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Dissipative kinetic equations and their applications to manipulations of particles using AFM tips

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Abstract—We derive a generalized law of dissipation in physical systems based on *force proportional to velocity* law. We apply this law to the derivation of dissipation in kinetic equations and discuss applications to mass spectrometers and sensors using the vibrating tips of atomic force microscopes. This theory is necessary to provide a theoretical background for recent experimental and numerical studies in this area.

1. The role of dissipation in single atom manipulation

Recently, much attention has been drawn to the possibility of the manipulation of single particles using a tip of atomic force microscope [1, 2, 3, 4, 5, 6]. The proven advantages of this technique involve amazing accuracy in the positioning of particles as small as single atoms. Most of the studies have concentrated on the manipulation of single – or a few – atoms. For industrial applications, however, we need to study the possibility of a massive *parallel application* of this technique. Of particular interest here is the recent work by Hikihara and Yamasuhe [7] which outlined the possibility of separation of particles using a two parallel AFM tips. It was demonstrated numerically that for a single atom, such a possibility of separation exists due to the presence of two potential wells in the Lennard-Jones potential. The dissipation in that system enforces the eventual collapse towards one of the potential wells. In order to make this technique applicable to industrially relevant processes like mass spectroscopy or element separation, we must understand the statistics of a large number of particles in the double potential well. The statistical behavior of a large number of particles in the momentum p and coordinate q space is usually described by the *probability distribution function* $f(p,q,t)$. As the initial step, we can assume the *collisionless plasma approximation* and say that in the absence of dissipation, the probability distribution function $f(p,q,t)$ satisfies the *Vlasov equation*

$$\frac{\partial f}{\partial t} + \left\{ f,\, \frac{\delta H}{\delta f} \right\} = 0\,, \tag{1}$$

where for any two functions $f(p,q)$ and $g(p,q)$ we define the canonical Poisson Bracket

$$\{f,\, q\} = \frac{\partial f}{\partial q}\frac{\partial g}{\partial p} - \frac{\partial g}{\partial q}\frac{\partial f}{\partial p}\,. \tag{2}$$

However, equation (1) does not include dissipation and therefore must be corrected, as dissipation plays an essential role in the choice of potential minima in the Lennard-Jones potential. The question is how to extend Vlasov kinetic equation (1) to include dissipation in a sensible way. In the case of dissipation caused by the collisions, it is customary to introduce the Boltzmann collision integral on the right hand side of the equation (1). However, this approach is extremely cumbersome and very little analytic progress can be achieved. We shall take an alternative approach and formulate the *Double bracket dissipation*. More precisely, we suggest the following dissipation term for the Vlasov equation (1)

$$\frac{\partial f}{\partial t} + \left\{ f,\, \frac{\delta H}{\delta f} \right\} = \left\{ f, \left\{ \mu[f],\, \frac{\delta H}{\delta f} \right\} \right\}\,, \tag{3}$$

where $\mu[f]$ is the mobility functional (in phase space). In this paper, we show that it is a consistent dissipation term based on the generalized Darcy's law of motion (force being proportional to the velocity).

2. Dissipation as the Darcy's law and disipative bracket

In general, dissipation may be understood as resistance to the motion. One can think that at the microscopic level, each individual molecule experiences resistance force that is proportional to the velocity. This law of resistance is expected to hold at small scales and we call it the *Darcy's law* which should viewed as a generalization of the Darcy's law of fluid motion in porous media.

If we consider density of particles ρ with the energy functional $E[\rho]$, the local potential of particle interaction at a point is $\delta E/\delta\rho$, Darcy's law says that local velocity is $\nabla\delta E/\delta\rho$ so the local Darcy's velocity is given by

$$\mathbf{u} = \mu\nabla\frac{\delta E}{\delta\rho}\,. \tag{4}$$

Then, conservation law for the density ρd^3x takes the well-known form

$$\frac{\partial \rho}{\partial t} = -\mathrm{div}\,(\rho \mathbf{u}) = -\pounds_u \rho\,. \tag{5}$$

where $\pounds_u \rho$ is the Lie derivative of the quantity ρd^3x (density) with respect to the vector field $\mathbf{u}$ [8].

Let us consider the evolution of more general quantity which is necessary for the description of particles that are non-spherical and thus need both density and orientation for complete microscopic description. The conservation law for density can be re-written as a generalization of (4,5) as follows [9, 10, 11]:

> "The local value of κ remains invariant along the characteristic curves of a flow, whose velocity depends on κ through an appropriate Darcy Law."

This principle may be formulated in symbols as,

$$\frac{d\kappa}{dt}(\mathbf{x}(t),t) = 0 \quad \text{along} \quad \frac{d\mathbf{x}}{dt} = \mathbf{u}[\kappa]\,, \tag{6}$$

which can again be written as

$$\frac{\partial \kappa}{\partial t} = -\mathrm{div}\,(\kappa \mathbf{u}) = -\pounds_u \kappa\,, \tag{7}$$

where the flow velocity $\mathbf{u}[\kappa]$ is to be determined for each type of order parameter κ and is a generalization of (4). The key question for understanding the physical modeling that would be needed in making such a generalization is, "What is its corresponding Darcy's Law?" Namely, how does one determine the vector field $u[\kappa]$ in (6) when κ is an arbitrary geometrical quantity?

3. The diamond operator

That second equality closing the problem has been identified in [9, 10, 11] using the *diamond* ($\diamond$) operation as the *dual* of the Lie derivative under integration by parts for any pair (κ, b) of dual variables and any vector field $\mathbf{v}$. That operator generalizes the gradient in the definition of Darcy's velocity (4). The diamond operator is defined as:

$$\langle \kappa \diamond b, \mathbf{v} \rangle = \langle \kappa, -\pounds_{\mathbf{v}} b \rangle\,. \tag{8}$$

Then , the generalized Darcy's velocity for an arbitrary geometric quantity κ is given by

$$\mathbf{u} = \left(\mu[\kappa] \diamond \frac{\delta E}{\delta \kappa} \right)^\sharp\,, \tag{9}$$

where the $\sharp$ raises indices to create a vector field from the result of diamond operator. Here, we have introduced the mobility $\mu[\kappa]$ that has the same geometric meaning (*i.e.* is a tensor of the same type) as κ. The reader is referred to the papers [9, 10, 11] for technical details and explicit expressions for the diamond operators for various tensor quantities.

4. The dissipative bracket

Very important for our further discussion of the dissipation is the notion of the *dissipative bracket*, describing the evolution of energy. Using (7,9) and the definition of diamond operator (8), we obtain the the corresponding energy equation: follows from (8, 6, 9) as

$$\begin{aligned} \frac{dE}{dt} &= \left\langle \frac{\partial \kappa}{\partial t}\,,\, \frac{\delta E}{\delta \kappa} \right\rangle \\ &= \left\langle -\pounds_{(\mu[\kappa] \diamond \frac{\delta E}{\delta \kappa})^\sharp} \kappa,\, \frac{\delta E}{\delta \kappa} \right\rangle \\ &= -\left\langle \left(\mu[\kappa] \diamond \frac{\delta E}{\delta \kappa} \right),\, \left(\kappa \diamond \frac{\delta E}{\delta \kappa} \right)^\sharp \right\rangle. \end{aligned} \tag{10}$$

The formula for energy in (10) suggests the following bracket notation for the time derivative of a functional $F[\kappa]$,

$$\begin{aligned} \frac{dF[\kappa]}{dt} &= \left\langle \frac{\partial \kappa}{\partial t}\,,\, \frac{\delta F}{\delta \kappa} \right\rangle \\ &= \left\langle -\pounds_{(\mu[\kappa] \diamond \frac{\delta E}{\delta \kappa})^\sharp} \kappa\,,\, \frac{\delta F}{\delta \kappa} \right\rangle \\ &= -\left\langle \left(\mu[\kappa] \diamond \frac{\delta E}{\delta \kappa} \right),\, \left(\kappa \diamond \frac{\delta F}{\delta \kappa} \right)^\sharp \right\rangle \\ &=: \{\!\{ E\,,\, F \}\!\}[\kappa] \end{aligned} \tag{11}$$

The properties of the GOP brackets $\{\!\{ E\,,\, F \}\!\}$ defined in equation (11) are determined by the diamond operation and the choice of the mobility $\mu[\kappa]$. For physical applications, one should choose a mobility that satisfies strict dissipation of energy, *i.e.* $\{\!\{ E\,,\, E \}\!\} \leq 0$. A particular example of mobility that satisfies the energy dissipation requirement is $\mu[\kappa] = \kappa M[\kappa]$, where $M[\kappa] \geq 0$ is a non-negative scalar functional of κ. (That is, $M[\kappa]$ is a number.) Requiring the mobility to produce energy dissipation does not limit the mathematical properties of the GOP bracket. For example, the dissipative bracket possesses the Leibnitz property with any choice of mobility. That is, it satisfies the Leibnitz rule for the derivative of a product of functionals. In addition, the dissipative bracket formulation (11) allows one to reformulate the GOP equation (6) in terms of flow on a Riemannian manifold with a metric defined through the dissipation bracket, as discussed in more detail in [9].

5. The dissipative bracket in the (p, q) space

We shall now turn our attention to the statistical description of the particle behavior in the phase space. It is common to involve the *distribution function* $f(p, q, t)$ as described in the introduction. For no dissipations and no collisions, the evolution equation for the distribution function is given by (1). The

dissipative bracket (11) and the concept of the diamond operator plays a crucial role in our further discussion of the dissipation in *phase space*. Namely, we define the dissipative bracket of two arbitrary functionals $E[f], G[f]$ of Darcy's velocity in (p, q) space as follows:

$$\begin{aligned} \{\{ E , F \}\} &= -\left\langle \left\{ \mu[f] , \frac{\delta E}{\delta f} \right\} , \left\{ f , \frac{\delta F}{\delta f} \right\} \right\rangle \\ &= \left\langle \left\{ f, \left\{ \mu[f] , \frac{\delta E}{\delta f} \right\} \right\} , \frac{\delta F}{\delta f} \right\rangle , \quad (12) \end{aligned}$$

where $< \cdot , \cdot >$ means, as usual, the scalar product and integral over the phase space. The bracket $\{\cdot , \cdot\}$ is simply the canonical Poisson bracket of two functions. The mobility $\mu[f]$ is a functional of f that has both p and q component and is a modeling choice, the restriction on μ is that the bracket (12) is positive definite. Since the functional $F[f]$ and therefore $\delta F/\delta f$ is arbitrary, we get equation (3) by integration by parts [12, 13].

It is interesting that the double bracket dissipation of the type (3) was suggested before, starting with Kandrup [14] within the framework of aggregation of galactic disks. Similar equations also arose in Kaufmann [15] and Morrisson [16] in the context of plasma physics. The concept of double bracket dissipation was also used in [17] to model dissipation in ideal fluids. All these works have used $\mu[f] = \alpha f$ where α is a constant. This approach does not allow for single-particle solutions $f = \delta(p-P(t), q-Q(t))$, whereas using a general mobility functional $\mu[f]$ retains the single-particle solutions. In addition, our equation (3) preserves the entropy $S = \int f \log f$, as well as arbitrary function of the entropy [12].

It has been further demonstrated that the double bracket dissipation (3) allows natural generalizations for the case when the interacting particles are not spherical, but have arbitrary shape [13]. This allows for derivation of a consistent dissipative kinetic equation for proteins of arbitrary shape (and not just rigid rods, as is common in polymer theory, for example). These interesting and important aspects of our theory will be pursued in the future.

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