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NON-EQUILIBRIUM THERMODYNAMICS BEYOND LINEARITY: SLIDING FRICTION

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ABSTRACT. Nevertheless, sliding friction is frequent and it was the first irreversible process we were faced in the school, very rare effort has been aimed to develop its non-equilibrium thermodynamic theory if ever. The reason may be guessed as Coulomb's (Amonton's 3rd) law is often taught as if it were the final solution, even the velocity dependence of the friction force is rarely mentioned in textbooks or in papers, looking away from its direction. On the other hand, the phenomenon can not be accounted with a linear theory even in the Onsagerian sense. Coulomb's law displays a strong singularity at equilibrium, which is, at least, extremely rare in nature.

On the ground of the thermodynamic theory of rheology, one can guess, that the singularity is virtual. The friction force do depend on the magnitude of the velocity and the function is continuous but it starts so steeply and falls back at practically very low values that to observe it is really difficult. If the two solids are separated with a thin layer of a non-Newtonian fluid the thermodynamic theory of the latter can be applied. This is not a nonsense; the independence of the friction force on the contact area is explained—by rather widely accepted ideas—with plastic flow of the materials at the surface region.

In the last decades the interest has increased and several theories was published and experimentally verified that explain friction and wear at different circumstances and the results are not like to each other nor to Coulomb's law.

Applying Onsager's thermodynamics beyond the realm of linearity is more or less like guessing. Not a free brain storm, but severely limited by observations.

Here a germ of a thermodynamic theory is sketched without acquiring generality and restricted to stationary sliding. Here the most simple model is looked for to eliminate the gap between static and kinetic friction. It is not a complete idea at all—the transients have been put aside—but may be a guideline for further modeling. The fork the train of thoughts stops at gives way to several kind of possibilities, a number of which—by the authors opinion—may have their own realm of application.

Finally, an accurately accountable model is given that may be assumed friction if we pretend not knowing its origin and the law differs significantly from the nearly exclusively used Coulomb's law. This example supports the idea that friction can not be described in a simple and uniform theory.

1. Introduction

Nevertheless, sliding friction is frequent (Persson and Tosatti 1996; Rabinowicz 1965) and it was the first irreversible process we were faced in the school and probable one of the most important from technological point of view, very rare (Ván, Mitsui, and Hatano 2015) has been aimed to develop its non-equilibrium thermodynamic theory if ever, even though, non-equilibrium thermodynamics (De Groot 1951; De Groot and Mazur 1962; Garcia-Colin and Uribe 1991; Gyarmati 1970, 1977; Hutter 1977; Jou, Casas-Vázques, and Lebon 1993; Jou, Casas-Vázquez, and Lebon 1992; Machlup and Onsager 1953; Müller and Ruggeri 1993; Onsager 1931a,b; Onsager and Maclup 1953; Prigogine 1961; Verhás 1997) has been applied to several phenomena with full success (Ciancio, Dolfin, and Ván 1996a,b; Holló and Nyíri 1992; G. A. Kluitenberg and Ciancio 1981; G. Kluitenberg, Turrisi, and Ciancio 1982; Muschik, Ehrentraut, and Papenfuss 1995; Nyíri 1989; Papenfuss, Ván, and Muschik 2003; Ván 2002; Ván, Papenfuss, and Muschik 2000; Ván and Ruszin 1990; Verhás 1997).

The reason may be guessed as Coulomb's law is often taught as if it where the final solution, even the velocity dependence of the magnitude of friction force is rarely mentioned in textbooks or in papers. On the other hand, the phenomenon can not be accounted with a linear theory even in the Onsagerian sense. Coulomb's law is highly non-linear and displays a strong singularity at equilibrium, which is, at least, extremely rare in nature (see Figure 1).

Starting from the fact that the static friction is larger than the kinetic one, we may assume that the friction force at very slow motion increases with decreasing velocity. At the end of the 19th century the low velocity meant from 3mm/s down to 0.061mm/s while nowadays from 1000nm/s down to 10nm/s, approximately 70 molecule per second. The experiments support the suspicion.

Amonton's 3rd law may be replaced with a function free of the strong singularity just at equilibrium. On the ground of the thermodynamic theory of rheology (Verhás 1997) one can guess, that the singularity is virtual. The friction force do depend on the magnitude of the velocity and the function is continuous, as shown in Figure 2, but it starts so steeply and falls back at practically very low velocities that it is really difficult to observe.

2. Thermodynamic theory

The assumed system is two rigid bodies in contact and sliding on each other. Motion is assumed tangential to the surface. The first law of thermodynamics reads

$$\frac{du}{dt} = \vec{F}\vec{v} + I_q, \tag{1}$$

where u is the internal energy, $\vec{F}$ is the applied force necessary for steady slip with velocity $\vec{v}$, I_q the heat flow, and t is the time. The second law reads

$$\frac{ds}{dt} = \frac{I_q}{T} + P_s \tag{2}$$

in general form. Here s is the entropy, T the temperature both of the system and the environment, [1] and P_s is the entropy production in unite time.

[1] The increase of temperature due to friction is neglected for convenience, not to entangle the complicated details of heat propagation studied a lot of times

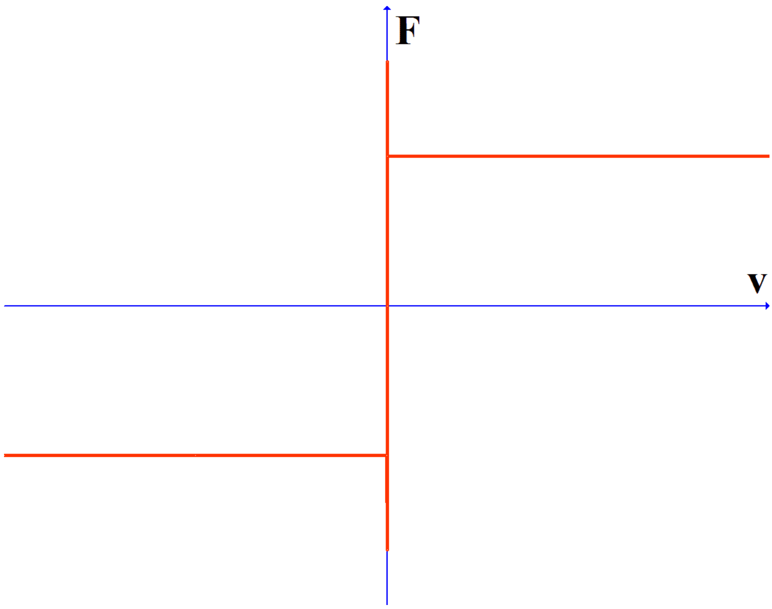

FIGURE 1. Coulomb's law

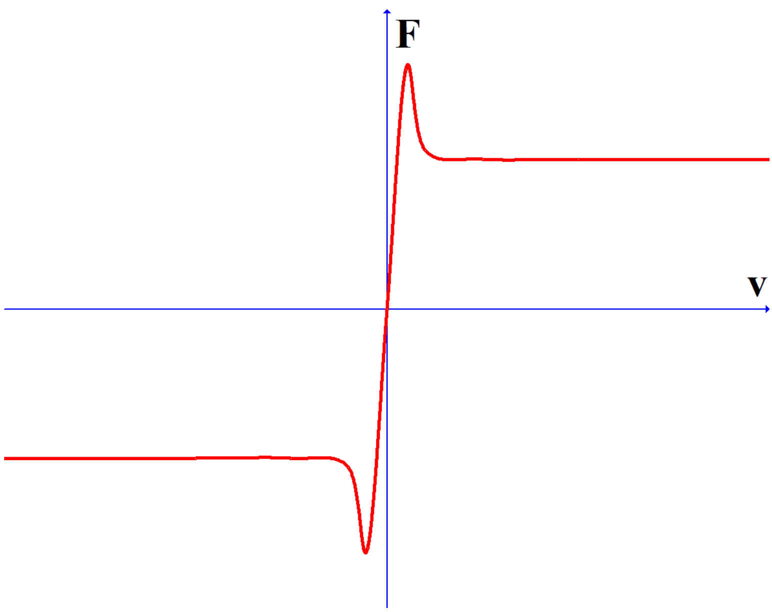

FIGURE 2. Possible modification of Coulomb's law

2.1. Model in local equilibrium. If local equilibrium is supposed than the entropy of the system depends on the internal energy alone;

$$s = s(u), \tag{3}$$

which results

$$TP_s = \frac{du}{dt} - I_q = \vec{F}\vec{v}, \tag{4}$$

and for the linear Onsager law

$$\vec{F} = L\vec{v}. \tag{5}$$

The linear approximation is obviously not able to fulfill the needs. In non linear approximation L may depend on the velocity rather arbitrarily; the only requirement of the second law is

$$L \geq 0. \tag{6}$$

The function

$$L = \frac{\mu N}{|\vec{v}|} \tag{7}$$

gives back Coulomb's law for sliding but knows nothing on static friction, moreover, L has severe singularity at equilibrium. The symbol μ stands for the coefficient of sliding friction and N for the normal force pressing the surfaces one to the other. If a function the graph of which is something like the line in Figure 2 is taken then a better formula is obtained. The disadvantages are that such a function is not very simple at all and the function has to be measured or guessed.

I incline to abandon the hypothesis of local equilibrium. [2]

2.2. Model with one dynamic variable. The first approximation out of local equilibrium is based on a single dynamic variable $\vec{\alpha}$ invariant under time inversion. It is assumed to be a vector because the local equilibrium theory contains vectorial force and flux. Basing on the Morse lemma (Morse 1925) the entropy is given as

$$s = s\left(u - \rho\vec{\alpha}^2\right) \tag{8}$$

leading to

$$TP_s = \vec{F}\vec{v} - 2\rho\vec{\alpha}\frac{d\vec{\alpha}}{dt}, \tag{9}$$

where ρ is a convenient constant not specified yet.

The linear laws take the form

$$\vec{F} = L_{11}\vec{v} + L_{12}\vec{\alpha} \tag{10}$$

$$-2\rho\frac{d\vec{\alpha}}{dt} = L_{21}\vec{v} + L_{22}\vec{\alpha}. \tag{11}$$

The thermodynamic forces are taken $\vec{v}$ and $\vec{\alpha}$. The Onsager-Casimir reciprocal relation (Casimir 1945; Onsager 1931a) reads

$$L_{21} = -L_{12} \tag{12}$$

and the second law prescribes

$$L_{11} \geq 0 \qquad \text{and} \qquad L_{22} \geq 0 \tag{13}$$

[2] The experimentally observed transients at the change of velocity make it mandatory.

and nothing else. The linear theory is again unsatisfactory as displays a force proportional with the velocity for motion; non-linear material laws are indispensable. The term $L_{11}\vec{v}$ is increasing without limit if L_{11} remain finite except it is zero or tends to zero. For low velocities $\vec{\alpha}$ is approximately proportional to the velocity, so for the starting section of the force, an L_{12} depending properly on $\vec{\alpha}$ is needed. Such a function can be found with the analogy to non-Newtonian fluids, especially, to Maxwell's fluid, in rather simple form, say

$$L_{12}(\vec{\alpha}) = \frac{L_{12}^0}{1+b^2\vec{\alpha}^2}, \tag{14}$$

which involves also

$$L_{21} = -L_{12}^0, \tag{15}$$

if L_{21} is assumed constant.

The analogy to the Maxwell-fluid is motivated by the idea that the parameter $\vec{\alpha}$ is something like an overall account on the rotation, as well as, the deformation of the bounds between the surfaces sliding on each other, whatever their physical nature is.

The proportionality of $\vec{\alpha}$ to the velocity in stationary motion has to be dropped for high velocities, because it leads to increasing force, contrary to Coulomb's law. The most simple choice is $L_{11} = 0$. With this choice, L_{21} can not be constant any longer, the second law requires the validity of equation (12) in complete generality.

This case the force tends to zero with increasing α. To get rid of the discrepancy, L_{22} is replaced by a function having a pole limiting the magnitude of $\vec{\alpha}$. The simplest function

$$L_{22}(\vec{\alpha}) = \frac{L_{22}^0}{1-\vec{\alpha}^2} \tag{16}$$

may lead to the needed rule for the force. Such a pole may be the consequence of the limited amount of undissipated energy. (The quantity ρ is chosen to that.)

The constitutive equations read

$$\vec{F} = L_{12}^0 \frac{\vec{\alpha}}{1+b^2\alpha^2} \tag{17}$$

$$-2\rho\frac{d\vec{\alpha}}{dt} = -L_{12}^0 \frac{\vec{v}}{1+b^2\alpha^2} + L_{22}^0 \frac{\vec{\alpha}}{1-\alpha^2}. \tag{18}$$

The coefficients L_{12}^0 and b can be determined from the static and dynamic coefficients of friction:

$$L_{12}^0 = \frac{\mu_0\mu}{\mu_0-\mu}, \qquad 2b^2 = \frac{\mu}{\mu_0-\mu} \tag{19}$$

The presented model is only one from many many other possibilities.

A very similar graph is resulted by the function

$$L_{12}(\vec{\alpha}) = L_{12}^0 e^{-b^2\vec{\alpha}^2}, \tag{20}$$

which is quite natural if friction is due to chemical bounds.

A non-linear law similar to the above is giving account on the static friction also with creep and that the friction force is independent of the velocity if it is high enough. For some materials, decreasing force has been reported at very low velocities (Baumberger 1996).

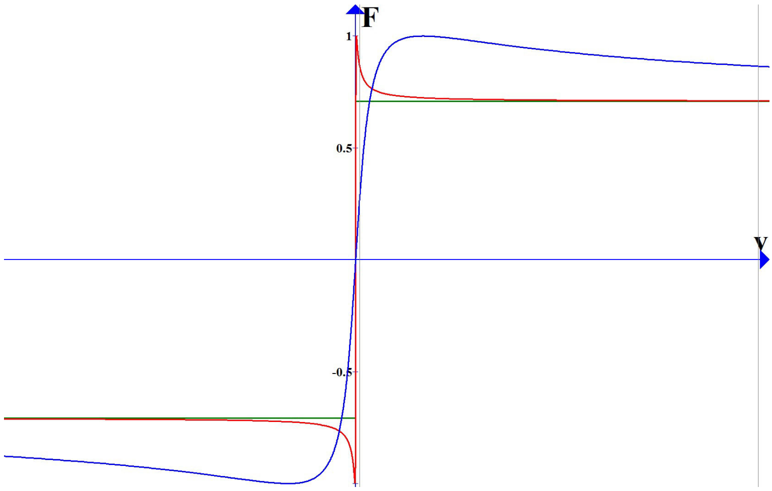

FIGURE 3. Result with equation (16). The blue line is the same function as the red one but stretched 100 times. The two gray vertical line are for reference.

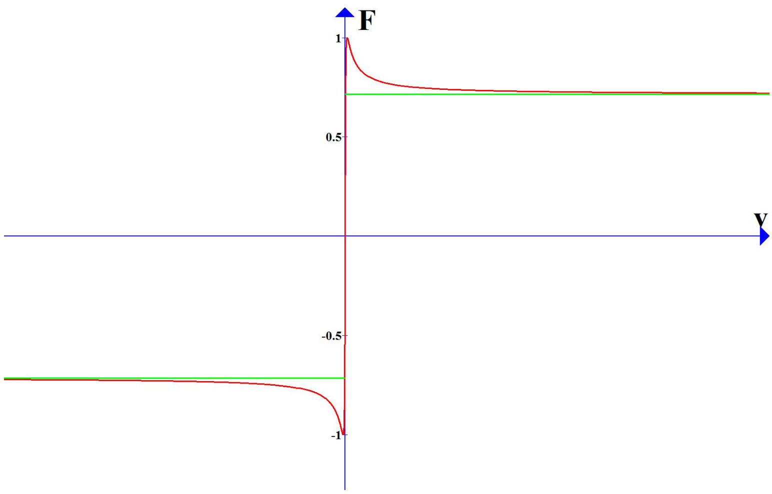

FIGURE 4. Result with equation (20).

3. Further considerations

The model presented here gives account on continuous and delayed change of the friction force when the velocity changes abruptly but the account is not good. This model does not display the overshot found experimentally.

This fact makes plausible that the coefficient $L_{11}(\vec{\alpha})$ can not be zero but at $\alpha = 1$. It may be something like

$$L_{11}(\vec{\alpha}) = L_{11}^{0}(1-\alpha^2), \tag{21}$$

and $L_{12}(\vec{\alpha})$—together with $L_{21}(\vec{\alpha})$, of course—may be stretched with a constant term; perhaps with a negative one. The unlimited validity of the Onsager-Casimir reciprocal relation—eq. (12)—ensures positive entropy production; it is sufficient but necessary condition. This sketch has to be examined in the future.

Here the skeleton of a thermodynamic theory has been sketched without acquiring generality. It is not a complete idea at all but may be a guideline for further development. The fork the train of thoughts stops at gives way to several kind of possibilities, a number of which—by the author's opinion—may have their own realm of application. I incline to believe that friction is a great family of processes and each kind needs its own theory.

If the two solids are separated with a thin layer of a non-Newtonian fluid—or if the contact area is surrounded with a thin fluidal layer (self-lubrication)—then the thermodynamic theory of the former can be applied. This is in the case of hydrodynamic lubrication and even without any lubricant; the independence of the friction force of the contact area is explained—by rather widely accepted ideas—with plastic flow of the materials at the surface region, etc.

In the last decades the interest has increased and several theories basing different mechanisms were published and experimentally examined that explain friction and wear at different circumstances and the results are not like to each other nor to Coulomb's law.

Finally, here an accurately accountable model has been given that may be assumed friction if we pretend not knowing its origin and the law differs significantly from the nearly exclusively used Coulomb's law. This example supports the idea that friction can be described but with a simple and uniform theory.

Assume that the roughness of the surfaces involves perpendicular motion and visco-elastic waves are generated. It is similar when a car goes on a rough road. The part of the driving force due to the energy loss in the shock absorber (visco-elastic loss in the bulks of the bodies) does not depend on the normal force but on the masses of the bodies and on the velocity. The function is rather complicated and at high velocities it is proportional to the velocity and independent of the masses or the normal force.

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