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REMARKS ABOUT METASTABILITY

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1. Introduction

Processes that involve disparate length scales and which are only metastable are inherent to the investigation of mesoscopic and microscopic systems. We focus here on a mechanism we believe to be deeply intertwined with these properties. Certainly the most established method for accomodating widely varying length scales is the use of stochastic analysis in the study of chemical systems. This is so famous that nothing more need be said about it. Let us recall that the distributions that describe these systems are usually solutions of a Fokker-Planck Equation, or forward Kolmogoroff Equation, determined by the stochastic process, [4]. New methods for the characterization of material microstructure have resulted in the development of weak convergence methods, often employing the Young measure and its generalizations, ([6],[7] are review papers). The Young measure solution of a typical nonconvex energy principle may be viewed as the zero temperature limit of a sequence of solutions of Fokker-Planck Equations, [8],[9].

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The compelling mechanism we wish to bring forward here is that the gradient flux of the native thermodynamic energy is the Fokker-Planck Equation, when taken in a suitable metric, [8],[9],[10]. This is the Wasserstein metric and it defines the weak* topology on the admissible class of probability densities. This immediately provides a deep connection between variational principles and stochastic differential equations. Moreover, we are allowed a format to discuss metastable systems: evolution may be interpreted as a competition between energy and distance in the weak* topology.

In this note, which is a plan for research more than a statement of results, we take up some of these issues. Our attention is confined to the simplest case.

2. A simple paradigm

For illustration, consider a potential $\psi(\xi)$, for a generalized snap spring or a shape memory element, for example, where ξ is the relative elongation of the spring or the shear length of the shape memory element, $-\infty < \xi < +\infty$. Let n_ξ denote the number of elements of elongation $\xi \in \{ \xi_1,\ldots,\xi_M \}$ so that

$$E = \sum \psi(\xi) n_\xi \quad \text{and} \quad d = \sum \xi\, n_\xi$$

are the total energy and elongation of the configuration. For such a system there is a configurational entropy or degeneracy given by Boltzmann's statistical definition

$$S = -\log \binom{|n_\xi|}{n_\xi},$$

where $\binom{|n_\xi|}{n_\xi}$ is the number of ways of arranging $|n_\xi|$ objects into M subsets with n_{ξ_j} elements in the j^{th} subset. The average free energy of the system is, $N = |n_\xi|$, $\sigma > 0$,

$$I_N = \frac{1}{|n_\xi|}\sum \psi(\xi) n_\xi + \sigma \log \binom{|n_\xi|}{n_\xi},$$

perhaps subject to an imposed constraint like $d = d_0$, with d_0 fixed. The parameter σ plays the role of the temperature. The potential energy of independent layers or springs, given by E, seeks to be minimum while the entropy seeks to be maximal by distributing elements evenly over the range. See Hou and Müller [5] for development of this sort of model in shape memory alloys. Passing to the limit as $N,M \to \infty$, gives, typically, the functional, defined on probability densities ρ,

$$F_\sigma(\rho) = \int_R \psi\rho \, d\xi + \sigma \int_R \rho \log \rho \, d\xi.$$

This is the type of functional we wish to consider.

A convex function of ρ, it admits a unique minimum, the (stationary) Gibbs distribution

$$\rho_s(\xi) = \frac{1}{Z(\sigma)} e^{-\frac{\psi(\xi)}{\sigma}}, \text{ with } Z(\sigma) = \int_R e^{-\frac{\psi(\xi)}{\sigma}} d\xi.$$

We witness in this construction virtually the paradigm of classical statistical statistical mechanics and, in the example as a particular case, the derivation of a Young measure formulation of a variational problem coupled to an entropic stabilization. The relaxation or Young measure distribution of a nonconvex variational principle may be realized as the zero temperature limit of F_σ. Namely,

$$I(\rho) = \int_R \psi\rho \, d\xi$$

represents the Young measure relaxation approach to a minimization problem and in our interpretation it has become ineluctably wedded to an entropy functional. Likewise, its driving force equation becomes linked to a Langevin Equation.

3. Fokker-Planck Dynamics

Were we to give and initial distribution of elements ρ_0 and ask how it relaxes to equilibrium, we might impose evolution of the probability flux or the Fokker-Planck Equation

$$\frac{\partial \rho}{\partial t} = \sigma \frac{\partial^2 \rho}{\partial \xi^2} + \frac{\partial}{\partial \xi}(\psi'\rho), \quad -\infty < \xi < \infty, \ t > 0, \qquad (3.1)$$

$$\rho|_{t=0} = \rho_0 .$$

The motivation for this is that the solution of (3.1) satisfies

$$\frac{d}{dt}F_\sigma(\rho) \leq 0 \quad \text{for solutions } \rho \text{ of } (3.1).$$

This is equivalent to seeking the distribution of the relaxation of the driving force equation of the strain rate, with a small stochastic force, given by the Langevin Equation

$$dX = -\psi'(X(t))dt + \sqrt{2\sigma}\, dB(t), \qquad (3.2)$$

where $B(t)$ is standard Brownian motion and $dB(t)$ represents white noise.

The compelling connection we wish to bring forward is that the implicit scheme

Determine $\rho^{(k)}$ that minimizes

$$\frac{1}{2h} d(\rho,\rho^{(k-1)})^2 + \int_R \psi\rho \, d\xi + \sigma \int_R \rho \log \rho \, d\xi, \qquad (3.3)$$

where d is the Wasserstein metric, briefly described below, gives rise to a solution of the Fokker-Planck Equation, [8],[9],[10].

The Wasserstein distance, [12], between two probability measures μ_1 and μ_2 on $\mathbf{R}$ is

$$d(\mu_1,\mu_2)^2 = \inf_{P} \int_{\mathbf{R}\times\mathbf{R}} |x-y|^2 \, dp(x,y), \qquad (3.4)$$

$P = P(\mu_1,\mu_2)$ = probability measures on $\mathbf{R}\times\mathbf{R}$ with first marginal μ_1 and second marginal μ_2.

So for $p \in P$, $p(A\times\mathbf{R}) = \mu_1(A)$ and $p(\mathbf{R}\times B) = \mu_2(B)$. It is well known that d defines a metric equivalent to the weak* topology on probability measures with the property

$$\int_{\mathbf{R}} |x|^2 \, d\mu(x) < \infty$$

when appropriately defined as contained in a dual space. Equivalently,

$$d(\mu_1,\mu_2)^2 = \inf E(|X-Y|^2),$$

where E denotes the expectation of the random variable and the infimum is taken over random variables (X,Y) where X has distribution μ_1 and Y has distribution μ_2. Since

$$E(|X-Y|^2) = E(|X|^2) + E(|Y|^2) - 2E(X\cdot Y) \text{ and}$$

$$E(|X|^2) = \int_{\mathbf{R}} |x|^2 \, d\mu_1(x), \quad E(|Y|^2) = \int_{\mathbf{R}} |y|^2 \, d\mu_2(y),$$

calculating the Wasserstein distance consists in maximizing the correlation between X and Y.

The variational problem (3.4) is an example of a Monge-Kantorovich mass transference problem with the cost function $c(x,y) = |x-y|^2$, [2],[3]. Variational problems of this type have applications in many disciplines. A minimizer in (3.4) is called an optimal transference plan is easily shown to exist. In our situation, μ_1

and μ_2 will always be absolutely continuous with respect to Lebesgue measure and so we shall not distinguish between them and their densities, say, ρ_1 and ρ_2.

4. A SYSTEM EXHIBITING HYSTERESIS

Systems that exhibit hysteresis are only metastable. Here we illustrate an extremely simple example determined by a family of double well potentials of varying relative heights $\psi(\xi,L)$. The two wells are at ± 1 and ψ is a step function of the parameter L. In this elementary testbed, the solution of the Fokker-Planck Equation which gives the distribution of the ξ is simulated by a straight forward

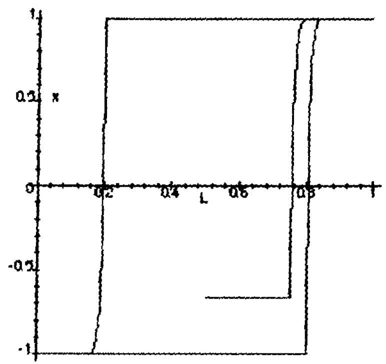

Figure 1 A hysteresis portrait determined by a Fokker-Planck Equation showing metastable states

explicit scheme and implemented with Maple. The first moment, or average ξ,

$$x = \langle \xi \rangle = \int_R \xi\, \rho(\xi,t)\, d\xi$$

is plotted as a function of the load parameter L. Although we lack the space to provide details, most of the outer loop does represent a distribution which is in equilibrium, which is the appropriate Gibbs distribution. But the inner segment and the portion of the outer loop from $0.5 < L < 0.8$, $x = -1$ is only metastable.

5. A BRIEF VIEW OF THE CONSTRAINED THEORY

In this section we give a schematic description of work with Richard James and Shlomo Ta'asan. The notion of the wiggly energy was first introduced by Abeyaratne, Chu, and James [1] in the shape memory CuAlNi system to interpret the hysteresis in evolution of the microstructure. A system similar to that of §2, governed by a Helmholtz free energy $W(\alpha)$ and an additional work of loading $T(\alpha)$ will have total energy, in its homogeneous Young measure form,

$$\int_R (W(\alpha) + T(\alpha))\, d\nu(\alpha).$$

Assume that the system is near equilibrium, which leads to the constraint

$$\operatorname{supp} \nu \subset \{W = \min W = 0\} \tag{5.1}$$

and energy

$$E = \min_\nu \int_R (W(\alpha) + T(\alpha))\, d\nu(\alpha) = \min_\nu \int_R T(\alpha)\, d\nu(\alpha).$$

Assume that the set of Young measures obeying (5.1) is a 1-parameter family $\nu^{(\xi)}$ depending on ξ. Then

$$E = \psi(\xi) = \min_\xi \int_R T(\alpha)\, d\nu^{(\xi)}(\alpha),$$

leading to the driving force equation, where $\mu > 0$ is a parameter,

$$\frac{d\xi}{dt} = -\mu\psi'(\xi).$$

We take $\mu = 1$ in the sequel.

Owing to the accomodation of a finer scale structure, whose details we do not describe here, we are led to augment ψ by a family ψ_ε which we take to be, with $\psi(\xi) = \frac{1}{2}|\xi|^2$,

$$\psi_\varepsilon(\xi) = \frac{1}{2}|\xi|^2 + \varepsilon\psi_o\left(\frac{\xi}{\varepsilon}\right), \ \varepsilon > 0,$$

$$\psi_o \text{ periodic of period 1, } |\psi_o'| \le a, \text{ and } \int_{[0,1]} \psi_o(y)\, dy = 0.$$

We arrive in this way at a Langevin Equation

$$dX_\varepsilon = -\psi_\varepsilon'(X_\varepsilon)dt + \sqrt{2\sigma}\, dB(t),$$

and corresponding Fokker-Planck Equation

$$\frac{\partial\rho}{\partial t} = \sigma\frac{\partial^2\rho}{\partial\xi^2} + \frac{\partial}{\partial\xi}(\psi_\varepsilon'\rho), \ -\infty < \xi < \infty, \ t > 0.$$

Our objective in this exercise is to show that the effective Fokker-Planck Equation, as $\sigma,\varepsilon \to 0$, has a greatly reduced drift. The perturbed system may dwell in states that are not equilibria of the original one.

Let us sketch a formal argument. Multiplying by a test function $\zeta \in C_0^\infty(\mathbf{R})$,

$$\left|\left\langle \sigma\frac{\partial^2\rho}{\partial\xi^2}, \zeta \right\rangle\right| = \left|\sigma\int_R \zeta''\rho\, d\xi\right| \le \sigma \max|\zeta''| \to 0 \text{ as } \sigma \to 0,$$

so,

$$-\int_R \zeta'\psi_\varepsilon'\rho\, d\xi = \int_R \zeta\frac{\partial\rho}{\partial t}\, d\xi.$$

This first order linear equation may be solved by differencing in time, as suggested by our discrete scheme, which leads to the approximating equation

$$\frac{\partial}{\partial \xi}(\psi_\varepsilon' \rho) = \frac{1}{h}(\rho - \rho^{(k-1)}),$$

or in weak form,

$$-\int_R \zeta' \psi_\varepsilon' \rho \, d\xi = \frac{1}{h}\int_R \zeta(\rho - \rho^{(k-1)})\, d\xi.$$

Choosing ζ a suitable Heaviside function with jump at a given ξ,

$$\psi_\varepsilon'(\xi)\rho(\xi) = \frac{1}{h}(F(\xi) - F^{(k-1)}(\xi)),$$

where F and $F^{(k-1)}$, the distribution functions of the probability densities ρ and $\rho^{(k-1)}$, converge pointwise as $\varepsilon \to 0$. From this and the fact that ψ_ε' has on the order of $2a/\varepsilon$ zeros in $[-a,a]$, we may infer the form of the limit transport equation

$$\frac{\partial}{\partial t}\rho = \frac{\partial}{\partial \xi}(b\rho) \quad \text{where} \quad b(\xi) = \left\{ \int_{[0,1]} (\xi + \psi_o(y))^{-1}\, dy \right\}^{-1} \text{ if } |\xi| > a,$$

$$b(\xi) = 0 \quad \text{if } |\xi| \leq a.$$

This is the form obtained in [1].

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