi,

- J. Phys. Conf. Series **89**, 012008 (2007).
- ¹⁶ G. He, and M. O. Robbins, Tribology Letters, **10**, 7, (2001).
 - ¹⁷ A. Vanossi, N. Manini, M. Urbakh, S. Zapperi and E. Tosatti, Rev. Mod. Phys. **85**, 529 (2013).
 - ¹⁸ Y. Lei and Y. Leng, Phys. Rev. Lett. **107**, 147801 (2011).
 - ¹⁹ M. H. Müser, and M. O. Robbins, Phys. Rev. B **61**, 2335 (2000).
 - ²⁰ Y. Qi, Y.-T. Cheng, T. Cagin, and W. A. Goddard III, Phys. Rev. B **66**, 085420 (2002).
 - ²¹ H. Yoshizawa, and J. Israelachvili, J. Phys. Chem. **97**, 11300 (1993).
 - ²² A. D. Berman, W. A. Ducker, and J. N. Israelachvili, Langmuir **12**, 4559 (1996).
 - ²³ E. Kumacheva, and J. Klein, J. Phys. Chem. B **108**, 7010 (1998).
 - ²⁴ A. Jabbarzadeh, P. Harrowell, and R. I Tanner, J. Phys. Chem. B **111**, 11354 (2007).
 - ²⁵ S.T. Cui, P.T. Cummings and H.D. Cochran J. Chem. Phys. **114**, 7189 (2001).
 - ²⁶ J. Klein, Phys. Rev. Lett. **98**, 056101 (2007).
 - ²⁷ C. Gattinoni, D. M. Heyes, C. D. Lorenz, and D. Dini, Phys. Rev. E **88**, 052406 (2013).
 - ²⁸ S. Butler, and P. Harrowell, Nature **415**, 1008 (2002).
 - ²⁹ J. Gao, W. D. Luedtke, and U. Landman, J. Phys. Chem. B **102**, 5033 (1998).
 - ³⁰ O. M. Braun, and M. Peyrard, Phys. Rev. E **63**, 046110 (2001).
 - ³¹ D. M. Heyes, E. R. Smith, D. Dini, H. A. Spikes, and T. A. Zaki, J. Chem. Phys. **136**, 134705 (2012).
 - ³² C. Gattinoni, Sz. Maćkowiak, D. M. Heyes, A. C. Brańka, and D. Dini, Phys. Rev. E **90**, 043302 (2014).
 - ³³ P. A. Thompson, and M. O. Robbins, Phys. Rev. A **41**, 6830 (1990).
 - ³⁴ G. Galmiche, A. Ponjavic and J. S. S. Wong, J. Phys.: Cond. Matt. **28**, 134005 (2016).
 - ³⁵ A. Ponjavic, J. Dench, N. Morgan, and J. S. S. Wong, RSC Adv. **5**, 99585 (2015) .

- ³⁶ A. Ponjavic, M. Chennaoui and J. S. S. Wong, Tribol. Lett. **50**, 261 (2013).
- ³⁷ L. Martinie, and P. Vergne, Tribol. Lett. **63**, 21 (2016).
- ³⁸ S. Plimpton, J. Comp. Phys. **117**, 1 (1995).
- ³⁹ B. D. Todd, D. J. Evans, and P. J. Daivis, Phys. Rev. E **52**, 1627 (1995).
- ⁴⁰ S. Butler, and P. Harrowell, J. Chem. Phys. **118**, 4115 (2003).
- ⁴¹ J. Petravic, and P. Harrowell, J. Chem. Phys. **124**, 014103 (2006).
- ⁴² D.J. Evans and G. Morriss, *Statistical mechanics of nonequilibrium liquids* (Cambridge Univ. Press, Cambridge, 2008).
- ⁴³ P. A. Thompson, and M. O. Robbins, Science, **250**, 792, (1990).
- ⁴⁴ L. Hromadová, R. Martoňák, and E. Tosatti, Phys. Rev. B **87**, 144105 (2013).
- ⁴⁵ M. Teodorescu, S. Theodossiades, and H. Rahnejat, Tribol. Int. **42**, 197 (2009).
- ⁴⁶ R. Khare, J. J. de Pablo, and A. Yethiraj, Macromolecules **29**, 7910 (1996).
- ⁴⁷ P. A. Thompson, G. S. Grest, and M. O. Robbins, Phys. Rev. Lett. **68**, 3448 (1992).
- ⁴⁸ M. Lupkowski, and F. van Swol, J. Chem. Phys. **93**, 737 (1990).
- ⁴⁹ M. Lupkowski, and F. van Swol, J. Chem. Phys. **95**, 1995(1991).
- ⁵⁰ L. Pastewka, S. Moser, and M. Moseler, Tribol. Lett. **39**, 49 (2010).
- ⁵¹ S. Bernardi, B. D. Todd and D. J. Searles, J. Chem. Phys. **132**, 244706 (2010).
- ⁵² X. Yong and L. T. Zhang, J. Chem. Phys. **138**, 084503 (2013).
- ⁵³ S. De Luca, B. D. Todd, J. S. Hansen, and P. J. Daivis, J. Chem. Phys. **140**, 054502 (2014).
- ⁵⁴ J. Petravic, J. Chem. Phys. **129**, 094503 (2008).
- ⁵⁵ D. M. Heyes, *The Liquid State*, (John Wiley & Sons, Chichester, 1997).
- ⁵⁶ A. J. C. Ladd, and L. V. Woodcock, Chem. Phys. Lett. **51**, 155 (1977).
- ⁵⁷ J. N. Cape, J. Chem. Soc. Faraday Trans. II, **78**, 317 (1982).
- ⁵⁸ D. W. Brazier and G.R. Freeman, Canad. J. Chemistry, 1969, **47**, 893 (1969).

- ⁵⁹ D. M. Heyes, J. J. Kim, C. J. Montrose, and T. A. Litovitz, J. Chem. Phys. **73**, 3987 (1980).
- ⁶⁰ C. Oligschleger and J.C. Schön, Phys. Rev. B. **59**, 4125 (1999).
- ⁶¹ A. M. Homola, J. N. Israelachvili, M. L. Gee, and P. M. McGuiggan, J. Tribol. **111**, 675 (1989).
- ⁶² P. M. McGuiggan, J. N. Israelachvili, M. L. Gee, and A. M. Homola, Mater. Res. Soc. Symp. Proc. **140**, 79 (1989).
- ⁶³ M. L. Gee, P. M. McGuiggan, J. N. Israelachvili, and A. M. Homola, J. Chem. Phys. **93**, 1895 (1990).
- ⁶⁴ J. N. Israelachvili, P. M. McGuiggan, and A. M. Homola, Science **240**, 189 (1988).
- ⁶⁵ P. A. Thompson, and G.S. Grest, Phys. Rev. Lett. **67**, 1751 (1991).
- ⁶⁶ H. A. Spikes, Langmuir, **12**, 4567 (1996).
- ⁶⁷ A. E. Filippov, and V. L. Popov, Phys. Rev. E **75**, 027103 (2007).
- ⁶⁸ Z. Deng, A. Smolyanitsky, Q. Li, X. Q Feng, and R. J. Cannara, Nature Materials, **11**, 1032 (2012).
- ⁶⁹ G. A. Tomlinson, Phil. Mag. **7(46)**, 905 (1929).
- ⁷⁰ A. Jabbarzadeh, P. Harrowell, and R. I Tanner, J. Chem. Phys. **125**, 034703 (2006).
- ⁷¹ N. V. Priezjev, J. Chem. Phys. **127**, 144708 (2007).
- ⁷² F. D. Sofos, T. E. Karakasidis and A. Liakopoulos, Phys. Rev. E. **79**, 026305 (2009).
- ⁷³ H. Spikes, Lubric. Sci., **18**, 265 (2006)
- ⁷⁴ T. M. Galea, and P. Attard, Langmuir **20**, 3477 (2004).
- ⁷⁵ T. Lee, E. Charraut, and C. Neto, Adv. Coll. & Interf. Sci. **210**, 21 (2014).
- ⁷⁶ W. M. Holmes, P. T. Callaghan, D. Vlassopoulos, and J. Roovers, J. Rheol. **48**, 1085 (2004).
- ⁷⁷ P. Schall, D. A. Weitz, and F. Spaegen, Science **318**, 1895 (2007).
- ⁷⁸ F. Varnik, L. Bocquet, J.-L. Barrat, and L. Berthier, Phys. Rev. Lett. **90**, 095702 (2003).

- ⁷⁹ K. E. Jensen, D. A. Weitz, and F. Spaepen, Phys. Rev. E **90**, 042305 (2014).
- ⁸⁰ P. Coussot, J. S. Raynaud, F. Bertrand, P. Moucheron, J. P. Guilbaud, H. T. Huynh, S. Jarny, and D. Lesueur, Phys. Rev. Lett. **88**, 218301 (2002).
- ⁸¹ P. C. F. Möller, S. Rodts, M. A. J. Michels, and D. Bonn, Phys. Rev. E **77**, 041507 (2008).
- ⁸² B. A. Sun, S. Pauly, J. Hu, W. H. Wang, U. Kühn, and J. Eckert, Phys. Rev. Lett. **110**, 225501 (2013).
- ⁸³ Y. Zhang, and A. L. Greer, Appl. Phys. Lett. **89**, 071907 (2006).
- ⁸⁴ M. Atzmon, and J. D. Ju, Phys. Rev. E **90**, 042313 (2014).
- ⁸⁵ S. Bair, F. Qureshi, and W. O. Winer, ASME J. Tribol. **115**, 507 (1993).
- ⁸⁶ S. Bair, F. Qureshi, and M. Khonsara, ASME J. Tribol. **116**, 705 (1994).
- ⁸⁷ S. Nosé, Mol. Phys. **52**, 255 (1984).
- ⁸⁸ W. G. Hoover, Phys. Rev. A **31**, 1695 (1985).
- ⁸⁹ L. V. Woodcock, Chem. Phys. Lett. **10**, 257 (1971).

APPENDIX: TEMPERATURE CONTROL IN THE SLAB GEOMETRY

In this appendix some consequences of using tethered wall atoms and schemes for controlling the temperature in the slab geometry are discussed.

1. The walls composed of tethered particles.

In the situation in which the solid walls A and C in Fig. 1 are composed of atoms tethered to notional lattice sites the entire system is defined by the following Hamiltonian,

$$H = U^{AA} + U^{AB} + U^A + U^{BB} + U^{BA} + U^{BC} + U^{CC} + U^{CB} + U^C + K^A + K^B + K^C. \quad (\text{A1})$$

The symbols K and U denote the kinetic and potential energy, respectively, within or between regions indicated by the superscripts. It is assumed that there are no (direct) interactions between the walls, A and C. The terms U^A and U^C represent the potential energy determined by the tethered particle displacements from the perfect crystal lattice points. The equations of motion derived from Eq. (A1) for region A containing atoms with indices, $i = 1, \dots, N_A$, are,

$$\begin{aligned} \dot{\underline{r}}_i^A &= \frac{\underline{p}_i^A}{m_i} \\ \dot{\underline{p}}_i^A &= - \sum_j^{N_A} \frac{\partial U_{ij}^{AA}}{\partial \underline{r}_{ij}} - \sum_j^{N_A} \frac{\partial U_{ij}^{AB}}{\partial \underline{r}_{ij}} - \frac{\partial U_i^A(\delta \underline{r}_i)}{\partial \underline{r}_i}. \end{aligned} \quad (\text{A2})$$

The corresponding equations of motion for region B, with molecule indices, $k = 1, \dots, N_B$ are,

$$\begin{aligned} \dot{\underline{r}}_k^B &= \frac{\underline{p}_k^B}{m_k} \\ \dot{\underline{p}}_k^B &= - \sum_j^{N_B} \frac{\partial U_{kj}^{BB}}{\partial \underline{r}_{kj}} - \sum_j^{N_B} \frac{\partial U_{kj}^{BA}}{\partial \underline{r}_{kj}} - \sum_j^{N_B} \frac{\partial U_{kj}^{BC}}{\partial \underline{r}_{kj}}. \end{aligned} \quad (\text{A3})$$

and for region C, with atom indices, $l = 1, \dots, N_C$ the equations of motion are,

$$\begin{aligned} \dot{\underline{r}}_l^C &= \frac{\underline{p}_l^C}{m_l} \\ \dot{\underline{p}}_l^C &= - \sum_j^{N_C} \frac{\partial U_{lj}^{CC}}{\partial \underline{r}_{lj}} - \sum_j^{N_C} \frac{\partial U_{lj}^{CB}}{\partial \underline{r}_{lj}} - \frac{\partial U_l^C(\delta \underline{r}_l)}{\partial \underline{r}_l}, \end{aligned} \quad (\text{A4})$$

where $U_{\lambda j}^{\alpha\beta}$ is the pair interaction potential between particles within the various regions, A, B and C. The term, U_{λ}^{α} is a single particle energy which comes from the tethering spring acting on a wall atom and $\delta \underline{r}$ is the atom's displacement from the crystal lattice point.

From the above equations of motion it can be shown that the total energy of the system is conserved (i.e., $\dot{H} = 0$), but for the total momentum, $\underline{P} = \underline{P}_A + \underline{P}_B + \underline{P}_C$ there is,

$$\dot{\underline{P}} = - \sum_{i=1}^{N_A} \frac{\partial U_i^A}{\partial \underline{r}_i} - \sum_{i=1}^{N_C} \frac{\partial U_i^C}{\partial \underline{r}_i}. \quad (\text{A5})$$

Thus the application of a tethered springs to the wall atoms leads to the nonconservation of the total linear momentum as the tethering acts as an external ‘confining’ force. The presence of the tethering springs in the system may lead to a problem in the direct application of some thermostatting schemes such as the Nosé-Hoover^{87,88} method where conservation of the total momentum is required.

2. Modified NH scheme

The following modification of the NH equations is proposed to enforce momentum conservation of the system in slab geometry (without tethering springs).

For region A, and $i = 1, \dots, N_A$,

$$\begin{aligned} \dot{\underline{r}}_i^A &= \underline{p}_i^A / m_i^A, \\ \dot{\underline{p}}_i^A &= - \frac{\partial (U_{AA} + U_{AB})}{\partial \underline{r}_i^A} - \zeta_A (\underline{p}_i^A - \frac{1}{N_A} \sum_{j=1}^{N_A} \underline{p}_j^A), \\ \dot{\zeta}_A &= \frac{1}{Q_A} \left[\sum_{i=1}^{N_A} \frac{\underline{p}_i^A}{m_i} \left(\underline{p}_i^A - \frac{1}{N_A} \sum_{j=1}^{N_A} \underline{p}_j^A \right) - g_A k_B T \right], \\ \dot{s}_A &= s_A \zeta_A, \end{aligned} \quad (\text{A6})$$

for region B, and $k = 1, \dots, N_B$,

$$\begin{aligned}\dot{\underline{r}}_k^B &= \underline{p}_k^B / m_k^B, \\ \dot{\underline{p}}_k^B &= - \frac{\partial(U_{BB} + U_{BA} + U_{BC})}{\partial \underline{r}_i^B},\end{aligned}\tag{A7}$$

for region C, where $l = 1, \dots, N_C$,

$$\begin{aligned}\dot{\underline{r}}_l^C &= \underline{p}_l^C / m_l^C, \\ \dot{\underline{p}}_l^C &= - \frac{\partial(U_{CC} + U_{BC})}{\partial \underline{r}_i^C} - \zeta_C (\underline{p}_i^C - \frac{1}{N_C} \sum_{j=1}^{N_C} \underline{p}_j^C), \\ \dot{\zeta}_C &= \frac{1}{Q_C} \left[\sum_{i=1}^{N_C} \frac{\underline{p}_i^C}{m_i} \left(\underline{p}_i^C - \frac{1}{N_C} \sum_{j=1}^{N_C} \underline{p}_j^C \right) - g_C k_B T \right], \\ \dot{s}_C &= s_C \zeta_C,\end{aligned}\tag{A8}$$

where $(\underline{p}_i^A - \frac{1}{N_A} \sum_{j=1}^{N_A} \underline{p}_j^A)$ and $(\underline{p}_i^C - \frac{1}{N_C} \sum_{j=1}^{N_C} \underline{p}_j^C)$ can be considered to be a type of peculiar momentum relative to the wall momentum, $\underline{P}^A$. The quantities, g_A and g_C are mechanical degrees of freedom within region A and B, while Q_A and Q_C , are the thermostat ‘mass’ for each region, respectively.

It can be shown that the following ‘energy’ like quantity,

$$\begin{aligned}H &= \sum_{i=1}^{N_A} \underline{p}_i^{A^2} / 2m_i^A + U_{AA} + U_{AB} + \frac{1}{2} Q_A \zeta_A^2 + g_A k_B T \ln(s_A) + \\ &\quad + \sum_{i=1}^{N_B} \underline{p}_i^{B^2} / 2m_i^B + U_{BB} + U_{BA} + U_{BC} + \\ &\quad + \sum_{i=1}^{N_C} \underline{p}_i^{C^2} / 2m_i^C + U_{CC} + U_{CB} + \frac{1}{2} Q_C \zeta_C^2 + g_C k_B T \ln(s_C),\end{aligned}\tag{A9}$$

is a constant of motion i.e., $\dot{H} = 0$. A straightforward derivation shows that, $\dot{\underline{P}} = \dot{\underline{P}}_A + \dot{\underline{P}}_B + \dot{\underline{P}}_C = 0$. Importantly, the proposed equations of motion in Eqs. (A6 - A8) generate the canonical distribution for particle momenta and positions, which can be shown by demonstrating that the density distribution $\rho = \rho(\underline{r}, \underline{p}, \zeta_A, \zeta_B) = \exp(-\beta \mathcal{H}(\underline{r}, \underline{p})) \exp(-\beta Q_A \zeta_A^2 / 2) \exp(-\beta Q_C \zeta_C^2 / 2)$ (where

$\beta = 1/k_B T$) is a stationary solution of the Liouville's equation. The modified Eqs. (A6) - (A8) apply the thermostat to the walls and generate a canonical temperature control in the whole system. The equations preserve total momentum $\underline{P}$ of the system. This scheme can be applied to the slab geometry without tethered springs.

3. The velocity scaling (VS) scheme

The efficient temperature control or equivalently heat extraction through the walls in a slab geometry can be performed also with a suitably modified version of the velocity scaling scheme,⁸⁹ which is achieved according to the following momentum recalling,

$$\begin{aligned}\underline{p}_i^{new} &= \underline{p}_i \lambda - (\lambda - 1) \frac{\mathbb{P}_A}{N_A}, & \text{for } i = 1 \dots N_A, \\ \underline{p}_k^{new} &= \underline{p}_k \lambda - (\lambda - 1) \frac{\mathbb{P}_C}{N_C}, & \text{for } k = 1 \dots N_C,\end{aligned}\tag{A10}$$

where $\mathbb{P}_A$, $\mathbb{P}_C$ is the total momentum of regions A and C , N_A , N_C is the number of atoms in each wall and $\lambda = \sqrt{T_0/T}$ and T_0 is the target temperature. In this scheme the momentum conservation is built on the subtraction of the rescaled particle's momentum (by the temperature factor, λ) and the one-particle contribution to the total momentum. In other words after every velocity rescaling applied to the wall, the total momentum of the wall is calculated and compared with the previous value. Then from each particle the correction divided by the number of particles in the wall is subtracted. In this way the total momentum in the system is conserved.

In a system without tethering springs the standard velocity scaling scheme⁸⁹ causes some spurious disturbances of the walls. The modified VS scheme, which includes the wall total momentum correction at every rescaling cycle allows the temperature to be controlled without such effects.