Uniqueness of thermodynamic projector and kinetic basis of molecular individualism

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Abstract

Two results are presented: First, we solve the problem of persistence of dissipation for reduction of kinetic models. Kinetic equations with thermodynamic Lyapunov functions are studied. Uniqueness of thermodynamic projector is proven: There exists only one projector which transforms the arbitrary vector field equipped with the given Lyapunov function into a vector field with the same Lyapunov function for a given anzatz manifold which is not tangent to the Lyapunov function levels. Moreover, from the requirement of persistence of the *sign* of dissipation follows that the *value* of dissipation (the entropy production) persists too. The explicit construction of this *thermodynamic projector* is described. In example we apply this projector to derivation the equations of reduced kinetics for the Fokker-Planck equation. This equation describes the polymer dynamics in flow. The new class of closures is developed: The kinetic multipeak polyhedrons. Distributions of this type are expected to appear in each kinetic model with multidimensional instability as universally, as Gaussian distribution appears for stable systems. The number of possible relatively stable states of polymer molecules grows as 2^m, and the number of macroscopic parameters is in order mn, where n is the dimension of configuration space, and m is the number of independent unstable directions in this space. The elaborated class of closures and equations pretends to describe the effects of "molecular individualism". This is the second result.

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Introduction

Reduction of description for dissipative kinetics assumes (explicitly or implicitly) the following picture: There exists a manifold of slow motions in the space of distributions. From the initial conditions the system goes quickly in a small neighborhood of the manifold, and after that moves slowly along it.

There are three basic problems in the model reduction:

1. How to **construct** the slow manifold;

2. How to **project** the initial equation onto the constructed slow manifold, i.e. how to split motions into fast and slow;

3. How to **improve** the constructed manifold and the projector in order to make the manifold more invariant and the motion along it slower.

The first problem is often named "the closure problem", and its solution is the closure assumption; the second problem is "the projection problem". Sometimes these problems are discussed and solved simultaneously (for example, for quasiequilibrium, or, what is the same, for MaxEnt closure assumptions [1, 2, 3, 4, 5]). Sometimes the time required for the solution of the projection problem after construction of anzatz may be rather long, as in the known case of the Tamm–Mott-Smith approximation in the theory of shock waves (see, for example, [6]). If one has constructed the closure assumption which is the *invariant manifold* [6, 7, 8], then the projection problem disappears, because the vector field is tangent to the invariant manifold.

Let us discuss the initial kinetic equation as the abstract ordinary differential equation,

$$\frac{d\Psi}{dt} = J(\Psi), \tag{1}$$

where $\Psi = \Psi(q)$ is the distribution function, q is the point in the configuration (for the Fokker-Planck equation) or phase (for the Liouville equation) space.

Let the closure assumption be given:

$$\Psi = \Psi(M|q), \tag{2}$$

where M is the set of macroscopic variables, which are coordinates on the manifold (2). The tangent space T_{M_0} for the manifold (2) in the point M_0 is the image of the differential:

$$T_{M_0} = \mathrm{im}(D_M(\Psi(M|q))_{M_0}. \tag{3}$$

How to construct the dynamic equation for the variables M? This is the projection problem. The equivalent setting is: how to project $J(\Psi(M_0|q))$ onto T_{M_0}? If $dM/dt = F(M)$ is the equation for M, then the equation on the manifold is $d\Psi(M|q)/dt = (D_M \Psi(M|q)) \cdot F(M)$.

There exist three common ways to construct the projector onto T_{M_0}:

1. Moment parametrization;

2. Spectral projectors of Jacobians for equation (1);

3. Spectral projectors of "symmetric part" of Jacobians for this equation.

The moment parametrization is the best way to "hide" the projector problem in a natural way: Let the macroscopic variables be defined not only on the manifold $\Psi(M|q)$, but in the neighborhood of this manifold: $M = m(\Psi)$, with the identity $m(\Psi(M|q)) \equiv M$. Then we can define dM/dt in a natural way:

$$\frac{dM}{dt} = (D_\Psi m(\Psi(M|q)))J(\Psi(M|q)). \tag{4}$$

As it will be demonstrated below, this simple formula is appropriate only for the quasiequilibrium (MaxEnt) approximation, because in other cases it leads to entropy decreasing for some initial conditions and, hence, to a perpetuum mobile of the second kind (this happens in reduced equations, of course, and not in reality).

The idea of slow-fast decomposition through spectral decomposition of Jacobian seems very attractive (see, for example, the theory of the so-called intrinsic low-dimensional manifold (ILDM) [9]): Let the spectrum of $D_\Psi J(\Psi)$ can be separated in two parts: $\mathrm{Re}\lambda_{\mathrm{sl}} < A \ll B < \mathrm{Re}\lambda_{\mathrm{fst}} < 0$. There are two invariant subspaces which correspond to slow (E_{sl}) and to fast (E_{fst}) points of the spectrum. The suggested solution of the projection problem is: The tangent space T_M of the slow manifold should be not very different from the slow invariant subspace E_{sl}, and the projection of J onto T_M should be done parallel to the fast invariant subspace E_{fst}.

The eigenvectors and eigenprojectors of the non-selfadjoint operators may be very unstable in calculations. So, it may be better to use the selfadjoint operator and it's spectral decomposition.

Dynamics of distances depends not on the Jacobian, but on the symmetrized Jacobian:

$$\frac{d(\Delta\Psi, \Delta\Psi)}{dt} = (\Delta\Psi, [D_\Psi J(\Psi) + (D_\Psi J(\Psi))^+]\Delta\Psi) + o(\Delta\Psi),$$

where $(\,,\,)$ is usual scalar product, $\Delta\Psi$ is difference between two solutions of equation (1), $\Psi = \Psi(t)$ is one of these solutions.

In the theory of inertial manifolds [10, 11, 12], for example, one usually uses the following form of equation (1) with selfadjoint linear operator A: $\dot\Psi + A\Psi = R(\Psi)$, and spectral decomposition of A rules the fast-slow splitting.

There are different physically motivated ways to select the scalar product and create the symmetrization [13, 14, 15]. But symmetrization does not provide termodinamicity and the entropy for the projected equations can decrease.

The construction of the thermodynamic projector which always preserve the dissipation is simple and transparent. We shall describe it now, in the introduction, and it's uniqueness will be proved in the next section. The proof of uniqueness will give us a demonstration, that all other ways of projection are thermodynamically inconsistent, and lead to entropy decrease, and, hence, to the perpetuum mobile of the second kind.

Let for the system (1) the entropy $S(\Psi)$ exist, and

$$\frac{dS}{dt} = (D_\Psi S)J(\Psi) \geq 0. \tag{5}$$

We introduce the entropic scalar product $\langle \,|\, \rangle_\Psi$:

$$\langle a \,|\, b \rangle_\Psi = -(a, (D_\Psi^2 S)(b)), \tag{6}$$

where D_Ψ^2 is the second differential of the entropy.

The thermodynamic projector is defined for a given point Ψ and a subspace T (the tangent space to an anzatz manifold). Let us consider a subspace $T_0 \subset T$ which is annulled by the differential S in the point Ψ: $(D_\Psi S)T_0 = 0$. If $T_0 = T$, then the thermodynamic projector is the orthogonal projector on T with respect to the entropic scalar product $\langle | \rangle_\Psi$. Suppose that $T_0 \neq T$. Let $e_g \in T$, $e_g \perp T_0$ with respect to the entropic scalar product $\langle | \rangle_\Psi$, and $(D_\Psi S)(e_g) = 1$. These conditions define vector e_g uniquely. The projector onto T is defined by the formula

$$P(J) = P_0(J) + e_g(D_\Psi S)(J), \tag{7}$$

where P_0 is the orthogonal projector onto T_0 with respect to the entropic scalar product $\langle | \rangle_\Psi$.

For example, if T a finite-dimensional space, then the projector (7) is constructed in the following way. Let $e_1, .., e_n$ be a basis in T, and for definiteness, $(D_\Psi S)(e_1) \neq 0$.
1) Let us construct a system of vectors

$$b_i = e_{i+1} - \lambda_i e_1, (i = 1, .., n-1), \tag{8}$$

where $\lambda_i = (D_\Psi S)(e_{i+1})/(D_\Psi S)(e_1)$, and hence $(D_\Psi S)(b_i) = 0$. Thus, $\{b_i\}_1^{n-1}$ is a basis in T_0.
2) Let us orthogonalize $\{b_i\}_1^{n-1}$ with respect to the entropic scalar product $\langle | \rangle_\Psi$. We get an orthonormal with respect to $\langle | \rangle_\Psi$ basis $\{g_i\}_1^{n-1}$ in T_0.
3) We find $e_g \in T$ from the conditions:

$$\langle e_g \mid g_i \rangle_\Psi = 0, (i = 1, .., n-1), (D_\Psi S)(e_g) = 1. \tag{9}$$

and, finally we get

$$P(J) = \sum_{i=1}^{n-1} g_i \langle g_i \mid J \rangle_\Psi + e_g(D_\Psi S)(J) \tag{10}$$

If $(D_\Psi S)(T) = 0$, then the projector P is simply the orthogonal projector with respect to the $\langle | \rangle_\Psi$ scalar product. This is possible if Ψ is the global maximum of entropy point (equilibrium). Then

$$P(J) = \sum_{i=1}^{n} g_i \langle g_i | J \rangle_\Psi, \langle g_i | g_j \rangle_\Psi = \delta_{ij}. \tag{11}$$

The entropy production for projected vector field (10) is the same, as for the initial vector field (1):

$$(D_\Psi S)(P(J)) = (D_\Psi S)(e_g)(D_\Psi S)(J). \tag{12}$$

The significance of the case $(D_\Psi S)(T) = 0$ may be not clear at the first glance, because such a state Ψ should be the equilibrium point with $J(\Psi) = 0$. Nevertheless, this case is important as a limit of nonequilibrium Ψ, and for discussion of persistence of the Onsager relations[1] as well, as for the proof of uniqueness the thermodynamic projector.

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[1]The preservation of the Onsager reciprocity relations for projected equations follows from the requirement of persistence of the *sign* of dissipation. This seems surprising, because these relations do not follow from the entropy grows. It should be stressed, that only the conditional statement can be proved: if for the initial system hold the Onsager reciprocity relations, then these relations hold for the projected system.

In this paper we do not discuss the third main problem of model reduction: How to improve the constructed manifold and the projector in order to make the manifold more invariant and the motion along it more slow. This discussion can be found in different works [6, 7, 8, 10, 11, 15].

The discovery of the molecular individualism for dilute polymers in the flow [16] was the challenge to theory from the very beginning. "Our data should serve as a guide in developing improved microscopic theories for polymer dynamics"... was the concluding sentence of the paper [16]. P. de Gennes invented the term "molecular individualism" [17]. He stressed that in this case the usual averaging procedures are not applicable. At the highest strain rates distinct conformation shapes with different dynamics were observed [16]. Further works for shear flow demonstrated not only shape differences, but different large temporal fluctuations [18].

Equation for the molecules in a flow are known. These are the Fokker-Planck equations with external force. The theory of the molecular individualism is hidden inside these equations. Following the logic of model reduction we should solve two problems: to construct the slow manifold, and to project the equation on this manifold. The second problem is solved: the thermodynamic projector is necessary for this projection. Why should we use this projector also for driven systems? These systems can be formally written as

$$\frac{d\Psi}{dt} = J(\Psi) + J_{\text{ex}}, \tag{13}$$

where J_{ex} is the external field (driven force).

The entropy for system (13) can decrease, but the thermodynamic processes modeled by the term $J(\Psi)$ should always produce the entropy (both in the initial and in the projected systems). This is the reason to use the thermodynamic projector also for open systems.

How to solve the first problem? We can find a hint in the paper [19]. The Gaussian distributions form the invariant manifold for the FENE-P model of polymer dynamics, but, as it was discovered in [19], this manifold can become unstable in the presence of a flow. We propose to model this instability as dissociation of the Gaussian peak into two peaks. This dissociation describes appearance of an unstable direction in the configuration space.

In the classical FENE-P model of polymer dynamics a polymer molecule is represented by one coordinate: the stretching of molecule (the connector vector between the beads). There exists a simple mean field generalized models for multidimensional configuration spaces of molecules. In these models dynamics of distribution functions is described by the Fokker-Planck equation in a quadratic potential well. The matrix of coefficients of this quadratic potential depends on the matrix of the second order moments of the distribution function. The Gaussian distributions form the invariant manifold for these models, and the first dissociation of the Gaussian peak after appearance of the unstable direction in the configuration space has the same nature and description, as for the one-dimensional models of molecules considered below.

At the highest strain there can appear new unstable directions, and corresponding dissociations of Gaussian peaks form a *cascade* of dissociation. For m unstable directions we get the Gaussian parallelepiped: The distribution function is represented as a sum of 2^m Gaussian peaks located in the vertixes of parallelepiped:

$$\Psi(q) = \frac{1}{2^m (2\pi)^{n/2} \sqrt{\det \Sigma}} \sum_{\varepsilon_i = \pm 1, \, (i=1,\ldots,m)} \exp\left(-\frac{1}{2}\left(\Sigma^{-1}\left(q + \sum_{i=1}^{m} \varepsilon_i \varsigma_i\right), \, q + \sum_{i=1}^{m} \varepsilon_i \varsigma_i\right)\right), \quad (14)$$

where n is dimension of configuration space, $2\varsigma_i$ is the vector of the ith edge of the parallelepiped, Σ is the one peak covariance matrix (in this model Σ is the same for all peaks). The macroscopic variables for this model are:

1. The covariance matrix Σ for one peak;

2. The set of vectors ς_i (or the parallelepiped edges).

The family of distributions (14) can be improved to include the proper equilibrium (this is important condition: the equilibrium should belong to the anzatz manifold). There may be different further refinements, some of them are discussed below.

1 Uniqueness of thermodynamic projector

In this section, the uniqueness theorem for thermodynamic projector will be proved.

1.1 Projection of linear vector field

Let E be a real Hilbert space with the scalar product $\langle \,|\, \rangle$, Q be a set of linear bounded operators in E with negatively definite quadratic form $\langle Ax \mid x \rangle \leq 0$ for every $A \in Q$, $T \subsetneq E$ be a nontrivial ($T \neq \{0\}$) closed subspace. For every projector $P : E \to T$ ($P^2 = P$) and linear operator $A : E \to E$ we define the projected operator $P(A) : T \to T$ in such a way:

$$P(A)x = PAx \equiv PAPx \text{ for } x \in T. \tag{15}$$

The space T is the Hilbert space with the scalar product $\langle \,|\, \rangle$. Let Q_T be a set of linear bounded operators in T with negatively define quadratic form $\langle Ax \mid x \rangle \leq 0$.

Proposition 1. *The inclusion $P(Q) \subseteq Q_T$ for a projector $P : E \to T$ holds if and only if P is the orthogonal projector with respect to the scalar product $\langle \,|\, \rangle$.*

Proof. If P is orthogonal (and, hence, selfadjoint) and $\langle Ax \mid x \rangle \leq 0$, then

$$\langle PAPx \mid x \rangle = \langle APx \mid Px \rangle \leq 0.$$

If P is not orthogonal, then $Px \neq 0$ for some vector $x \in T^{\perp}$ in orthogonal complement of T. Let us consider the negatively defined selfadjoint operator

$$A_x = -\mid Px - ax\rangle\langle Px - ax \mid$$

($A_x y = -(Px - ax)\langle Px - ax \mid y\rangle$). The projection of A_x on T is:

$$P(A_x) = (a-1)\mid Px\rangle\langle Px \mid .$$

This operator is not negatively definite for $a > 1$. $\square$

Immediately from this proof follows the Corollary 1.

Corollary 1. *Let $Q^{\mathrm{sym}} \subset Q$ be a subset of selfadjoint operators in E. The inclusion $P(Q^{\mathrm{sym}}) \subseteq Q_T$ for a projector $P : E \to T$ holds if and only if P is the orthogonal projector with respect to the scalar product $\langle\,|\,\rangle$.* $\square$

Corollary 2. *Let $Q_T^{\mathrm{sym}} \subset Q_T$ be a subset of selfadjoint operators in T. If $P(Q) \subseteq Q_T$ for a projector $P : E \to T$, then $P(Q^{\mathrm{sym}}) \subseteq Q_T^{\mathrm{sym}}$.*

It follows from the Proposition 1 and the obvious remark: If operators A and P are selfadjoint, then operator PAP is selfadjoint too. $\square$

The Proposition 1 means that a projector which transforms every linear vector field Ax with Lyapunov function $\langle x \mid x \rangle$ into projected vector field $PAPx$ with the same Lyapunov function is orthogonal with respect to the scalar product $\langle\,|\,\rangle$.

According to the Corollary 1, the conditions of the Proposition 1 can be made weaker: A projector which transforms every *selfadjoint* linear vector field Ax with Lyapunov function $\langle x \mid x \rangle$ into projected vector field $PAPx$ with the same Lyapunov function is orthogonal with respect to the scalar product $\langle\,|\,\rangle$. In physical applications it means, that we can deal with requirement of dissipation persistence for vector field with Onsager reciprocity relations. The consequence of such a requirement will be the same, as for the class of all continuous linear vector field: The projector should be orthogonal.

The Corollary 2 is a statement about persistence of the reciprocity relations.

1.2 The uniqueness theorem

In this subsection we will discuss finite-dimensional systems. There are technical details which make the theory of nonlinear infinite-dimensional case too cumbersome: the Hilbert space equipped with entropic scalar product $\langle\,|\,\rangle_\Psi$ (12) for different Ψ consists of different functions. Of course, there exists a common dense subspace, and geometrical sense remains the same, as for the finite-dimensional space, but we prefer to defer the discussion of all these details till a special mathematical publication.

Let E be n-dimensional real vector space, $U \subset E$ be a domain in E, and a m-dimensional space of parameters L be defined, $m < n$, and let W be a domain in L. We consider differentiable maps, $F : W \to U$, such that, for every $y \in W$, the differential of F, $D_y F : L \to E$, is an isomorphism of L on a subspace of E. That is, F are the manifolds, immersed in the phase space of the dynamic system (1), and parametrized by parameter set W.

Let the twice differentiable function S on U be given (the entropy). We assume that S is strictly concave in the second approximation: The quadratic form defined by second differential of the entropy $D_\Psi^2 S(x, x)$ is strictly negative definite in E for every $\Psi \in U$. We will use the entropic scalar product (6). Let S have the interior point of maximum in U: $\Psi^{eq} \in \mathrm{int} U$.

The function S is Lyapunov function for a vector field J in U, if $(D_\Psi S)(J(\Psi)) \geq 0$ for every $\Psi \in U$.

First of all, we shall study vector fields with Lyapunov function S in the neighborhood of Ψ^{eq}. Let $0 \in \mathrm{int} W$, $F : W \to U$ be an immersion, and $F(0) = \Psi^{eq}$. Let us define $T_y = \mathrm{im} D_y F(y)$ for each $y \in W$. This T_y is the tangent space to $F(W)$ in the point y. Suppose that the mapping F is sufficiently smooth, and $F(W)$ is not tangent to entropy levels:

$$T_y \nsubseteq D_\Psi S|_{\Psi = F(y)}$$

for every $y \neq 0$. The thermodynamic projector for a given F is a projector-valued function $y \mapsto P_y$, where $P_y : E \to T_y$ is a projector. The **thermodynamic conditions** reads: *For every smooth vector field $J(\Psi)$ in U with Lyapunov function S the projected vector field $P_y(J(F(y)))$ on $F(W)$ has the same Lyapunov function $S(F(y))$.*

Proposition 1 and Corollaries 1, 2 make it possible to prove uniqueness of the thermodynamic projector for the weakened thermodynamic conditions too: *For every smooth vector field $J(\Psi)$ in U with Lyapunov function S and selfadjoint Jacobian operator for every equilibrium point (zero of $J(\Psi)$) the projected vector field $P_y(J(F(y)))$ on $F(W)$ has the same Lyapunov function $S(F(y))$.* We shall not discuss it separately.

Proposition 2. *Let the thermodynamic projector P_y be a smooth function of y. Then*

$$P_0 = P_0^\perp \text{ and } P_y = P_y^\perp + O(y), \tag{16}$$

where $P_y^\perp$ is orthogonal projector onto T_y with respect to the entropic scalar product $\langle | \rangle_{F(y)}$.

Proof. A smooth vector field in the neighborhood of $F(0) = \Psi^{eq}$ can be presented as $A(\Psi - \Psi^{eq}) + o(\|\Psi - \Psi^{eq}\|)$, where A is a linear operator. If S is Lyapunov function for this vector field, then the quadratic form $\langle Ax \mid x \rangle_{\Psi^{eq}}$ is negatively definite. $P_y = P_0 + O(y)$, because P_y is a continuous function. Hence, for P_0 we have the problem solved by the Proposition 1, and $P_0 = P_0^\perp$. $\square$

Theorem. *Let the thermodynamic projector P_y be a smooth function of y. Then*

$$P_y = P_{0y} + e_g D_\Psi S|_{\Psi = F(y)}, \tag{17}$$

where notations of formula (7) are used: T_{0y} is the kernel of linear functional $D_\Psi S|_{\Psi = F(y)}$ in T_y, $P_{0y} : T_{0y} \to E$ is the orthogonal projector with respect to the entropic scalar product $\langle \mid \rangle_{F(y)}$ (12). Vector $e_g \in T$ is proportional to the Riesz representation g_y of linear functional $D_\Psi S|_{\Psi = F(y)}$ in T_y with respect to the entropic scalar product:

$$\langle g_y \mid x \rangle_{F(y)} = (D_\Psi S|_{\Psi = F(y)})(x)$$

for every $x \in T_y$, $e_g = g_y / \langle g_y \mid g_y \rangle_{F(y)}$.

Proof. Let $y \neq 0$. Let us consider auxiliary class of vector fields J on U with additional linear balance $(D_\Psi S)_{\Psi = F(y)})(J) = 0$. If such a vector field has Lyapunov function S, then $\Psi = F(y)$ is its equilibrium point: $J(F(y)) = 0$. The class of vector fields with this additional linear balance and Lyapunov function S is sufficiently rich and we can use the Propositions 1, 2 for dynamics on the auxiliary phase space

$$\{x \in U | (D_\Psi S|_{\Psi = F(y)})(x - F(y)) = 0\}.$$

Hence, the restriction of P_y on the hyperplane $\ker D_\Psi S|_{\Psi = F(y)}$ is P_{0y}. Formula (17) gives the unique continuation of this projector on the whole E. $\square$

1.3 Thermodynamic projector, quasiequilibrium, and entropy maximum

The thermodynamic projector projects any vector field which satisfies the second law of thermodynamics into the vector field which satisfies the second law too. Another projectors violate the second law. But what does it mean? Each projector P_Ψ onto tangent space to an anzatz manifold in a point Ψ induces the fast-slow motion splitting:

Fast motion is the motion parallel to $\ker P_\Psi$ (on the affine subspace $\Psi + \ker P_\Psi$ in the neighborhood of Ψ), slow motion is the motion on the slow manifold and in the first order it is parallel to the tangent space T_Ψ in the point Ψ (in the first order this slow manifold is the affine subspace $\Psi + \mathrm{im}P_\Psi$, $T_\Psi = \mathrm{im}P_\Psi$), and velocity of the slow motion in point Ψ belongs to image P_Ψ.

If P_Ψ is the thermodynamic projector, then Ψ is the point of entropy maximum on the affine subspace of fast motion $\Psi + \ker P_\Psi$. It gives the solution to the problem

$$S(x) \to \max,\ x \in \Psi + \ker P_\Psi. \tag{18}$$

This is the most important property of thermodynamic projector [6]. Let us call it for nonequilibrium points Ψ *the property* **A**:

$$\textbf{A.} \qquad \ker P_\Psi \subset \ker D_\Psi S. \tag{19}$$

If the projector P_Ψ with the property **A** can be continued to the equilibrium point, Ψ^{eq}, as a smooth function of Ψ, then in this point $\ker P_\Psi \perp \mathrm{im}P_\Psi$. If this is valid for all systems (including systems with additional linear balances), then the following *property* **B** holds:

$$\textbf{B.} \qquad (\ker P_\Psi \bigcap \ker D_\Psi S) \perp (\mathrm{im}P_\Psi \bigcap \ker D_\Psi S). \tag{20}$$

Of course, orthogonality in formulae (19,20) is considered with respect to the entropic scalar product in point Ψ.

The property **A** means that the value of entropy production persists for all nonequilibrium points. The sense of property **B** is: each point of the slow manifold can be made an equilibrium point (after the deformation of the system which leads to appearance on additional balance). And for equilibrium points the orthogonality condition (20) follows from the property **A**.

If P_Ψ does not have the property **A**, then Ψ is not the point of entropy maximum on the affine subspace of fast motion $\Psi + \ker P_\Psi$, so either the fast motion along this subspace does not leads to Ψ (and, hence, the point Ψ does not belong to slow manifold), or this motion violates the second law, and the entropy decreases. This is the violation of the second law of thermodynamics during the fast motion. If P_Ψ does not have the property **A**, then such a violation is expected for almost every system.

On the other hand, if P_Ψ is not the thermodynamic projector, then there exists a thermodynamic vector field J, with non-thermodynamic projection: S is Lyapunov function for J (it increases), and is not Lyapunov function for $P_\Psi(J)$ (it decreases in the neighborhood of Ψ). The difference between violation of the second law of thermodynamics in fast and slow motions for a projector without the property **A** is: for the fast motion this violation typically exists, for the slow (projected) motion there exist some thermodynamic systems with such a violation. On the other hand, the violation in slow motion is more important for applications, if we use the slow dynamics as an answer (and assume that the fast dynamics is relaxed).

If P_Ψ does not have the property **B**, then there exist systems with violation of the second law of thermodynamics in fast and slow motions. Here we can not claim that the second law violates for almost every system, but such systems exist.

One particular case of thermodynamic projector is known during several decades. It is the quasiequilibrium projector on the tangent space of the quasiequilibrium (MaxEnt) manifold.

Let a set of macroscopic (slow) variables be given: $M = m(\Psi)$. The vector of macroscopic variables M is a continuous linear function of microscopic variables Ψ. Let the anzatz manifold be the manifold of conditional entropy maximum:

$$S(\Psi) \to \max,\ m(\Psi) = M. \qquad (21)$$

The solution of the problem (21) Ψ_M^{qe} parametrized by values of the macroscopic variables M is the quasiequilibrium manifold.

The projector on the tangent space to the quasiequilibrium manifold is:

$$\pi_M^{\mathrm{qe}} = (D_M \Psi_M^{\mathrm{qe}})_M\, m = \left(D_\Psi^2 S\right)_{\Psi_M^{\mathrm{qe}}}^{-1} m^T \left(m \left(D_\Psi^2 S\right)_{\Psi_M^{\mathrm{qe}}}^{-1} m^T\right)^{-1} m. \qquad (22)$$

This formula was essentially obtained by Robertson [20].

First of all, the thermodynamic projector (22) for the quasiequilibrium manifold (21) is the orthogonal projector with respect to the entropic scalar product (6). In this case both terms in the thermodynamic projector (7) are orthogonal projectors with respect to the entropic scalar product (6). The first term, P_0, is orthogonal projector by construction. For the second term, $e_g(D_\Psi S)$, it means that the Riesz representation of the linear functional $D_\Psi S$ in the whole space E with respect to the entropic scalar product belongs to the tangent space of the quasiequilibrium manifold. This Riesz representation is the gradient of S with respect to $\langle\,|\,\rangle_\Psi$. The following Proposition gives simple and important condition of orthogonality of the thermodynamic projector (7). Let $\boldsymbol{M}$ be an anzatz manifold, and let $\boldsymbol{V}$ be some quasiequilibrium manifold, $\Psi \in \boldsymbol{M} \bigcap \boldsymbol{V}$, T_Ψ be the tangent space to the anzatz manifold $\boldsymbol{M}$ in the point Ψ. Suppose that there exists a neighborhood of Ψ where $\boldsymbol{V} \subseteq \boldsymbol{M}$. We will use the notation $\mathrm{grad}_\Psi S$ for the Riesz representation of the linear functional $D_\Psi S$ in the scalar product $\langle\,|\,\rangle_\Psi$: $\langle\mathrm{grad}_\Psi S|f\rangle_\Psi \equiv (D_\Psi S)(f)$ for $f \in E$.

Proposition 3. *Under given assumptions, $\mathrm{grad}_\Psi S \in T_\Psi$, and the thermodynamic projector P_Ψ is the orthogonal projector onto T_Ψ with respect to the entropic scalar product (6).* $\square$

So, if a point Ψ on the anzatz manifold $\boldsymbol{M}$ belongs to some quasiequilibrium submanifold $\boldsymbol{V} \subseteq \boldsymbol{M}$, then the thermodynamic projector in this point is simply the orthogonal projector with respect to the entropic scalar product (6).

Proposition 3 is useful in the following situation. Let the quasiequilibrium approximation be more or less satisfactory, but the "relevant degrees of freedom" depend on the current state of the system. It means that for some changes of the state we should change the list of relevant macroscopic variables (moments of distribution function for generation the quasiequilibrium). Sometimes it can be described as presence of hidden degrees of freedom, which are not moments. In these cases the manifold of reduced description should be extended. We have a family of systems of moments $M_\alpha = m_\alpha(\Psi)$, and a family of corresponding quasiequilibrium manifolds $\boldsymbol{M}_\alpha$: The manifold $\boldsymbol{M}_\alpha$ consist of solutions of optimization problem $S(\Psi) \to \max,\ m_\alpha(\Psi) = M$ for given α and all admissible values for M. To create a manifold of reduced description it is possible to join all the moments M_α in one family, and construct the corresponding quasiequilibrium manifold. Points on this manifold are parametrized by the family of moments values $\{M_\alpha\}$ for all possible α. It leads to a huge increase of the quasiequilibrium manifold. Another way to extension of the quasiequilibrium manifold is a union of all the manifolds $\boldsymbol{M}_\alpha$ for all α. In accordance with the Proposition 3, the thermodynamic projector for this union is simply the orthogonal projector with respect to the entropic scalar product. This kind of manifolds

gives a closest generalization of the quasiequilibrium manifolds. An example of such a construction will be described below.

Quasiequilibrium approximation became very popular after works of Jaynes [1][2].

Thermodynamic projector gives the presentation of almost arbitrary anzatz as the quasiequilibrium manifold. This property opens the natural field for applications of thermodynamic projector: construction of Galerkin approximations with thermodynamic properties. Of course, there is a "law of the difficulty conservation": for the quasiequilibrium with the moment parameterization the slow manifold is usually not explicitly given, and it can be difficult to calculate it. Thermodynamic projector completely eliminates this difficulty. On the other side, on the quasiequilibrium manifold with the moment parameterization (if it is found) it is easy to find the dynamics: simply write $\dot{M} = m(J)$. The building of the thermodynamic projector may require some efforts. Finally, for each of the distributions Ψ it is easy to find its projection on the classical quasiequilibrium manifold $\Psi \to \Psi^{qe}_{M(\Psi)}$: it requires just calculation of the moments $M(\Psi)$. The analogue projection for the general thermodynamic projector is not so easy: $\Psi \to f$ with the condition $P_f(\Psi - f) = 0$. This equation defines the projection of some neighborhood of the manifold Ω on Ω, but the solution of this equation is rather difficult. Fortunately, we need to build such operators only to analyze the fast processes of the initial relaxation layer, and it is not necessary to investigate the slow dynamics.

Is it necessary to use the thermodynamic projector everywhere? The persistence of dissipation is necessary, because the violation of the second law may lead to strange non-physical effects. If one creates a very accurate method for solution of initial equation (1), then it may be possible to expect that the persistence of dissipation will hold without additional efforts. But this situation yet have not appeared. All methods of model reduction need a special tool to control the persistence of dissipation.

In order to summarize, let us give three reasons to use the thermodynamic projector:

1. It guarantees the persistence of dissipation: all the thermodynamic processes which should product the entropy conserve this property after projecting, moreover, not only the sign of dissipation conserves, but the value of entropy production and the reciprocity relations too;

2. The coefficients (and, more generally speaking, the right hand part) of kinetic equations are known significantly worse then the thermodynamic functionals, so, the

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[2]From time to time it is discussed in the literature, who was the first to introduce the quasiequilibrium approximations, and how to interpret them. At least a part of the discussion is due to a different role the quasiequilibrium plays in the entropy–conserving and the dissipative dynamics. The very first use of the entropy maximization dates back to the classical work of G. W. Gibbs [21], but it was first claimed for a principle by E. T. Jaynes [1]. Probably the first explicit and systematic use of quasiequilibria to derive dissipation from entropy–conserving systems is due to the works of D. N. Zubarev. Recent detailed exposition is given in [2]. For dissipative systems, the use of the quasiequilibrium to reduce description can be traced to the works of H. Grad on the Boltzmann equation [22]. The viewpoint of the present authors was influenced by the papers by L. I. Rozonoer and co-workers, in particular, [3, 4, 23]. A detailed exposition of the quasiequilibrium approximation for Markov chains is given in the book [24] (Chapter 3, *Quasiequilibrium and entropy maximum*, pp. 92-122), and for the BBGKY hierarchy in the paper [5]. We have applied maximum entropy principle to the description the universal dependence the 3-particle distribution function F_3 on the 2-particle distribution function F_2 in classical systems with binary interactions [25]. A general discussion of the maximum entropy principle with applications to dissipative kinetics is given in the review [26]. The methods for corrections the quasiequilibrium approximations are developed in [6, 7, 27, 28]

universality of the thermodynamic projector (it depends only on thermodynamic data) makes the thermodynamic properties of projected system as reliable, as for the initial system;

3. It is easy (much more easy than spectral projector, for example).

2 The art of anzatz: Multi-peak polyhedrons in kinetic systems with instabilities

2.1 How to evaluate the anzatz?

Thermodynamic projector transforms almost arbitrary ansatz into thermodynamically consistent model. So, the simplest criteria of quality of an anzatz (entropy grows, reciprocity relations, etc.) are satisfied by the construction of the projector. How to evaluate the anzatz now?

First of all, we can estimate the *defect of invariance* $\Delta = J(\Psi) - P_\Psi(J(\Psi))$. If Δ is not small (in comparison with the typical value of J), then the anzatz should be improved (for details see, for example, [29, 30]). It is possible to use Δ for error estimation and correction of an anzatz *after* solution of projected equations too (it is so-called post-processing [31, 15]). Let $\Psi^0(t)$, ($t \in [0, T]$) be the solution of projected equations $d\Psi(t)/dt = P_\Psi(J(\Psi))$, and $\Delta(t) = J(\Psi^0(t)) - P_{\Psi^0(t)}(J(\Psi^0(t)))$. Then the following formula

$$\Psi^1(t) = \Psi^0(t) + \int_0^t \Delta(\tau)d\tau \tag{23}$$

gives the Picard iteration for solution of the initial kinetic equation $d\Psi(t)/dt = J(\Psi)$, with initial approximation $\Psi^0(t)$. The integral in the right hand side of equation (23) gives the estimation of the deviation the anzatz solution $\Psi^0(t)$ from the true solution as well, as the correction for this anzatz solution. For a better estimation we can take into account not only $\Delta(t)$, but the linear part of the vector field $J(\Psi)$ near $\Psi^0(t)$, and use different approximations of this linear part [15]. The following representation gives us one of the simplest approximations: $\Psi^1(t) = \Psi^0(t) + \delta\Psi(t)$;

$$\frac{d(\delta\Psi(t))}{dt} = \Delta(t) + \frac{\langle\Delta(t)|(DJ)_{\Psi^0(t)}\Delta(t)\rangle_{\Psi^0(t)}}{\langle\Delta(t)|\Delta(t)\rangle_{\Psi^0(t)}}\delta\Psi(t). \tag{24}$$

where $\Delta(t) = J(\Psi^0(t)) - P_{\Psi^0(t)}(J(\Psi^0(t)))$, $(DJ)_{\Psi^0(t)}$ is the differential of $J(\Psi(t))$ in the point $\Psi^0(t)$, $\langle \, | \, \rangle_{\Psi^0(t)}$ is the entropic scalar product (6) in the point $\Psi^0(t)$.

The solution of equation (24) is

$$\delta\Psi(t) = \int_0^t \exp\left(\int_\tau^t k(\theta)d\theta\right)\Delta(\tau)d\tau, \tag{25}$$

where

$$k(t) = \frac{\langle\Delta(t)|(DJ)_{\Psi^0(t)}\Delta(t)\rangle_{\Psi^0(t)}}{\langle\Delta(t)|\Delta(t)\rangle_{\Psi^0(t)}}.$$

The right hand side of equation (25) improves the simplest Picard iteration (23) and gives both the estimation of the error of the anzatz, and the correction for the solution $\Psi^0(t)$.

The projection of Δ on the slow motion anzatz is zero, hence, for post-processing analysis of the slow motion, the estimation (25) should be supplemented by one more Picard iteration:

$$\delta\Psi_{sl}(t) = P_{\Psi^0(t)}\delta\Psi(t) + \int_0^t P_{\Psi^0(\tau)}((DJ)_{\Psi^0(\tau)})\delta\Psi(\tau)d\tau, \qquad (26)$$

where $\delta\Psi(t)$ is calculated by formula (25).

The thermodynamic projector guarantees the thermodynamic consistence of anzatz, and post-processing gives both the estimations of the error and correction for the solution. So, the main requirement to an anzatz now is: to capture the essence of the phenomenon. This is *the art of anzatz*. Is it possible to formalize this art? In the next subsection we discuss two special anzatz which are known for several decades and mysteriously are at the same time simplest and reliable nonperturbative approximations in the domains of their application. The requested formalization seems to be possible, at least, partially.

2.2 Two-peak approximations

2.2.1 Tamm–Mott-Smith approximation for kinetics of shock waves

Shock waves in gas flows are important from practical, as well, as from theoretical points of view. Some integral parameters of the shock wave front can be obtained by gas dynamics equations with additional thermodynamic relations, for weak shocks the hydrodynamic approach can give the shock front structure too [32]. For strong shocks it is necessary to use the kinetic representation, for rarefied gases the Boltzmann kinetic equation gives the framework for studying the structure of strong shocks [33]. This equation describes the dynamics of the one-particle distribution function $f(\boldsymbol{v}, \boldsymbol{x})$, where $\boldsymbol{v}$ is the vector of particle velocity, and $\boldsymbol{x}$ is the particle position in space. One of the common ways to use the Boltzmann equation in physics away from exact solutions and perturbation expansions consists of three steps:

1. Construction of a specific anzatz for the distribution function for a given physical problem;

2. Projection of the Boltzmann equation on the anzatz;

3. Estimation and correction of the anzatz (optional).

The first and, at the same time, the most successful anzatz for the distribution function in the shock layer was invented in the middle of the XX century. It is the bimodal Tamm–Mott-Smith approximation (see, for example, the book [33]):

$$f(\boldsymbol{v}, \boldsymbol{x}) = f_{\mathrm{TMS}}(\boldsymbol{v}, z) = a_-(z)f_-(\boldsymbol{v}) + a_+(z)f_+(\boldsymbol{v}), \qquad (27)$$

where z is the space coordinate in the direction of the shock wave motion, $f_{\pm}(\boldsymbol{v})$ are the downstream and the upstream Maxwellian distributions, respectively.

Direct molecular dynamics simulation for the Lennard-Jones gas shows good *quantitative* agreement of the Tamm–Mott-Smith anzatz (27) with the simulated velocity distribution functions in the shock fronts for a wide range of Mach number (between 1 and 8.19) [35]. For different points in the shock front the bimodal approximation (27) of the

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simulated velocity distribution function has appropriate accuracy, but the question about approximation of the $a_\pm(z)$ remained open in the paper [35], because the authors of this paper had "no way to decide which of the equations proposed in the literature yields better results".

The thermodynamic projector gives the unique thermodynamically consistent equation for the Tamm–Mott-Smith approximation (27) [6]. These equations have a simple form for the variables:

$$n(z) = \int f_{\mathrm{TMS}}(\boldsymbol{v}, z)d^3\boldsymbol{v}; \; s(z) = -k_{\mathrm{B}} \int f_{\mathrm{TMS}}(\boldsymbol{v}, z) \ln f_{\mathrm{TMS}}(\boldsymbol{v}, z)d^3\boldsymbol{v}.$$

The particles density $n(z)$ is linear function of $a_\pm(z)$. The entropy density s is a more complicated function of $a_\pm$, but there are simple expansions both for weak and for strong shocks [6, 34].

The equations for $n(z, t)$, $s(z, t)$ in the Tamm–Mott-Smith approximation have the form:

$$\frac{\partial s}{\partial t} + \frac{\partial j_s}{\partial z} = \sigma, \; \frac{\partial n}{\partial t} + \frac{\partial j_n}{\partial z} = 0, \tag{28}$$

where

$$j_s(z) = -k_{\mathrm{B}} \int v_z f_{\mathrm{TMS}}(\boldsymbol{v}, z) \ln f_{\mathrm{TMS}}(\boldsymbol{v}, z)d^3\boldsymbol{v}, \; j_n(z) = \int v_z f_{\mathrm{TMS}}(\boldsymbol{v}, z)d^3\boldsymbol{v},$$

and σ is the Boltzmann density of entropy production for the TMS distribution (27):

$$\sigma = -k_{\mathrm{B}} \int J(f_{\mathrm{TMS}})(\boldsymbol{v}, z) \ln f_{\mathrm{TMS}}(\boldsymbol{v}, z)d^3\boldsymbol{v},$$

where $J(f)$ is the Boltzmann collision integral.

The stationary version of equations (28) was first introduced by M. Lampis [34]. in the ad hoc manner. Direct numerical simulation demonstrated that all other known equations for the Tamm–Mott-Smith anzatz violate the second law [36].

2.2.2 Langer–Baron–Miller approximation for spinodal decomposition

The spinodal decomposition is the initial stage of a phase separation in thermodynamically unstable solid solution. It requires no activation energy (unstable does not mean metastable). The order parameter is the composition variable (concentration c of one of components, for example). Hence, the rate of the spinodal decomposition is limited by diffusion processes.

The process of spinodal decomposition was described quantitatively in the paper [37]. This model consists of two coupled equations: for the single-point distribution function of fluctuations, and for the pair correlation function. The fluctuation $u(\boldsymbol{r}) = c(\boldsymbol{r}) - c_0$ is deviation of the concentration c from the average concentration c_0. The time evolution of the single-point distribution density of fluctuation, $\rho_1(u)$ is described by the one-dimensional Fokker-Planck equation:

$$\frac{\partial \rho_1}{\partial t} = M \frac{\partial}{\partial u} \left(\rho_1 \frac{\partial F(u)}{\partial u} + k_{\mathrm{B}} T b \frac{\partial \rho_1}{\partial u} \right), \tag{29}$$

where b is a constant, $F(u)$ is a mean-field free energy which depends on the value of u, on the whole function ρ_1 (because $F(u)$ includes some averages in the mean field approximation), and on the two-point correlation function (because it depends on average square of $\nabla u(\boldsymbol{r})$). The assumption

$$\rho_2[u(\boldsymbol{r}), u(\boldsymbol{r}_0)] \cong \rho_1[u(\boldsymbol{r})]\rho_1[u(\boldsymbol{r}_0)]\{1 + \gamma(|\boldsymbol{r} - \boldsymbol{r}_0|)u(\boldsymbol{r})u(\boldsymbol{r}_0)\} \tag{30}$$

allows to truncate the infinite chain of equations for all correlation functions, and to write the equation for the two-point correlation function. Details are presented in the paper [37].

The mean-field free energy function $F(u)$ is non-stationary and may be non-convex. Thus, the one-peak representations for $\rho_1(u)$ are far from a physical sense, but it is possible to try the two-peak anzatz:

$$\rho_1(u) = a_1 G_\sigma(u - \varsigma_1) + a_2 G_\sigma(u + \varsigma_2), \tag{31}$$

where $a_1 = \varsigma_2/(\varsigma_1 + \varsigma_2)$, $a_2 = \varsigma_1/(\varsigma_1 + \varsigma_2)$ (because obvious normalization conditions), and $G_\sigma(u)$ is the Gaussian distribution: $G_\sigma(u) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{u^2}{2\sigma^2}\right)$.

The systematic use of this two-peak anzatz (31) allowed to get the satisfactory quantitative description for some features of spinodal decomposition. The authors of the paper [37] mentioned that the present computational scheme does appear to be accurate enough to justify its use in the study of realistic metallurgical systems. Instead of thermodynamic projector which was not known in 1975, they used the projection onto the first three non-trivial moments ($\langle u^2 \rangle$, $\langle u^3 \rangle$, $\langle u^4 \rangle$).

2.3 Multi-peak anzatz and mean-field theory of molecular individualism

2.3.1 Two-peak approximation for polymer stretching in flow, and explosion of the Gaussian manifold

We shall consider the simplest case of dilute polymer solutions represented by dumbbell models. The dumbbell model reflects the two features of real–world macromolecules to be orientable and stretchable by a flowing solvent [39].

Let us consider the simplest one-dimensional kinetic equation for the configuration distribution function $\Psi(q, t)$, where q is the reduced vector connecting the beads of the dumbbell. This equation is slightly different from the usual Fokker-Planck equation. It is nonlinear, because of the dependence of potential energy U on the moment $M_2[\Psi] = \int q^2 \Psi(q)dq$. This dependence allows us to get the exact quasiequilibrium equations on M_2, but this equations are not solving the problem: this quasiequilibrium manifold may become unstable when the flow is present [19]. Here is this model:

$$\partial_t \Psi = -\partial_q\{\alpha(t)q\Psi\} + \frac{1}{2}\partial_q^2 \Psi. \tag{32}$$

Here

$$\alpha(t) = \kappa(t) - \frac{1}{2}f(M_2(t)), \tag{33}$$

$\kappa(t)$ is the given time-independent velocity gradient, t is the reduced time, and the function $-fq$ is the reduced spring force. Function f may depend on the second moment of the

distribution function $M_2 = \int q^2 \Psi(q,t)dq$. In particular, the case $f \equiv 1$ corresponds to the linear Hookean spring, while $f = [1 - M_2(t)/b]^{-1}$ corresponds to the self-consistent finite extension nonlinear elastic spring (the FENE-P model, first introduced in [40]). The second moment M_2 occurs in the FENE-P force f as the result of the pre-averaging approximation to the original FENE model (with nonlinear spring force $f = [1 - q^2/b]^{-1}$). The parameter b changes the characteristics of the force law from Hookean at small extensions to a confining force for $q^2 \to b$. Parameter b is roughly equal to the number of monomer units represented by the dumbell and should therefore be a large number. In the limit $b \to \infty$, the Hookean spring is recovered. Recently, it has been demonstrated that FENE-P model appears as first approximation within a systematic self-confident expansion of nonlinear forces [29].

Equation (32) describes an ensemble of non-interacting dumbells subject to a pseudo-elongational flow with fixed kinematics. As is well known, the Gaussian distribution function,

$$\Psi^G(M_2) = \frac{1}{\sqrt{2\pi M_2}} \exp\left[-\frac{q^2}{2M_2}\right], \tag{34}$$

solves equation (32) provided the second moment M_2 satisfies

$$\frac{dM_2}{dt} = 1 + 2\alpha(t)M_2. \tag{35}$$

Solution (34) and (35) is the valid macroscopic description if all other solutions of the equation (32) are rapidly attracted to the family of Gaussian distributions (34). In other words [7], the special solution (34) and (35) is the macroscopic description if equation (34) is the stable invariant manifold of the kinetic equation (32). If not, then the Gaussian solution is just a member of the family of solutions, and equation (35) has no meaning of the macroscopic equation. Thus, the complete answer to the question of validity of the equation (35) as the macroscopic equation requires a study of dynamics in the neighborhood of the manifold (34). Because of the simplicity of the model (32), this is possible to a satisfactory level even for M_2-dependent spring forces.

In the paper [19] it was shown, that there is a possibility of "explosion" of the Gaussian manifold: with the small initial deviation from it, the solutions of the equation (32) are very fast going far from, and then slowly come back to the stationary point which is located on the Gaussian manifold. The distribution function Ψ is stretched fast, but looses the Gaussian form, and after that the Gaussian form recovers slowly with the new value of M_2. Let us describe briefly the results of [19].

Let $M_{2n} = \int q^{2n} \Psi dq$ denote the even moments (odd moments vanish by symmetry). We consider deviations $\mu_{2n} = M_{2n} - M_{2n}^G$, where $M_{2n}^G = \int q^{2n} \Psi^G dq$ are moments of the Gaussian distribution function (34). Let $\Psi(q, t_0)$ be the initial condition to the Eq. (32) at time $t = t_0$. Introducing functions,

$$p_{2n}(t, t_0) = \exp\left[4n \int_{t_0}^{t} \alpha(t')dt'\right], \tag{36}$$

where $t \geq t_0$, and $2n \geq 4$, the *exact* time evolution of the deviations μ_{2n} for $2n \geq 4$ reads

$$\mu_4(t) = p_4(t, t_0)\mu_4(t_0), \tag{37}$$

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and

$$\mu_{2n}(t) = \left[\mu_{2n}(t_0) + 2n(4n-1) \int_{t_0}^t \mu_{2n-2}(t') p_{2n}^{-1}(t', t_0) dt' \right] p_{2n}(t, t_0), \qquad (38)$$

for $2n \geq 6$. Equations (36), (37) and (38) describe evolution near the Gaussian solution for arbitrary initial condition $\Psi(q, t_0)$. Notice that explicit evaluation of the integral in the Eq. (36) requires solution to the moment equation (35) which is not available in the analytical form for the FENE-P model.

It is straightforward to conclude that any solution with a non-Gaussian initial condition converges to the Gaussian solution asymptotically as $t \to \infty$ if

$$\lim_{t \to \infty} \int_{t_0}^t \alpha(t') dt' < 0. \qquad (39)$$

However, even if this asymptotic condition is met, deviations from the Gaussian solution may survive for considerable *finite* times. For example, if for some finite time T, the integral in the Eq. (36) is estimated as $\int_{t_0}^t \alpha(t') dt' > \alpha(t - t_0)$, $\alpha > 0$, $t \leq T$, then the Gaussian solution becomes exponentially unstable during this time interval. If this is the case, the moment equation (35) cannot be regarded as the macroscopic equation. Let us consider specific examples.

For the Hookean spring ($f \equiv 1$) under a constant elongation ($\kappa = \text{const}$), the Gaussian solution is exponentially stable for $\kappa < 0.5$, and it becomes exponentially unstable for $\kappa > 0.5$. The exponential instability in this case is accompanied by the well known breakdown of the solution to the Eq. (35) due to infinite stretching of the dumbbell. The situation is much more interesting for the FENE-P model because this nonlinear spring force does not allow the infinite stretching of the dumbbell.

Eqs. (35) and (37) were integrated by the 5-th order Runge-Kutta method with adaptive time step. The FENE-P parameter b was set equal to 50. The initial condition was $\Psi(q, 0) = C(1 - q^2/b)^{b/2}$, where C is the normalization (the equilibrium of the FENE model, notoriously close to the FENE-P equilibrium [41]). For this initial condition, in particular, $\mu_4(0) = -6b^2/[(b+3)^2(b+5)]$ which is about 4% of the value of M_4 in the Gaussian equilibrium for $b = 50$. In Fig. 1 we demonstrate deviation $\mu_4(t)$ as a function of time for several values of the flow. Function $M_2(t)$ is also given for comparison. For small enough κ we find an adiabatic regime, that is μ_4 relaxes exponentially to zero. For stronger flows, we observe an initial *fast runaway* from the invariant manifold with $|\mu_4|$ growing over three orders of magnitude compared to its initial value. After the maximum deviation has been reached, μ_4 relaxes to zero. This relaxation is exponential as soon as the solution to Eq. (35) approaches the steady state. However, the time constant for this exponential relaxation $|\alpha_\infty|$ is very small. Specifically, for large κ,

$$\alpha_\infty = \lim_{t \to \infty} \alpha(t) = -\frac{1}{2b} + O(\kappa^{-1}). \qquad (40)$$

Thus, the steady state solution is unique and Gaussian but the stronger is the flow, the larger is the initial runaway from the Gaussian solution, while the return to it thereafter becomes flow-independent. Our observation demonstrates that, though the stability condition (39) is met, *significant deviations from the Gaussian solution persist over the times when the solution of Eq. (35) is already reasonably close to the stationary state.* If we accept the usually quoted physically reasonable minimal value of parameter b of the order
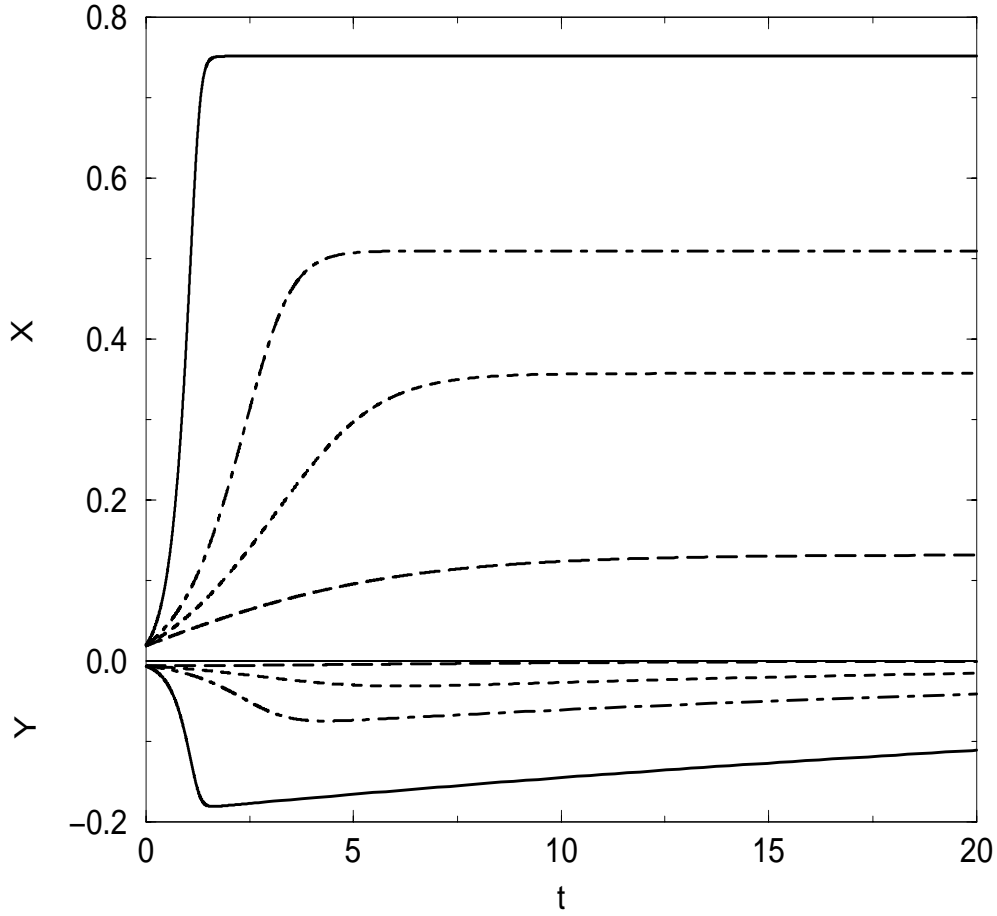
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Figure 1: Deviations of reduced moments from the Gaussian solution as a function of reduced time t in pseudo-elongation flow for the FENE-P model. Upper part: Reduced second moment $X = M_2/b$. Lower part: Reduced deviation of fourth moment from Gaussian solution $Y = -\mu_4^{1/2}/b$. Solid: $\kappa = 2$, dash-dot: $\kappa = 1$, dash: $\kappa = 0.75$, long dash: $\kappa = 0.5$. (The figure from the paper [19], computed by P. Ilg.)

20 then the minimal relaxation time is of order 40 in the reduced time units of Fig. 1. We should also stress that the two limits, $\kappa \to \infty$ and $b \to \infty$, are not commutative, thus it is not surprising that the estimation (40) does not reduce to the above mentioned Hookean result as $b \to \infty$. Finally, peculiarities of convergence to the Gaussian solution are even furthered if we consider more complicated (in particular, oscillating) flows $\kappa(t)$. Further numerical experiments are presented in [42]. The statistics of FENE-P solutions with random strains was studied recently by J.-L. Thiffeault [43]

In accordance with [38] the anzatz for Ψ can be suggested in the following form:

$$\Psi^{An}(\{\sigma, \varsigma\}, q) = \frac{1}{2\sigma\sqrt{2\pi}} \left(e^{-\frac{(q+\varsigma)^2}{2\sigma^2}} + e^{-\frac{(q-\varsigma)^2}{2\sigma^2}} \right). \tag{41}$$

Natural inner coordinates on this manifold are σ and ς. Note, that now $\sigma^2 \neq M_2$. The value σ^2 is a dispersion of one of the Gaussian summands in (41),

$$M_2(\Psi^{An}(\{\sigma, \varsigma\}, q)) = \sigma^2 + \varsigma^2.$$

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To build the thermodynamic projector on the manifold (41), the thermodynamic Lyapunov function is necessary. It is necessary to emphasize, that equations (32) are nonlinear. For such equations, the arbitrarity in the choice of the thermodynamic Lyapunov function is much smaller than for the linear Fokker Planck equation. Nevertheless, such a function exists. It is the free energy

$$F = U(M_2[\Psi]) - TS[\Psi], \tag{42}$$

where

$$S[\Psi] = -\int \Psi(\ln \Psi - 1)dq,$$

$U(M_2[\Psi])$ is the potential energy in the mean field approximation, T is the temperature (further we assume that $T = 1$).

Note, that Kullback-form entropy $S_k = -\int \Psi \ln\left(\frac{\Psi}{\Psi^*}\right)$ also has the form $S_k = -F/T$:

$$\Psi^* = \exp(-U),$$
$$S_k[\Psi] = -\langle U \rangle - \int \Psi \ln \Psi dq.$$

If $U(M_2[\Psi])$ in the mean field approximation is the convex function of M_2, then the free energy (42) is the convex functional too.

For the FENE-P model $U = -\ln[1 - M_2/b]$.

In accordance to the thermodynamics the vector of flow of Ψ must be proportional to the gradient of the corresponding chemical potential μ:

$$J = -B(\Psi)\nabla_q \mu, \tag{43}$$

where $\mu = \frac{\delta F}{\delta \Psi}$, $B \geq 0$. From the equation (42) it follows, that

$$\mu = \frac{dU(M_2)}{dM_2} \cdot q^2 + \ln \Psi$$
$$J = -B(\Psi)\left[2\frac{dU}{dM_2} \cdot q + \Psi^{-1}\nabla_q \Psi\right]. \tag{44}$$

If we suppose here $B = \frac{D}{2}\Psi$, then we get

$$J = -D\left[\frac{dU}{dM_2} \cdot q\Psi + \frac{1}{2}\nabla_q \Psi\right]$$
$$\frac{\partial \Psi}{\partial t} = div_q J = D\frac{dU(M_2)}{dM_2}\partial_q(q\Psi) + \frac{D}{2}\partial^2 q\Psi, \tag{45}$$

When $D = 1$ this equations coincide with (32) in the absence of the flow: due to equation (45) $dF/dt \leq 0$.

Let us construct the thermodynamic projector with the help of the thermodynamic Lyapunov function F (42). Corresponding entropic scalar product in the point Ψ has the form

$$\langle f|g\rangle_\Psi = \frac{d^2U}{dM_2^2}\bigg|_{M_2=M_2[\Psi]} \cdot \int q^2 f(q)dq \cdot \int q^2 g(q)dq + \int \frac{f(q)g(q)}{\Psi(q)}dq \tag{46}$$

During the investigation of the anzatz (41) the scalar product (46), constructed for the corresponding point of the Gaussian manifold with $M_2 = \sigma^2$, will be used. It will let us to investigate the neighborhood of the Gaussian manifold (and to get all the results in the analytical form):

$$\langle f|g\rangle_{\sigma^2} = \frac{d^2 U}{dM_2^2}\bigg|_{M_2=\sigma^2} \cdot \int q^2 f(q) dq \cdot \int q^2 g(q) dq + \sigma\sqrt{2\pi} \int e^{\frac{q^2}{2\sigma^2}} f(q) g(q) dq \qquad (47)$$

Also we will need to know the functional DF in the point of Gaussian manifold:

$$DF_{\sigma^2}(f) = \left(\frac{dU(M_2)}{dM_2}\bigg|_{M_2=\sigma^2} - \frac{1}{2\sigma^2} \right) \int q^2 f(q) dq, \qquad (48)$$

(with the condition $\int f(q) dq = 0$). The point

$$\frac{dU(M_2)}{dM_2}\bigg|_{M_2=\sigma^2} = \frac{1}{2\sigma^2},$$

corresponds to the equilibrium.

The tangent space to the manifold (41) is spanned by the vectors

$$f_\sigma = \frac{\partial \Psi^{An}}{\partial(\sigma^2)}; \ f_\varsigma = \frac{\partial \Psi^{An}}{\partial(\varsigma^2)};$$

$$f_\sigma = \frac{1}{4\sigma^3\sqrt{2\pi}} \left[e^{-\frac{(q+\varsigma)^2}{2\sigma^2}} \frac{(q+\varsigma)^2 - \sigma^2}{\sigma^2} + e^{-\frac{(q-\varsigma)^2}{2\sigma^2}} \frac{(q-\varsigma)^2 - \sigma^2}{\sigma^2} \right]; \qquad (49)$$

$$f_\varsigma = \frac{1}{4\sigma^2\varsigma\sqrt{2\pi}} \left[-e^{-\frac{(q+\varsigma)^2}{2\sigma^2}} \frac{q+\varsigma}{\sigma} + e^{-\frac{(q-\varsigma)^2}{2\sigma^2}} \frac{(q-\varsigma)}{\sigma} \right];$$

The Gaussian entropy (free energy) production in the directions f_σ and f_ς (48) has a very simple form:

$$DF_{\sigma^2}(f_\varsigma) = DF_{\sigma^2}(f_\sigma) = \frac{dU(M_2)}{dM_2}\bigg|_{M_2=\sigma^2} - \frac{1}{2\sigma^2}. \qquad (50)$$

The linear subspace $\ker DF_{\sigma^2}$ in $lin\{f_\sigma, f_\varsigma\}$ is spanned by the vector $f_\varsigma - f_\sigma$.

Let us have the given vector field $d\Psi/dt = \Phi(\Psi)$ in the point $\Psi(\{\sigma, \varsigma\})$. We need to build the projection of Φ onto the tangent space $T_{\sigma,\varsigma}$ in the point $\Psi(\{\sigma, \varsigma\})$:

$$P^{th}_{\sigma,\varsigma}(\Phi) = \varphi_\sigma f_\sigma + \varphi_\varsigma f_\varsigma. \qquad (51)$$

This equation means, that the equations for σ^2 and ς^2 will have the form

$$\frac{d\sigma^2}{dt} = \varphi_\sigma; \ \frac{d\varsigma^2}{dt} = \varphi_\varsigma \qquad (52)$$

Projection $(\varphi_\sigma, \varphi_\varsigma)$ can be found from the following two equations:

$$\varphi_\sigma + \varphi_\varsigma = \int q^2 \Phi(\Psi)(q) dq;$$

$$\langle \varphi_\sigma f_\sigma + \varphi_\varsigma f_\varsigma | f_\sigma - f_\varsigma \rangle_{\sigma^2} = \langle \Phi(\Psi) | f_\sigma - f_\varsigma \rangle_{\sigma^2}, \qquad (53)$$
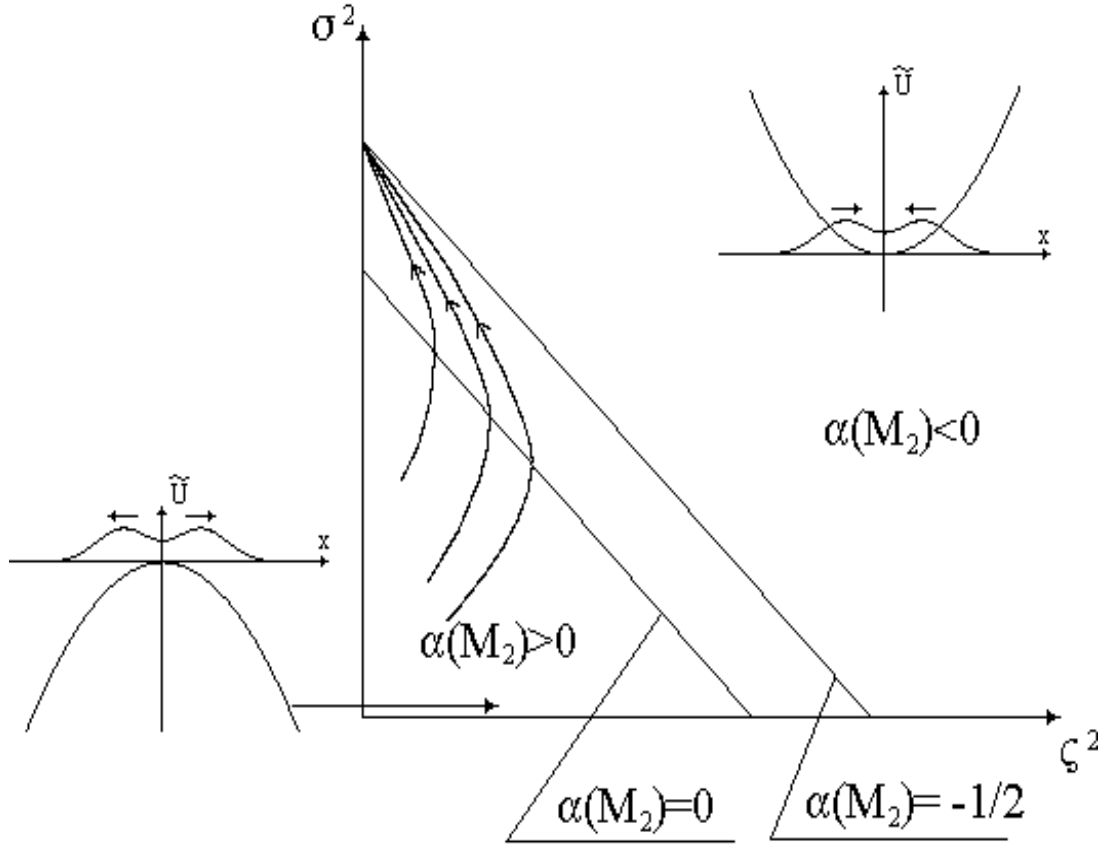
21

Figure 2: Phase trajectories for the two-peak approximation, FENE-P model. The vertical axis ($\varsigma = 0$) corresponds to the Gaussian manifold. The triangle with $\alpha(M_2) > 0$ is the domain of exponential instability.

where $\langle f|g \rangle_{\sigma^2} = \langle \Phi(\Psi)|f_\sigma - f_\varsigma \rangle_{\sigma^2}$, (46). First equation of (53) means, that the time derivative dM_2/dt is the same for the initial and the reduced equations. Due to the formula for the dissipation of the free energy (48), this equality is equivalent to the persistence of the dissipation in the neighborhood of the Gaussian manifold.

The second equation in (53) means, that Φ is projected orthogonally on ker $DS \bigcap T_{\sigma,\varsigma}$. Let us use the orthogonality with respect to the entropic scalar product (47). The solution of equations (53) has the form

$$\frac{d\sigma^2}{dt} = \varphi_\sigma = \frac{\langle \Phi|f_\sigma - f_\varsigma \rangle_{\sigma^2} + M_2(\Phi)(\langle f_\varsigma|f_\varsigma \rangle_{\sigma^2} - \langle f_\sigma|f_\varsigma \rangle_{\sigma^2})}{\langle f_\sigma - f_\varsigma|f_\sigma - f_\varsigma \rangle_{\sigma^2}},$$

(54)

$$\frac{d\varsigma^2}{dt} = \varphi_\varsigma = \frac{-\langle \Phi|f_\sigma - f_\varsigma \rangle_{\sigma^2} + M_2(\Phi)(\langle f_\sigma|f_\sigma \rangle_{\sigma^2} - \langle f_\sigma|f_\varsigma \rangle_{\sigma^2})}{\langle f_\sigma - f_\varsigma|f_\sigma - f_\varsigma \rangle_{\sigma^2}},$$

where $\Phi = \Phi(\Psi)$, $M_2(\Phi) = \int q^2 \Phi(\Psi)dq$.

It is easy to check, that the formulas (54) are indeed defining the projector: if f_σ (or f_ς) is substituted there instead of the function Φ, then we will get $\varphi_\sigma = 1, \varphi_\varsigma = 0$
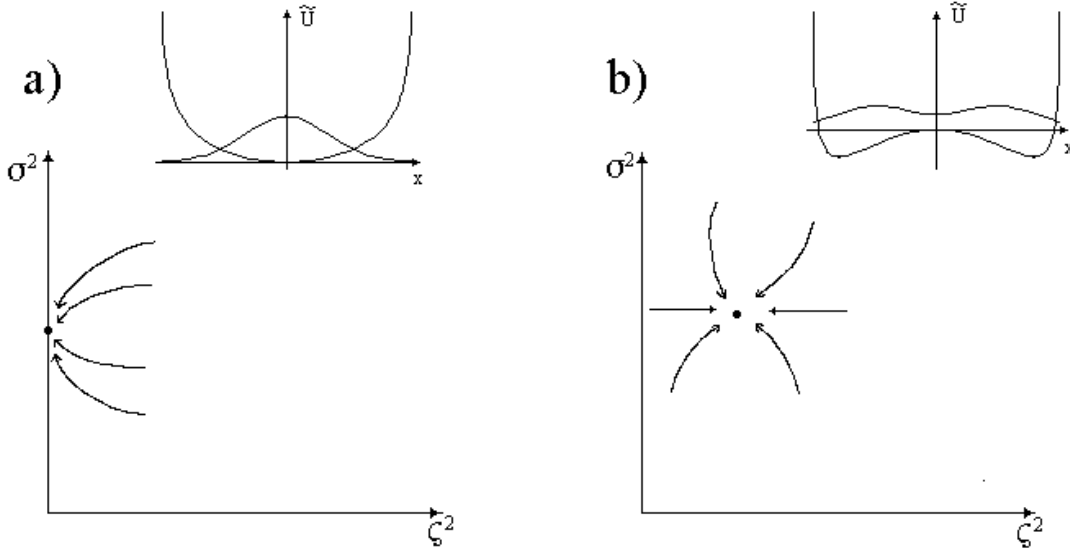
Figure 3: Phase trajectories for the two-peak approximation, FENE model: **a)** A stable equilibrium on the vertical axis, one stable peak; **b)** A stable equilibrium with $\varsigma > 0$, stable two-peak configuration.

(or $\varphi_\sigma = 0, \varphi_\varsigma = 1$, respectively). Let us substitute the right part of the initial kinetic equations (32), calculated in the point $\Psi(q) = \Psi(\{\sigma, \varsigma\}, q)$ (see the equation (41)) in the equation (54) instead of Φ. We will get the closed system of equations on σ^2, ς^2 in the neighborhood of the Gaussian manifold.

This system describes the dynamics of the distribution function Ψ. The distribution function is represented as the half-sum of two Gaussian distributions with the averages of distribution $\pm\varsigma$ and mean-square deviations σ. All integrals in the right-hand part of (54) are possible to calculate analytically.

Basis (f_σ, f_ς) is convenient to use everywhere, except the points in the Gaussian manifold, $\varsigma = 0$, because if $\varsigma \to 0$, then

$$ f_\sigma - f_\varsigma = O\left(\frac{\varsigma^2}{\sigma^2}\right) \to 0. $$

Let us analyze the stability of the Gaussian manifold to the "dissociation" of the Gaussian peak in two peaks (41). To do this, it is necessary to find first nonzero term in the Taylor expansion in ς^2 of the right-hand side of the second equation in the system (54). The denominator has the order of ς^4, the numerator has, as it is easy to see, the order not less, than ς^6 (because the Gaussian manifold is invariant with respect to the initial system).

With the accuracy up to ς^4:

$$ \frac{1}{\sigma^2}\frac{d\varsigma^2}{dt} = 2\alpha\frac{\varsigma^2}{\sigma^2} + o\left(\frac{\varsigma^4}{\sigma^4}\right), \tag{55} $$

where

$$\alpha = \kappa - \left.\frac{dU(M_2)}{dM_2}\right|_{M_2=\sigma^2}.$$

So, if $\alpha > 0$, then ς^2 grows exponentially ($\varsigma \sim e^{\alpha t}$) and the Gaussian manifold is unstable; if $\alpha < 0$, then ς^2 decreases exponentially and the Gaussian manifold is stable.

Near the vertical axis $d\sigma^2/dt = 1 + 2\alpha\sigma^2$. The form of the phase trajectories is shown qualitative on Fig. 2. Note that this result completely agrees with equation (37).

For the real equation FPE (for example, with the FENE potential) the motion in presence of the flow can be represented as the motion in the effective potential well $\tilde{U}(q) = U(q) - \frac{1}{2}\kappa q^2$. Different variants of the phase portrait for the FENE potential are present on Fig. 3. Instability and dissociation of the unimodal distribution functions ("peaks") for the FPE is the general effect when the flow is present.

The instability occurs when the matrix $\partial^2 \tilde{U}/\partial q_i \partial q_j$ starts to have negative eigenvalues ($\tilde{U}$ is the effective potential energy, $\tilde{U}(q) = U(q) - \frac{1}{2}\sum_{i,j}\kappa_{i,j}q_i q_j$).

2.3.2 Polymodal polyhedron

The stationary polymodal distribution for the Fokker-Planck equation corresponds to the persistence of several local minima of the function $\tilde{U}(q)$. The multidimensional case is different from one-dimensional because it has the huge amount of possible configurations. All normal forms of the catastrophe of "birth of the critical point" are well investigated and known [44]. Every dissociation of the peak is connected with such a catastrophe. The number of the new peaks is equal to the number of the new local minima of U.

The possible cascade of peaks dissociation is presented qualitatively on Fig. 4. The important property of this qualitative picture is the linear complexity of dynamical description with exponential complexity of geometrical picture. Let m be the number of bifurcation steps in the cascade. Then

- For description of parallelepiped it is sufficient to describe m edges;

- There are 2^{m-1} geometrically different conformations associated with 2^m vertex of parallelepiped (central symmetry halved this number).

Another important property is the *threshold* nature of each dissociation: It appears in points of stability loss for new directions, in these points the dimension of unstable direction increases.

The simplest multidimensional dynamic model is the Fokker-Planck equation with quadratic mean field potential. This is direct generalization of the FENE-P model: the quadratic potential $U(q)$ depends on the tensor of second moments $\boldsymbol{M}_2 = \langle q_i q_j \rangle$ (here the angle brackets denote the averaging). This dependence should provide the finite extensibility. This may be, for example, a simple matrix generalization of the FENE-P energy:

$$U(q) = \sum_{ij} K_{ij}q_i q_j, \ \boldsymbol{K} = \boldsymbol{K}^0 + \phi(\boldsymbol{M}_2/b), \ \langle U(q) \rangle = \mathrm{tr}(\boldsymbol{K}\boldsymbol{M}_2/b)$$

where b is a constant (the limit of extensibility), $\boldsymbol{K}^0$ is a constant matrix, $\boldsymbol{M}_2$ is the matrix of second moments, and ϕ is a positive analytical monotone increasing function of one variable on the interval $(0, 1)$, $\phi(x) \to \infty$ for $x \to 1$ (for example, $\phi(x) = -\ln(1-x)/x$, or $\phi(x) = (1-x)^{-1}$).
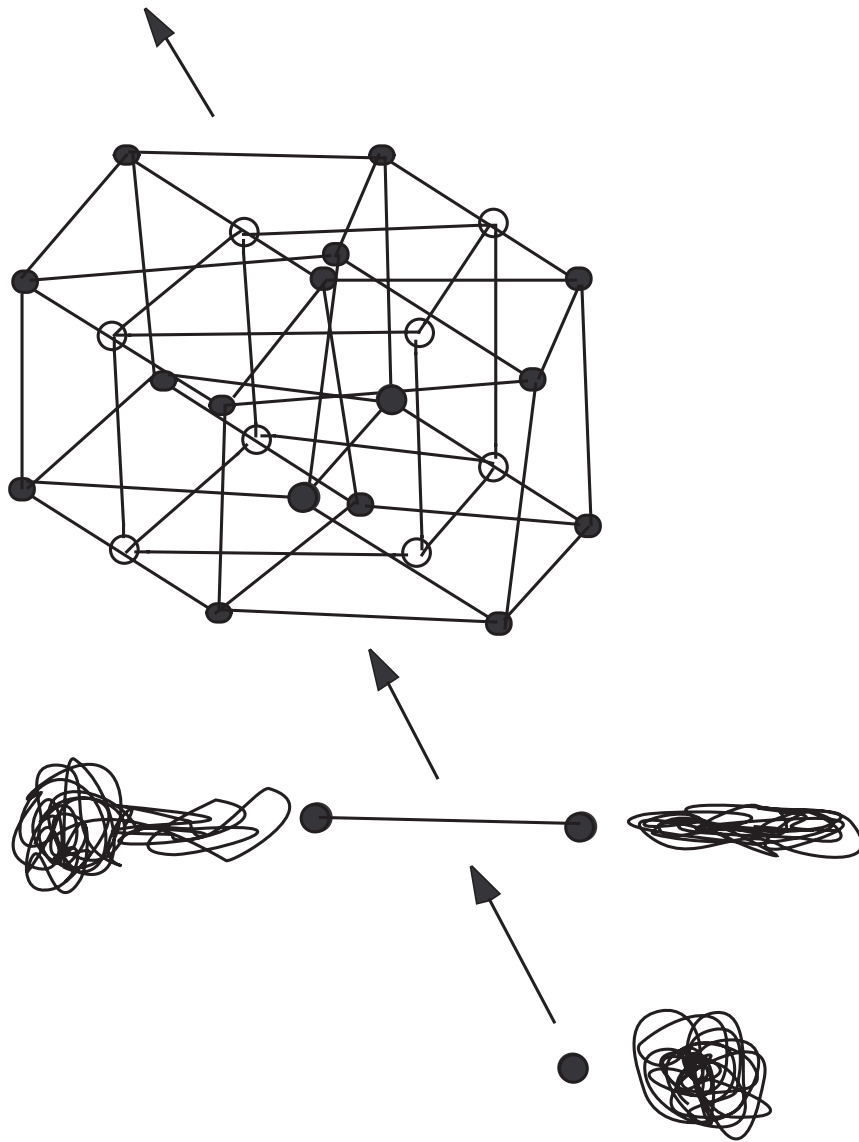
Figure 4: Cartoon representing the steps of molecular individualism. Black dots are vertices of Gaussian parallelepiped. Zero, one, and four-dimensional polyhedrons are drawn. Dashed is the three-dimensional polyhedron used to draw the four-dimensional object. Each new dimension of the polyhedron adds as soon as the corresponding bifurcation occurs. Quasi-stable polymeric conformations are associated with each vertex. First bifurcation pertinent to the instability of a dumbbell model in elongational flow is described in the text.

For quadratic multidimensional mean field models persists the qualitative picture of Fig. 2: there is *non-stationary moleqular individualism for stationary "molecular collectivism"*. The stationary distribution is the Gaussian distribution, and on the way to this stationary point there exists an unstable region, where the distribution dissociates onto 2^m peaks (m is the number of unstable degrees of freedom).

Dispersion of individual peak in unstable region increases too. This effect can deform the observed situation: If some of the peaks have significant intersection, then these peaks join into new extended classes of observed molecules. The stochastic walk of molecules between connected peaks can be observed as "large non-periodical fluctuations". This walk can be unexpected fast, because it can be effectively a *motion in a low-dimensional space*, for example, in one-dimensional space (in a neighborhood of a part of one-dimensional skeleton of the polyhedron).

2.4 Generalization: neurons and particles

The Gaussian parallelepiped (14) seems to be a "rigid" structure: the possibilities to extend this anzatz, to make it more exact, but with preservation of more or less transparent structure, are not obvious. The simple transformation can improve this situation. Let us mention the obvious relation: $\exp(-(x-a)^2) = \exp(-x^2)\exp(2ax)\exp(-a^2)$. We can write the simple generalization of equation (14):

$$\Psi(q) = \Psi^*(q) \prod_{i=1}^{m} \varphi_i((\varsigma_i, q)), \tag{56}$$

where $\Psi^*(q)$ is the distribution density for one peak, for example, it may be the multidimensional Gaussian distribution $\Psi^*(q) = \frac{1}{(2\pi)^{n/2}\sqrt{\det \Sigma}} \exp\left(-\frac{1}{2}\left(\Sigma^{-1}q, q\right)\right)$, ς_i, ($i = 1, \ldots, m$) are vectors in the configuration space, (ς_i, q) is the usual scalar product, $\varphi_i(x)$ are nonnegative functions of one variable x. for example, $\varphi_i(x) = A_i \text{ch}(\alpha_i x + \beta_i)$.

The form (56) is more flexible then original Gaussian parallelepiped (14). It gives the possibility to extend the space for model adaptation. Functions of one variable $\varphi_i(x)$ are additional variables. They can form a finite-parametric family: For example, $\varphi_i(x) = A_i \text{ch}(\alpha_i x)$ give the Gaussian peaks, and if we use $\varphi_i(x) = A_i^+ \exp(\alpha_i^+ x) + A_i^- \exp(\alpha_i^- x)$, then we obtain a non-symmetric picture of shifted peaks. On following steps we may use different spaces (or manifolds) of functions $\varphi_i(x)$ to extend the approximation capacity of the anzatz (56).

Let us describe the tangent space T for the anzatz (56) with functions $\lambda_i(x) = \ln \varphi_i(x)$ from some space L. The space of functions of n variables

$$L((\varsigma, q)) = \{\lambda((\varsigma, q)) | \varphi \in L\}$$

corresponds to a given vector ς and the space L. The tangent space T_Ψ for the anzatz (56) in a point Ψ has a form:

$$T_\Psi = \Psi \left[\sum_{i=1}^{m} L((\varsigma_i, q)) + \sum_{i=1}^{m} \left(\frac{d\lambda_i(x)}{dx}\right)_{x=(\varsigma_i, q)} E^* \right], \tag{57}$$

where E^* is the space of linear functions of q.

If the space L includes all sufficiently smooth functions, then to avoid intersection between $L((\varsigma_i, q))$ and $\left(\frac{d\lambda_i(x)}{dx}\right)_{x=(\varsigma_i,q)} E^*$ it is convenient to change in equation (57) the space of all linear functions E^* to the space of linear functions orthogonal to (ς_i, q), $E_i^* = \{(\varsigma, q) | \varsigma \perp \varsigma_i\}$ (without any change in the resulting space):

$$T_\Psi = \Psi \left[\sum_{i=1}^m L((\varsigma_i, q)) + \sum_{i=1}^m \left(\frac{d\lambda_i(x)}{dx}\right)_{x=(\varsigma_i,q)} E_i^* \right]. \tag{58}$$

It means that for sufficiently rich spaces L the vectors ς_i in the anzatz (56) could be chosen on the sphere, $(\varsigma_i, \varsigma_i) = 1$, to provide the independence of variables.

The form (56) appears as a quasiequilibrium distribution density in the following particular case of the problem (21):

$$S(\Psi) \to \max, \ \int \delta(x - (\varsigma_i, q)) \Psi(q) d^n q = f_i(x), \ i = 1, \ldots, m, \tag{59}$$

where $S(\Psi)$ is the Kullback-form Bolzmann-Gibbs-Shannon entropy which measures a deviation of the distribution density $\Psi(q)$ from the equilibrium density $\Psi^*(q)$:

$$S(\Psi) = - \int \Psi(q) \ln \left(\frac{\Psi(q)}{\Psi^*(q)}\right) d^n q. \tag{60}$$

Hence, for fixed values of ς_i and for a space of arbitrary nonnegative smooth functions $\varphi_i(x)$ the anzatz (56) is the quasiequilibrium approximation with macroscopic variables

$$f_i(x) = \int \delta(x - (\varsigma_i, q)) \Psi(q) d^n q.$$

Let us define the anzatz manifold (56) as a union of the quasiequilibrium manifolds (59) for all sets of values $\{\varsigma_i\}_{i=1}^m$ on the unit sphere. In this case we can apply Proposition 3: The thermodynamic projector is the orthogonal projector on T_Ψ with respect to the entropic scalar product in the point Ψ: In the space of density functions

$$\langle f | g \rangle_\Psi = \int \frac{f(q)g(q)}{\Psi(q)} dq, \tag{61}$$

and in the conjugated space (for example, for functions λ from space L in (57),(58))

$$\langle \mu | \lambda \rangle_\Psi^c = \int \mu(q)\lambda(q)\Psi(q) dq, \tag{62}$$

where the scalar product for the conjugated space is marked by the upper index c.

The orthogonal projector P on the direct sum of subspaces

$$\sum_{i=1}^m L((\varsigma_i, q)) + \sum_{i=1}^m \left(\frac{d\lambda_i(x)}{dx}\right)_{x=(\varsigma_i,q)} E_i^* \tag{63}$$

is a sum of operators: $P = \sum_{i=1}^m (P_{\lambda_i} + P_{\varsigma_i})$, where

$$\mathrm{im} P_{\lambda_i} = L((\varsigma_i, q)), \ \mathrm{im} P_{\varsigma_i} = \left(\frac{d\lambda_i(x)}{dx}\right)_{x=(\varsigma_i,q)} E_i^*. \tag{64}$$

Operators P_{λ_i}, $P_{\varsigma i}$ can be founded from the definition of their images (64) and the conditions: $P^2 = P$, $P^+ = P$, where P^+ is the conjugated to P operator with respect of the scalar product $\langle \ | \ \rangle^c$ (62). From the first equation of ($P^2 = P$) it follows that each operator A from the set $\boldsymbol{Q} = \{P_{\lambda_i}\}_{i=1}^m \bigcup \{P_{\varsigma_j}\}_{j=1}^m$ is a projector, $A^2 = A$ (it may be not orthogonal), and for any pair of distinct projectors $A, B \in \boldsymbol{Q}$ the following inclusions hold: $\mathrm{im}A \subseteq \ker B$, $\mathrm{im}B \subseteq \ker A$.

In a general case, the constructive realization of orthogonal projector requires solution of systems of linear equations, or orthogonalization of systems of vectors, etc. We shall not discuss the details of computational algorithms here, but one important possibility should be stressed. *The orthogonal projection $P(J)$ can be computed by adaptive minimization of a quadratic form* :

$$\langle J - P(J) | J - P(J) \rangle_\Psi \to \min \text{ for } P(J) \in T_\Psi \tag{65}$$

The gradient methods for solution of the problem (65) are based on the following simple observation: Let a subspace $L \subset E$ of the Hilbert space E be the direct sum of subspaces L_i: $L = \sum_i L_i$. The orthogonal projection of a vector $J \in E$ onto L has an unique representation in a form: $P(J) = x = \sum_i x_i$, $x_i \in L_i$. The gradient of the quadratic form $(J - x, J - x)$ in the space L has the form:

$$\mathrm{grad}_x(J - x, J - x) = 2 \sum_i P_i^\perp(J - x), \tag{66}$$

where $P_i^\perp$ is the orthogonal projector on the space L_i. It means: if one has the orthogonal projectors on the spaces L_i, then he can easy write the gradient method for the problem (65).

The projected kinetic equations, $\dot\Psi = x$, $x \in T_\Psi$, with the equations for this adaptive method, for example $\dot x = -h\mathrm{grad}_x\langle J - x | J - x \rangle_\Psi$, can be solved together. For a rational choice of the step h this system is stable, and has a Lyapunov functional (for closed systems). This functional can be found as a linear combination of the entropy and the minimized quadratic form $\langle J - x | J - x \rangle_\Psi$.

We consider the FPE of the form

$$\frac{\partial \Psi(q, t)}{\partial t} = \nabla_q \left\{ D(q) \left[\Psi(q, t)(\nabla_q U(q) - F_{ex}(q, t)) + \nabla_q \Psi(q, t) \right] \right\}. \tag{67}$$

Here $\Psi(q, t)$ is the probability density over the configuration space q, at the time t, while $U(q)$ and $D(q)$ are the potential and the positively semi-definite $((r, D(q)r) \geq 0)$ symmetric diffusion matrix, $F_{ex}(q, t)$ is an external force (we omit here such multipliers as $k_{\mathrm{B}}T$, friction coefficients, etc). Another form of equation (67) is:

$$\frac{\partial \Psi(q, t)}{\partial t} = \nabla_q \left\{ D(q) \Psi^*(q)(\nabla_q - F_{ex}(q, t)) \left(\frac{\Psi(q, t)}{\Psi^*(q)} \right) \right\}, \tag{68}$$

where $\Psi^*(q)$ is the equilibrium density: $\Psi^*(q, t) = \exp(-U(q))/ \int \exp(-U(p))dp$. For the anzatz (56) $\Psi(q, t) = \Psi^*(q) \exp \sum_i \lambda_i((\varsigma_i, q), t)$. For this anzatz the left hand side of equation (68) has the form

$$J(\Psi) = \Psi \left[\sum_i (\varsigma_i, D(q)\varsigma_i) \left(\frac{\partial^2 \lambda_i}{\partial x^2} \right)_{x=(\varsigma_i, q)} + \sum_{i,j} (\varsigma_j, D(q)\varsigma_i) \left(\frac{\partial \lambda_i}{\partial x} \right)_{x=(\varsigma_i, q)} \left(\frac{\partial \lambda_j}{\partial x} \right)_{x=(\varsigma_j, q)} - \right.$$

$$\sum_i \left(\frac{\partial \lambda_i}{\partial x}\right)_{x=(\varsigma_i,q)} ((\varsigma_i, D(q)(\nabla_q U(q) + F_{ex}(q,t))) - (\nabla_q, D(q)\varsigma_i)) +$$
$$(\nabla_q U(q), D(q)F_{ex}(q,t)) - (\nabla_q, D(q)F_{ex}(q,t))] , \tag{69}$$

where $\lambda_i = \lambda_i(x,t)$, and $(\ ,\ )$ is the usual scalar product in the configuration space.

The projected equations have the form:

$$\frac{\partial \lambda_i}{\partial t} = P_{\lambda_i} J(\Psi), \ \frac{d\varsigma_i}{dt} = P_{\varsigma_i} J(\Psi), \tag{70}$$

where the vector field $J(\Psi)$ is calculated by formula (69), and the projectors P_{λ_i}, P_{ς_i} are defined by equations (64). For adaptive methods the right hand parts of equations (70) are solutions of auxiliary equations.

We can return from the anzatz (56) to the polymodal polyhedron: It corresponds to a finite-dimensional multimodal approximation for each of equations (70). If the number of maxima in the approximation of $\lambda_i(x)$ is k_i, then the number of peaks in the polymodal polyhedron is $k = \prod_i k_i$.

For the further development of the approximation (56) it is possible add some usual moments to the system (59). These additional moments can include a stress tensor, and some other polynomial moments. As a result of such an addition the equilibrium density in anzatz (56) will be replaced to a more general nonconstant quasiequilibrium density.

The anzatz (56) can be discussed and studied from different points of view:

1. It is a *uncorrelated particles* representation of kinetics: The distribution density function (56) is a product of equilibrium density and one-particle distributions, φ_i. Each particle has it's own one-dimensional configuration space with coordinate $x = (\varsigma_i, q)$. The representation of uncorrelated particles is well known in statistical physics, for example, the Vlasov equation is the projection of the Liouville equation onto uncorrelated anzatz [51]. There are three significant differences between the anzatz (56) and usual uncorrelated anzatz: First, the anzatz (56) is not symmetric with respect to particles permutation, second, the configuration spaces of particles for this anzatz are dynamic variables. The third difference is: The anzatz (56) includes the equilibrium density function explicitly, hence, the *uncorrelated particles* represent the *nonequlibrium* factor of distribution, and equilibrium correlations are taken into account completely.

2. It is a version of a *neural-network approximation* [45]. The components of the vector ς_i are input synaptic weights for the ith neuron of the hidden layer, and $\ln \varphi_i(x)$ is the activation function of this neuron. The activation function of the output neuron is $\exp(x)$. There is no need in different input synaptic weights for the output neuron, because possible activation functions of the neurons of the hidden layer form the linear space L, and any real multiplier can be included into $\ln \varphi_i(x)$. The only difference from usual neural networks is a relatively big space of activation functions on the hidden layer. Usually, the most part of network abilities is hidden in the net of connections, and the only requirement to the activation function is their nonlinearity, it is sufficient for the approximation omnipotence of connectionism [46, 47, 48]. Nevertheless, the neural networks with relatively rich spaces of activation functions are in use too [49, 50].

Conclusion: POET and the difference between ellipsoid and parallelepiped

Let us introduce an abbreviation "POET" (Projection-Of-Everything-Thermodynamic) for the thermodynamic projector. POET transforms the arbitrary vector field equipped with the given Lyapunov function into a vector field with the same Lyapunov function. It projects each term in kinetic equations into the term with the same entropy production. Moreover, POET conserves the reciprocity relations: if initial kinetics satisfies the Onsager relations, then the projected system satisfies these relations too. Thus, the problem of persistence of thermodynamical properties in model reduction is solved. POET is **unique** operator which always preserves the sign of dissipation, any other important features of this operator follow from this preservation.

It is necessary to use POET even for reduction of kinetic models for open systems, because the processes which produce the entropy in a closed system should produce the entropy in open system too: The difference between open and closed systems is the presence of entropy outflow (or, what is the same, of the free energy inflow), and the dissipative processes preserve their dissipativity.

One of the most important impact of POET on the model reduction technology is the new possibility of constructing thermodynamically consistent reduced model with almost arbitrary anzatz.

In this paper we discussed the important example of such an anzatz: the multi-peak models. Two examples of these type of models demonstrated high efficiency during decades: the Tamm–Mott-Smith bimodal anzatz for shock waves, and the the Langer–Baron–Miller approximation for spinodal decomposition.

The multimodal polyhedron appears every time as an appropriate approximation for distribution functions for systems with instabilities. We create such an approximation for the Fokker–Planck equation for polymer molecules in a flow.

The usual point of view is: The shape of the polymers in a flow is either a coiled ball, or a stretched ellipsoid, and the Fokker–Planck equation describes the stretching from the ball to the ellipsoid. It is not the whole truth, even for the FENE-P equation, as it was shown in ref. [19, 38]. The Fokker-Planck equation describes the shape of a probability cloud in the space of conformations. In the flow with increasing strain this shape changes from the ball to the ellipsoid, but, after some thresholds, this ellipsoid transforms into a multimodal distribution which can be modeled as the peak parallelepiped. The peaks describe the finite number of possible molecule conformations. The number of this distinct conformations grows for a parallelepiped as 2^m with the number m of independent unstable direction.

These models pretend to be the kinetic basis for the theory of molecular individualism. The detailed computations will be presented in following works, but the qualitative features of the models are in good agreement with qualitative picture observed in experiment [16, 17, 18]. Some questions remain open:

- Of course, appearance of 2^m peaks in the Gaussian parallelepiped is possible, but some of these peaks can join in following dynamics, hence the first question is: what is the typical number of significantly different peaks for a $m-$dimensional instability?

- How can we decide what scenario is more realistic from the experimental point of view: the proposed universal kinetic mechanism, or the scenario with long living metastable states (for example, the relaxation of knoted molecules in the flow can give an other picture than the relaxation of unknoted molecules)?

- The analysis of random walk of molecules from peak to peak should be done, and results of this analysis should be compared with observed large fluctuations.

May be, the most important result of this paper is the systematic discussion of a difference between the Gaussian elipsoid (and its generalizations) and the Gaussian multipeak polyhedron (and its generalizations). This polyhedron appears generically as the effective anzatz for kinetic systems with instabilities.

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