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Uniqueness of thermodynamic projector and kinetic basis of molecular individualism

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Abstract

Three 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 the *thermodynamic projector* is proven: There exists only one projector which transforms any 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.

Second, we use the thermodynamic projector for developing the short memory approximation and coarse-graining for general nonlinear dynamic systems. We prove that in this approximation the entropy production increases. (*The theorem about entropy overproduction.*)

In example, we apply the thermodynamic projector to derive the equations of reduced kinetics for the Fokker–Planck equation. A new class of closures is developed, the kinetic multi-peak polyhedra. Distributions of this type are expected in kinetic models with multidimensional instability as universally as the Gaussian distribution appears for stable systems. The number of possible relatively stable states of a nonequilibrium system 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 third result.

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1. 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 the quasiequilibrium, or, which is the same, for MaxEnt closure assumptions [1–5]). Sometimes solution of the projection problem after construction of anzatz takes a long time. The known case of such a problem gives us the Tamm–Mott-Smith approximation in the theory of shock waves (see, for example, [6]). However if one has constructed the closure assumption which is at the same time the *invariant manifold* [6–8], then the projection problem disappears, because the vector field is always tangent to the invariant manifold.

Let us discuss the initial kinetic equation as an abstract ordinary differential equation,[1]

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

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

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

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[1] Many of partial differential kinetic equations or integro-differential kinetic equations with suitable boundary conditions (or conditions at infinity) can be discussed as abstract ordinary differential equation in the appropriate space of functions. The corresponding *semigroup* of shifts in time can be considered too. For example, the Fokker–Planck equation in a potential well $U(q)$ with a condition $U(q)/\|q\|^{\alpha} \to \infty$ for $\|q\| \to \infty$ and some $\alpha > 0$ generates an analytical semigroup. It allows to discuss the Fokker–Planck equation in such a well on the same way as an ordinary differential equation. Sometimes, when an essential theorem of existence and uniqueness of solution is not proven, it is possible to discuss a corresponding shift in time with the support of physical sense: the shift in time for physical system should exist. Benefits from the latter approach are obvious as well as its risk.

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 $\mathrm{d}M/\mathrm{d}t = F(M)$ is the equation for M, then the equation on the manifold is $\mathrm{d}\Psi(M|q)/\mathrm{d}t = (D_M\Psi(M|q)) \cdot F(M)$.

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

(1) Moment parametrization.
(2) Spectral projectors of Jacobians for Eq. (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 $\mathrm{d}M/\mathrm{d}t$ in a natural way:

$$\frac{\mathrm{d}M}{\mathrm{d}t} = (D_\Psi m(\Psi(M|q)))J(\Psi(M|q)) \; . \tag{4}$$

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 attractive (see, for example, the theory of the so-called intrinsic low-dimensional manifold (ILDM) [9]): Let the spectrum of $D_\Psi J(\Psi)$ be separated into 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 not be 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 nonself-adjoint operators may be very unstable in calculations. So, it may be better to use the self-adjoint operator and its spectral decomposition.

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

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

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

In the theory of inertial manifolds [10–12], for example, one usually uses the following form of Eq. (1) with self-adjoint 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 [13–15]. But symmetrization does not provide thermodynamicity and the entropy for the projected equations can decrease.

The construction of the thermodynamic projector that always preserves the dissipation is simple and transparent. We shall describe it now, in the introduction, and its uniqueness will be proved in the next section. The proof of uniqueness will demonstrate, 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 system (1) the entropy $S(\Psi)$ exist, and

$$\frac{\mathrm{d}S}{\mathrm{d}t} = (D_\Psi S)J(\Psi) \geqslant 0 \, . \tag{5}$$

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

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

where $D^2_\Psi S$ 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 is a finite-dimensional space, then projector (7) is constructed in the following way. Let $e_1, \ldots, e_n$ be a basis in T, and for definiteness, $(D_\Psi S)(e_1) \neq 0$.

(1) Let us construct a system of vectors

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

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:

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

and, finally we get

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

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

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

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 not be 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[2] [16] as well, as for the proof of uniqueness the thermodynamic projector.

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 [6–8,10,11,15].

The discovery of the molecular individualism for dilute polymers in the flow [17] 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 Ref. [17]. de Gennes invented the term “molecular individualism” [18]. 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 [17]. Further works for shear flow demonstrated not only shape differences, but different large temporal fluctuations [19].

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

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

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

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[2] 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 growths. 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.

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 Ref. [20]. The Gaussian distributions form the invariant manifold for the FENE-P model of polymer dynamics, but, as it was discovered in Ref. [20], 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 the 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 exist 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 the 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:

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

where n is the dimension of configuration space, $2\varsigma_i$ is the vector of the ith edge of the parallelepiped, and 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.

2. Uniqueness of thermodynamic projector

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

2.1. 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 $\langle Ax\,|\,x\rangle \leqslant 0$ 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 defined quadratic form $\langle Ax\,|\,x\rangle \leqslant 0$.

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, self-adjoint) and $\langle Ax\,|\,x\rangle \leqslant 0$, then

$$\langle PAPx\,|\,x\rangle = \langle APx\,|\,Px\rangle \leqslant 0 \,.$$

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 self-adjoint operator

$$A_x = -\,|\,Px - ax\rangle\langle Px - ax\,|$$

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

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

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

Immediately from this proof follows the Corollary 1.

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

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

It follows from the Proposition 1 and the obvious remark: If operators A and P are self-adjoint, then operator PAP is self-adjoint too.

The Proposition 1 means that a projector which transforms every linear vector field Ax with Lyapunov function $\langle x\,|\,x\rangle$ 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 *self-adjoint* linear vector field Ax with Lyapunov function $\langle x\,|\,x\rangle$ 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 the 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.

2.2. 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, $D_yF : L \to E$, 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 $D^2_\Psi S(x,x)$ 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: $\Psi^{\mathrm{eq}} \in \mathrm{int}U$.

The function S is Lyapunov function for a vector field J in U, if $(D_\Psi S)(J(\Psi)) \geqslant 0$ 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 $F(0) = \Psi^{\mathrm{eq}}$. Let us define $T_y = \mathrm{im}D_yF(y)$ 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:

$$T_y \not\subseteq \ker D_\Psi S|_{\Psi = F(y)}$$

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* read: *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 self-adjoint 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*

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

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 $F(0) = \Psi^{\mathrm{eq}}$ can be presented as $A(\Psi - \Psi^{\mathrm{eq}}) + \mathrm{o}(\|\Psi - \Psi^{\mathrm{eq}}\|)$, where A is a linear operator. If S is Lyapunov function for this vector field, then the quadratic form $\langle Ax\,|\,x\rangle_{\Psi^{\mathrm{eq}}}$ 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 $P_0 = P_0^{\perp}$. □

Theorem 1. *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* $\langle\,|\,\rangle_{F(y)}$ (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*:

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

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

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. □

2.3. Orthogonality of the thermodynamic projector and entropic gradient models

In Euclidean spaces with given scalar product, we often identify the differential of a function $f(x)$ with its gradient: in orthogonal coordinate system $(\mathrm{grad}\, f(x))_i = \partial f(x)/\partial x_i$. However, when dealing with a more general setting, one can run into problems making sense out of such a definition. What to do if there is no distinguished scalar product, and no given orthogonality?

For a given scalar product $\langle\,|\,\rangle$ the gradient $\mathrm{grad}_x f(x)$ of a function $f(x)$ at a point x is such a vector g that $\langle g|y\rangle = D_x f(y)$ for any vector y, where $D_x f$ is the differential of function f at a point x. The differential of function f is the linear functional that provides the best linear approximation near the given point.

To transform a vector into a linear functional one needs a *pairing*, that means a bilinear form $\langle \,|\, \rangle$. This pairing transforms vector g into linear functional $\langle g|$: $\langle g|(x) = \langle g|x\rangle$. Any twice differentiable function $f(x)$ generates a field of pairings: at any point x there exists a second differential of f, a quadratic form $(D_x^2 f)(\Delta x, \Delta x)$. For a convex function these forms are positively defined, and we return to the concept of scalar product. Let us calculate a gradient of f using this scalar product. In coordinate representation

$$\sum_i (\mathrm{grad} f(x))_i \frac{\partial^2 f}{\partial x_i \partial x_j} = \frac{\partial f}{\partial x_j}, \text{ hence, } (\mathrm{grad}\, f(x))_i = \sum_i (D_x^2 f)^{-1}_{ij} \frac{\partial f}{\partial x_j} \,. \tag{18}$$

As we can see, this $\mathrm{grad}\, f(x)$ is the *Newtonian* direction, and with this gradient the method of steepest descent transforms into the Newton's method of optimization.

Entropy is the concave function and we defined the entropic scalar product through negative second differential of entropy (6). Let us define the gradient of entropy by means of this scalar product: $\langle \mathrm{grad}_\Psi S|x\rangle_\Psi = (D_\Psi S)(x)$. The *entropic gradient system* is

$$\frac{\mathrm{d}\Psi}{\mathrm{d}t} = \varphi(\Psi)\mathrm{grad}_\Psi S \,, \tag{19}$$

where $\varphi(\Psi) > 0$ is a positive kinetic multiplier.

System (19) is a representative of a family of *model kinetic equations*. One replaces complicated kinetic equations by model equations for simplicity. The main requirements to such models are: they should be as simple as possible and should not violate the basic physical laws. The most known model equation is the BGK model [21] for substitution of collision integral in the Boltzmann equation. There are different models for simplifying kinetics [22,23]. The entropic gradient models (19) possesses all the required properties (if the entropy Hessian is sufficiently simple). It was invented first for Lattice–Boltzmann kinetics [24]. In many cases it is more simple than the BGK model, because the gradient model is *local* in the sense that it uses only the entropy function and its derivatives at a current state, and it is not necessary to compute the equilibrium (or quasiequilibrium for quasiequilibrium models [14,22]. The entropic gradient model has a one-point relaxation spectrum, because the gradient vector field (19) has near an equilibrium Ψ^{eq} an extremely simple linear approximation: $\mathrm{d}(\Delta\Psi)/\mathrm{d}t = -\varphi(\Psi^{\mathrm{eq}})\Delta\Psi$. It corresponds to a well-known fact that the Newton's method minimizes a positively defined quadratic form in one step.

Direct calculation shows that the thermodynamic projector P (7) in a point Ψ onto the tangent space T can be rewritten as

$$P(J) = P^\perp(J) + \frac{\mathrm{grad}_\Psi S^{\|}}{\langle \mathrm{grad}_\Psi S^{\|} | \mathrm{grad}_\Psi S^{\|}\rangle_\Psi} \langle \mathrm{grad}_\Psi S^\perp | J\rangle_\Psi \,, \tag{20}$$

where $P^\perp$ is the orthogonal projector onto T with respect the entropic scalar product, and the gradient $\mathrm{grad}_\Psi S$ is splitted onto tangent and orthogonal components:

$$\mathrm{grad}_\Psi S = \mathrm{grad}_\Psi S^{\|} + \mathrm{grad}_\Psi S^\perp; \;\; \mathrm{grad}_\Psi S^{\|} = P^\perp \mathrm{grad}_\Psi S;$$

$$\mathrm{grad}_\Psi S^\perp = (1 - P^\perp)\mathrm{grad}_\Psi S \,.$$

From Eq. (20) it follows that two properties of an anzatz manifolds are equivalent: orthogonality of the thermodynamic projector and invariance of the manifold with respect to the entropic gradient system (19).

Proposition 3. *The thermodynamic projector for an anzatz manifold* Ω *is orthogonal at any point* $\Psi \in \Omega$ *if and only if* $\mathrm{grad}_\Psi S \in T_\Psi(\Omega)$ *at any point* $\Psi \in \Omega$.

It should be stressed that it should be possible to think of gradients as infinitesimal displacements of points Ψ. Usually there are some balances, at least the conservation of the total probability, and the gradient should belong to a given subspace of zero balances change. For example, for the classical Boltzmann–Gibbs–Shannon entropy $S = -\int \Psi(q)(\ln \Psi(q) - 1)\,\mathrm{d}^n q$ the entropic scalar product is $\langle g(q)|f(q)\rangle_\Psi = \int g(q)f(q)/\Psi(q)\,\mathrm{d}^n q$ and $\mathrm{grad}_\Psi S = -\Psi(q)\ln(\Psi(q)) + c(q)$, where function (vector) $c(q)$ is orthogonal to a given subspace of zero balances. This function has to be founded from the conditions of zero balances for the gradient $\mathrm{grad}_\Psi S$. For example, if the only balance is the conservation of the total probability, $\int \Psi(q)\,\mathrm{d}^n q \equiv 1$, then for the classical Boltzmann–Gibbs–Shannon entropy S

$$\mathrm{grad}_\Psi S = -\Psi(q)\left(\ln(\Psi(q)) - \int \Psi(q')\ln(\Psi(q'))\,\mathrm{d}^n q'\right) . \tag{21}$$

For the Kullback-form entropy (the negative free energy)

$$S = -F/T = -\int \Psi(q)\left(\ln\left(\frac{\Psi(q)}{\Psi^{\mathrm{eq}}(q)}\right) - 1\right)\mathrm{d}^n q$$

the second differential and the entropic scalar product are the same, as for the classical Boltzmann–Gibbs–Shannon entropy, and

$$\mathrm{grad}_\Psi S = -\Psi(q)\left(\ln\left(\frac{\Psi(q)}{\Psi^{\mathrm{eq}}(q)}\right) - \int \Psi(q')\ln\left(\frac{\Psi(q)}{\Psi^{\mathrm{eq}}(q)}\right)\mathrm{d}^n q'\right) . \tag{22}$$

For more complicated system of balances, linear or nonlinear, the system of linear equations for $c(q)$ can also be written explicitly.

2.4. Violation of transversality condition, singularity of thermodynamic projection and steps of relaxation

The thermodynamic projector 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. Sometimes it is useful to create an anzatz in violation of this transversality condition. The point of entropy maximum on this anzatz is not the equilibrium. The usual examples are: the noncorrelated approximation $\Psi(x_1,\dots,x_n) = \prod_i f(x_i)$, the Gaussian manifold, etc. For these manifolds the thermodynamic projector becomes singular near the point of entropy maximum Ψ^* on the anzatz manifold. It is obvious from Eq. (20): in the neighborhood of Ψ^* it has the form

$$P(J) = P^{\perp}(J) + \frac{\mathrm{grad}_{\Psi} S^{\|}}{\langle \mathrm{grad}_{\Psi} S^{\|} | \mathrm{grad}_{\Psi} S^{\|} \rangle_{\Psi}} \langle \mathrm{grad}_{\Psi} S^{\perp} | J \rangle_{\Psi}$$

$$= - \frac{\Delta\Psi}{\langle \Delta\Psi | \Delta\Psi \rangle_{\Psi^*}} \sigma(\Psi^*) + O(1) , \tag{23}$$

where $\Delta\Psi = \Psi - \Psi^*$ is the deviation of Ψ from Ψ^*, $\sigma(\Psi^*) = \langle \mathrm{grad}_{\Psi^*} S^{\perp} | J \rangle_{\Psi^*}$ is the entropy production at the point Ψ^*, $\sigma(\Psi^*) \neq 0$, because the point of entropy maximum Ψ^* is not the equilibrium. In this case the projected system in the neighborhood of Ψ^* reaches the point Ψ^* at finite time t^* as $\sqrt{t^* - t}$. The entropy difference $\Delta S = S(\Psi) - S(\Psi^*) = -\frac{1}{2} \langle \Delta\Psi | \Delta\Psi \rangle_{\Psi^*} + \mathrm{o}(\langle \Delta\Psi | \Delta\Psi \rangle_{\Psi^*})$ goes to zero as $-\sigma(\Psi^*)$ $(t^* - t)$ $(t \leqslant t^*)$.

The singularity of projection has a transparent physical sense. The relaxation along the anzatz manifold to the point Ψ^* is not complete, because this point is not the equilibrium. This motion should be rated as a step of relaxation, and after it was completed, the next step should start. In this sense it is obvious that the motion to the point Ψ^* along the anzatz manifold should take the finite time. The results of this step-by-step relaxation can represent the whole process (with smoothing [25], or without it [26]). The experience of such step-by-step computing of relaxation trajectories in the initial layer problem for the Boltzmann kinetics demonstrated its efficiency [25,26].

2.5. 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. Other 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

$$S(x) \to \max, \quad x \in \Psi + \ker P_{\Psi} . \tag{24}$$

This is the most important property of thermodynamic projector. It was introduced in our paper [6] as a main thermodynamic condition for model reduction. Let us call it for nonequilibrium points Ψ *the property* A:

$$\mathrm{A} \quad \ker P_{\Psi} \subset \ker D_{\Psi} S . \tag{25}$$

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 $\ker P_\Psi \perp \operatorname{im} P_\Psi$. If this is valid for all systems (including systems with additional linear balances), then the following *property* B holds:

$$\mathrm{B} \quad \left(\ker P_\Psi \bigcap \ker D_\Psi S\right) \perp \left(\operatorname{im} P_\Psi \bigcap \ker D_\Psi S\right) . \tag{26}$$

Of course, orthogonality in formulae (25), (26) is considered with respect to the entropic scalar product in point Ψ.

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 (26) follows from the property A.

If P_Ψ does not have 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 lead 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 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 nonthermodynamic 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 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 property B, then there exist systems with violation of the second law of thermodynamics in fast and slow motions. Here we cannot 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:

$$S(\Psi) \to \max, \quad m(\Psi) = M . \tag{27}$$

The solution of problem (27) 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:

$$\pi_M^{\mathrm{qe}} = (D_M \Psi_M^{\mathrm{qe}})_M m = (D^2_{\Psi} S)^{-1}_{\Psi_M^{\mathrm{qe}}} m^T (m (D^2_{\Psi} S)^{-1}_{\Psi_M^{\mathrm{qe}}} m^T)^{-1} m \, . \tag{28}$$

This formula was essentially obtained by Robertson [27].[3]

First of all, the thermodynamic projector (28) for the quasiequilibrium manifold (27) 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 Ω be an anzatz manifold, and let $\boldsymbol{V}$ be some quasiequilibrium manifold, $\Psi \in \Omega \bigcap \boldsymbol{V}$, T_{Ψ} be the tangent space to the anzatz manifold Ω in the point Ψ. Suppose that there exists a neighborhood of Ψ where $\boldsymbol{V} \subseteq \Omega$. We use the notation $\mathrm{grad}_{\Psi} S$ for the Riesz representation of the linear functional $D_{\Psi}S$ in the entropic scalar product $\langle | \rangle_{\Psi}$: $\langle \mathrm{grad}_{\Psi} S | f \rangle_{\Psi} \equiv (D_{\Psi}S)(f)$ for $f \in E$.

Proposition 4. *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).

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

Proposition 4 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

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[3] In his dissertation [27] Robertson has studied “the equation of motion for the generalized canonical density operator”. The generalized canonical density renders entropy a maximum for given statistical expectations of the thermodynamic coordinates. He started from the Liouville equation for a general quantum system. The first main result of Robertson’s paper is the explicit expression for splitting of the motion onto two components: projection of the motion onto generalized canonical density and the motion in the kernel of this projection. The obtained projector operator is a specific particular case of the quasiequilibrium projector (28). The second result is the exclusion of the motion in the kernel of quasiequilibrium projector from the dynamic equation. This operation is similar to the Zwanzig formalism [28]. It leads to the integro-differential equation with delay in time for the generalized canonical density. The quasiequilibrium projector (28) is more general than the projector obtained by Robertson [27] in the following sense: It is derived for any functional S with nondegenerate second differential $D^2_{\Psi} S$, for manifold of condition maxima of S and for any (nonlinear) differential equation. B. Robertson emphasized that this operator is non-Hermitian with respect to standard L^2 scalar product and in this sense is not a projector at all. Nevertheless it is self-adjoint (and, hence, orthogonal), but with respect to another (entropic) scalar product. The general thermodynamic projector (7) acts with an arbitrary anzatz manifolds and in that sense is much more general. The motion in transversal direction will be discussed below together with post-processing algorithms.

generating the quasiequilibrium). Sometimes it can be described as the 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 Ω_α: The manifold Ω_α 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 moment values $\{M_\alpha\}$ for all possible α. It leads to a huge increase of the quasiequilibrium manifold. Another way to extension of the quasiequlibrium manifold is a union of all the manifolds Ω_α for all α. In accordance with Proposition 4, 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].[4] Due to Eq. (24) the 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 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: we can use almost any manifold as appropriate anzatz now. 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, if the classical quasiequilibrium manifold is found, then it is easy to find the projection of any distributions Ψ on the quasiequilibrium manifold: $\Psi \mapsto m(\Psi) \mapsto \Psi^{\mathrm{qe}}_{m(\Psi)}$. It requires just a calculation of the moments $m(\Psi)$. The preimage of the point $\Psi^{\mathrm{qe}}_{m(\Psi)}$ is a set (an affine manifold) of distributions

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[4] 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 dissipative dynamics. The very first use of the entropy maximization dates back to the classical work of Gibbs [29], but it was first claimed for a principle by Jaynes [1]. Probably the first explicit and systematic use of quasiequilibria to derive dissipation from entropy–conserving systems is due to the works of Zubarev. Recent detailed exposition is given in Ref. [2]. For dissipative systems, the use of the quasiequilibrium to reduce description can be traced to the works of Grad on the Boltzmann equation [30]. The viewpoint of the present authors was influenced by the papers by Rozonoer and co-workers, in particular, [3,4,31]. A detailed exposition of the quasiequilibrium approximation for Markov chains is given in the book [32] (Chapter 3, *Quasiequilibrium and entropy maximum*, pp. 92–122), and for the BBGKY hierarchy in Ref. [5]. We have applied maximum entropy principle to the description of the universal dependence of the 3-particle distribution function F_3 on the 2-particle distribution function F_2 in classical systems with binary interactions [33]. A general discussion of the maximum entropy principle with applications to dissipative kinetics is given in the review [34]. The methods for corrections of quasiequilibrium approximations are developed in Refs. [6,7,35,36].

$\{\Psi | m(\Psi - \Psi^{\mathrm{qe}}_{m(\Psi)}) = 0\}$, and $\Psi^{\mathrm{qe}}_{m(\Psi)}$ is the point of entropy maximum on this set. It is possible, but not so easy, to construct such a projector of some neighborhood of the manifold Ω onto Ω for general thermodynamic projector P_Ψ too: for a point Φ from this neighborhood

$$\Phi \mapsto \Psi \in \Omega, \quad \text{if } P_\Psi(\Phi - \Psi) = 0 \ . \tag{29}$$

A point $\Psi \in \Omega$ is the point of entropy maximum on the preimage of Ψ, i.e., on the affine manifold $\{\Phi | P_\Psi(\Phi - \Psi) = 0\}$. It is necessary to emphasize that the map (29) can be defined only in a neighborhood of the manifold Ω, but not in the whole space, because some of affine subspaces $\{\Phi | P_\Psi(\Phi - \Psi) = 0\}$ for different $\Psi \in \Omega$ can intersect. Let us introduce a special denotation for projection of some neighborhood of the manifold Ω onto Ω, associated with the thermodynamic projector P_Ψ (29): $\mathbf{P}_\Omega : \Phi \mapsto \Psi$. The preimage of a point $\Psi \in \Omega$ is:

$$\mathbf{P}_\Omega^{-1} \Psi = \Psi + \ker P_\Psi \tag{30}$$

(or, strictly speaking, a vicinity of Ψ in this affine manifold). Differential of the operator $\mathbf{P}_\Omega$ at a point $\Psi \in \Omega$ from the manifold Ω is simply the projector P_Ψ:

$$\mathbf{P}_\Omega(\Psi + \varepsilon\Phi) = \Psi + \epsilon P_\Psi \Phi + \mathrm{o}(\varepsilon) \ . \tag{31}$$

Generally, differential $\mathbf{P}_\Omega$ at a point Ψ has not so simple form, if Ψ does not belong Ω.

The "global extension" $\mathbf{P}_\Omega$ of a field of "infinitesimal" projectors P_f $(f \in \Omega)$ is needed for discussion of projector operator technique, memory functions and short memory approximation below.

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 nonphysical 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 has yet 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 produce 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 than the thermodynamic functionals, so, the *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 easier than spectral projector, for example).

3. Post-processing, memory and natural projector

3.1. How to evaluate the anzatz?

Thermodynamic projector transforms almost arbitrary anzatz 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, [37,38]). 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 [39,15]). Let $\Psi^0(t)$, $(t \in [0,T])$ be the solution of projected equations $\mathrm{d}\Psi(t)/\mathrm{d}t = P_\Psi(J(\Psi))$, and $\Delta(t) = J(\Psi^0(t)) - P_{\Psi^0(t)}(J(\Psi^0(t)))$. Then the following formula:

$$\Psi^1(t) = \Psi^0(t) + \int_0^t \Delta(\tau)\,\mathrm{d}\tau \tag{32}$$

gives the Picard iteration for solution of the initial kinetic equation $\mathrm{d}\Psi(t)/\mathrm{d}t = J(\Psi)$, with initial approximation $\Psi^0(t)$. The integral in the right-hand side of Eq. (32) 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: $\Psi^1(t) = \Psi^0(t) + \delta\Psi(t)$;

$$\frac{\mathrm{d}(\delta\Psi(t))}{\mathrm{d}t} = \Delta(t) + \frac{\langle \Delta(t) | (DJ)_{\Psi^0(t)} \Delta(t) \rangle_{\Psi^0(t)}}{\langle \Delta(t) | \Delta(t) \rangle_{\Psi^0(t)}}\,\delta\Psi(t)\,. \tag{33}$$

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 Eq. (33) is

$$\delta\Psi(t) = \int_0^t \exp\left(\int_\tau^t k(\theta)\,\mathrm{d}\theta\right) \Delta(\tau)\,\mathrm{d}\tau\,, \tag{34}$$

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 Eq. (34) improves the simplest Picard iteration (32) and gives both the estimation of the error of the anzatz, and 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 (34) should be supplemented by one more Picard iteration:

$$\delta\Psi_{sl}(t) = P_{\Psi^0(t)}\delta\Psi(t) + \int_0^t P_{\Psi^0(\tau)}((DJ)_{\Psi^0(\tau)})\delta\Psi(\tau)\,\mathrm{d}\tau\,, \tag{35}$$

where $\delta\Psi(t)$ is calculated by formula (34).

3.2. Short memory and natural projector

At the middle of XX century S. Nakajima (1958), R. Zwanzig (1960), and H. Mori (1965) discovered a new approach to model reduction in statistical physics: the method of projection operators. (Relevant bibliography and detailed presentation of this technique can be found in two books [40,41].) In this section we contrast our approach with the Nakajima–Zwanzig–Mori theory of projection operators. This theory is based upon two technical steps: (i) a projection technique for creation of exact integro-differential equations that describe dynamics of "relevant" variables for given initial conditions, (ii) and various Marcovian, short memory, adiabatic, or other assumptions of this type that allow us to simplify the exact integro-differential equations. Without such a simplification the theory is simply equivalent to the initial detailed microscopic dynamics.

The projection operators approach (it is more adequate to call it "the memory function approach" [40]) deals with linear equations of microscopic description: Liouville equation (or generalized quantum Liouville equation). The thermodynamic projector developed in this paper and a series of previous works [6,7,14,25] can be applied to any system with entropy, i.e., to a system with a specified function (functional) whose time derivative should be preserved in model reduction. Of course, it can be applied to the systems considered in the memory function approach to project the initial equations onto the manifold of relevant distribution functions. Moreover, the particular case of the thermodynamic projector, namely the quasiequilibrium projector, was developed for this purpose by Robertson in the context of Nakajima–Zwanzig approach [27].

In this paper we have discussed only the simple infinitesimal projection of the vector field onto the tangent space to anzatz manifold, but it is possible to develop a hierarchy of short-memory approximations even for general nonlinear equations and an arbitrary anzatz manifold [35–37,42–45]. This approach joins ideas of Ehrenfests on coarse-graining [46], methods of projection operators, and methods of invariant manifold [6,7,14]. The essence of this approach can be formulated very simply: we turn from infinitesimal projection of vector fields to "natural projection" of segments of trajectories.

Let us consider a dynamical system (1) $\mathrm{d}\Psi/\mathrm{d}t = J(\Psi)$, an anzatz manifold Ω, a field of projectors on $\Omega : P_\Psi : E \to T_\Psi$ for $\Psi \in \Omega$, and a global extension $\mathbf{P}_\Omega$ (29), (30) of this field of infinitesimal projectors. In this construction the field of projectors P_Ψ is arbitrary, and thermodynamic condition will be necessary only for estimation of the entropy production (see the next subsection). Let $\mathbf{T}_t$ be the shift in time t due to the dynamical system (1) (the phase flow). We are looking for a phase flow $\mathbf{\Theta}_t$ on Ω that should be a coarse-grained dynamical system in a short memory approximation. The matching equation for the short memory approximation is

$$\mathbf{\Theta}_\tau(\Psi) = \mathbf{P}_\Omega(\mathbf{T}_\tau(\Psi)) \quad \text{for all } \Psi \in \Omega , \tag{36}$$

where $\tau > 0$ is the time of memory (it may be a function of Ψ: $\tau = \tau(\Psi)$).

The phase flow $\mathbf{\Theta}_t$ on Ω is generated by a vector field on Ω:

$$\frac{\mathrm{d}\Psi}{\mathrm{d}t} = \Upsilon(\Psi) = \left.\frac{\mathrm{d}\mathbf{\Theta}_\tau(\Psi)}{\mathrm{d}\tau}\right|_{\tau=0} \in T_\Psi . \tag{37}$$

For the short memory it may be natural to seek a vector field $\Upsilon(\Psi)$ on the anzatz manifold Ω in a form of Taylor series in powers of τ: $\Upsilon(\Psi) = \Upsilon_0(\Psi) + \tau\Upsilon_1(\Psi) + \cdots$. Let us expand the right-hand side of the matching equation (36) into Taylor series in powers of τ. In zero order we get an equality $\Psi = \Psi$. In first order we obtain an expected trivial "infinitesimal" result $\Upsilon_0(\Psi) = P_\Psi(J(\Psi))$. First nontrivial result is an expression for $\Upsilon_1(\Psi)$:

$$\Upsilon_1(\Psi) = \tfrac{1}{2}\,\{P_\Psi[(D_\Psi J(\Psi))J(\Psi)] - [D_\Psi(P_\Psi J(\Psi))](P_\Psi J(\Psi))\} + \tfrac{1}{2}\,[D^2_\Psi \boldsymbol{P}_\Omega(\Psi)](J(\Psi), J(\Psi))\,. \tag{38}$$

In this order we obtain the first short-memory approximation:

$$\frac{\mathrm{d}\Psi}{\mathrm{d}t} = P_\Psi(J(\Psi)) + \frac{\tau}{2}\,\{P_\Psi[(D_\Psi J(\Psi))J(\Psi)] - [D_\Psi(P_\Psi J(\Psi))](P_\Psi J(\Psi))\} + \frac{\tau}{2}\,[D^2_\Psi \mathbf{P}_\Omega(\Psi)](J(\Psi), J(\Psi))\,. \tag{39}$$

If $\ker P_\Psi$ does not depend on Ψ, then it is possible to choose such a coordinate system on Ω where linear operator P_Ψ does not depend on Ψ. Then the last term in Eqs. (38), (39) vanishes. It is the case of quasiequilibrium manifolds, for example [37,42].

Various physical examples of application of these formulae with quasiequilibrium manifolds are presented in Refs. [37,42–44,35].

The theory of short memory and coarse-graining in the form given by Eqs. (36), (38), (39) has one free parameter: the memory time $\tau(\Psi)$. The next step is the development of the theory without such free parameters [45,36].

The first attempt to formalize the short memory approximation and coarse-graining on the base of the matching equation (36) was made by Lewis [47], but he expanded only the right-hand side of Eq. (36), and the result was not a solution of this equation. Very recently the short memory approximation became more popular [48,49].

3.3. *The theorem about entropy overproduction in the short memory approximation*

The short memory approximation (39) has one important property: it increases the entropy production for the thermodynamic projectors P_Ψ: if for any vector field the field of projectors P_Ψ preserves dissipation, then for any vector field the short memory approximation increases dissipation (and it strictly increases dissipation, if the vector field is not tangent to anzatz manifold Ω).

This *theorem about entropy overproduction* can be formulated as an expression for the entropy production.

Theorem 2. *Let P_Ψ be the field of thermodynamic projectors. Then, due to the short memory approximation* (39) *for $\Psi \in \Omega$*

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \sigma_0(\Psi) + \frac{\tau}{2}\,\sigma_1(\Psi) + \frac{\tau}{2}\,\langle \Delta(\Psi) | \Delta(\Psi)\rangle_\Psi\,, \tag{40}$$

where Δ is defect of invariance: $\Delta = J(\Psi) - P_\Psi(J(\Psi))$,

$$\sigma_0(\Psi) = \left.\frac{\mathrm{d}S(\mathbf{T}_\tau(\Psi))}{\mathrm{d}\tau}\right|_{\tau=0} = (D_\Psi S(\Psi))(J(\Psi))\ ;$$

$$\sigma_1(\Psi) = \left.\frac{\mathrm{d}^2S(\mathbf{T}_\tau(\Psi))}{\mathrm{d}\tau^2}\right|_{\tau=0} = (D_\Psi S(\Psi))[(D_\Psi J(\Psi))(J(\Psi))] - \langle J(\Psi)|J(\Psi)\rangle_\Psi\ . \tag{41}$$

($\sigma_0(\Psi)$ is the entropy production due to initial system at a point Ψ.) The geometrical proof of this formula (40) is simple. The matching condition (36) represents a motion according to a short memory approximation as two steps: (i) the motion along trajectories of initial system during time τ, and (ii) the projection onto manifold Ω by means of the operator $\mathbf{P}_\Omega$ (29), (30). The entropy increment on the first step is

$$S(\mathbf{T}_\tau(\Psi)) - S(\Psi) = \tau\sigma_0(\Psi) + \frac{\tau^2}{2}\sigma_1(\Psi) + \mathrm{o}(\tau^2)\ .$$

To calculate the entropy increment on the projection step with accuracy τ^2 we need to calculate the motion with accuracy τ^1 only, because the point $\Psi \in \Omega$ is the point of entropy maximum on its preimage $\mathbf{P}_\Omega^{-1}(\Psi)$ (here it is crucial that P_Ψ is the field of thermodynamic projectors with the property A (25)). In the first order $\mathbf{T}_\tau(\Psi) - \mathbf{P}_\Omega(\mathbf{T}_\tau(\Psi)) = \tau\Delta(\Psi)$ and the last term in Eq. (40) is just the Taylor formula for S of the second order.

First two terms in Eq. (40) give the average entropy production by the initial system in time τ (up to the second order in τ). The third term is always non-negative, and is zero only for zero defect of invariance. In this sense Theorem 2 is *the theorem about entropy overproduction*. The following corollary gives an obvious, but physically important consequence of this theorem.

Corollary 3. *Let the initial system* (1) *be conservative*: $\mathrm{d}S/\mathrm{d}t = (D_\Psi S(\Psi))(J(\Psi)) \equiv 0$. *Then for the short memory approximation* (39) *entropy production is non-negative*:

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \frac{\tau}{2}\langle\Delta(\Psi)|\Delta(\Psi)\rangle_\Psi \geqslant 0\ , \tag{42}$$

and $\mathrm{d}S/\mathrm{d}t = 0$ *if and only if the vector field* $J(\Psi)$ *is tangent to anzatz manifold.*

The short-memory approximation equipped by the thermodynamic projector gives us the simplest way to introduce dissipation into a conservative system.

4. The art of anzatz: multi-peak polyhedrons in kinetic systems with instabilities

4.1. Two-peak approximations

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 this subsection we discuss two special anzatz which have been 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.

4.1.1. 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 [50]. 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 [51]. 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, Ref. [51]):

$$f(\boldsymbol{v},\boldsymbol{x}) = f_{\mathrm{TMS}}(\boldsymbol{v},z) = a_-(z)f_-(\boldsymbol{v}) + a_+(z)f_+(\boldsymbol{v}) , \tag{43}$$

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

Direct molecular dynamic simulation for the Lennard-Jones gas shows good *quantitative* agreement of the Tamm–Mott-Smith anzatz (43) with the simulated velocity distribution functions in the shock fronts for a wide range of Mach number (between 1 and 8.19) [52]. For different points in the shock front the bimodal approximation (43) of the simulated velocity distribution function has appropriate accuracy, but the question about the approximation of the $a_\pm(z)$ remained open in the paper [52], 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 (43) [6] (in our paper [6] we have used only *property* A, but for this one-dimensional anzatz it was sufficient for uniqueness of the projector). These equations have a simple form for the variables:

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

The particle density $n(z)$ is a 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 [6,53].

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

$$\frac{\partial s}{\partial t} + \frac{\partial j_s}{\partial z} = \sigma, \quad \frac{\partial n}{\partial t} + \frac{\partial j_n}{\partial z} = 0 \,, \tag{44}$$

where

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

and σ is the Boltzmann density of entropy production for the TMS distribution (43):

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

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

Eqs. (44) were first introduced by Lampis [53] in the ad hoc manner. Direct numerical simulation demonstrated that all other known equations for the Tamm–Mott-Smith anzatz violate the second law [54].

4.1.2. Langer–Bar-on–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 Ref. [55]. 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 a 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:

$$\frac{\partial \rho_1}{\partial t} = M \frac{\partial}{\partial u} \left(\rho_1 \frac{\partial F(u)}{\partial u} + k_{\mathrm{B}} T b \frac{\partial \rho_1}{\partial u} \right) \,, \tag{45}$$

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

$$\rho_2[u(\boldsymbol{r}), u(\boldsymbol{r}_0)] \cong \rho_1[u(\boldsymbol{r})]\rho_1[u(\boldsymbol{r}_0)]\{1 + \gamma(|\boldsymbol{r} - \boldsymbol{r}_0|)u(\boldsymbol{r})u(\boldsymbol{r}_0)\} \tag{46}$$

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 Ref. [55].

The mean-field free energy function $F(u)$ is nonstationary and may be nonconvex. 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:

$$\rho_1(u) = a_1 G_\sigma(u - \varsigma_1) + a_2 G_\sigma(u + \varsigma_2) , \tag{47}$$

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 (47) allowed to get the satisfactory quantitative description for some features of spinodal decomposition. The authors of the paper [55] 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 nontrivial moments ($\langle u^2\rangle$, $\langle u^3\rangle$, $\langle u^4\rangle$).

The Langer–Bar-on–Miller bimodal anzatz has a long history of criticizing and comparison with experiments and other calculations. During 10 years after this publication there were some attempts to criticize and improve this theory. Nevertheless, at 1985 this theory was called “the most successful “early-time” theory yet available” [56]. In this paper the nonlinear Langer–Bar-on–Miller theory was again criticized as nonsystematic, “since there is no smallness parameter”.[5] Nevertheless, 20 years of various attempts to improve this theory of bimodal anzatz were resumed in Ref. [57]: “There have been many theories that attempt to incorporate nonlinear effects in the description of the spinodal decomposition process. The most successful of these was devised by Langer, Baron, and Miller”. This situation reminds the situation with TMS anzatz for shock waves.

More recently, applications of Monte Carlo methods to the self-consistent calculation of a Ginzburg–Landau free energy functional for Lennard-Jones systems in three dimensions were discussed [58]. It was demonstrated that the parameters in the coarse-grained free energy can be extracted from a multivariate distribution of energies and particle densities. Histograms of calculated unimodal and bimodal density distributions are presented.

4.2. Multi-peak anzatz and mean-field theory of molecular individualism

4.2.1. 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 [59].

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.

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[5] This explicit belief in small parameters and Taylor expansion remains widespread in spite of many well-known computational algorithms that use no explicit small parameters both in computational mathematics and mathematical physics.

It is nonlinear, because of the dependence of potential energy U on the moment $M_2[\Psi] = \int q^2\Psi(q)\,\mathrm{d}q$. 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 [20]. Here is this model:

$$\partial_t\Psi = -\partial_q\{\alpha(t)q\Psi\} + \tfrac{1}{2}\,\partial_q^2\Psi\,. \tag{48}$$

Here

$$\alpha(t) = \kappa(t) - \tfrac{1}{2}\,f(M_2(t))\,, \tag{49}$$

$\kappa(t)$ 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 $M_2 = \int q^2\Psi(q,t)\,\mathrm{d}q$. 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 Ref. [60]). 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 [37].

Eq. (48) describes an ensemble of non-interacting dumbells subject to a pseudo-elongational flow with fixed kinematics. As is well known, the Gaussian distribution function,

$$\Psi^G(M_2) = \frac{1}{\sqrt{2\pi M_2}}\exp\left[-\frac{q^2}{2M_2}\right]\,, \tag{50}$$

solves Eq. (48) provided the second moment M_2 satisfies

$$\frac{\mathrm{d}M_2}{\mathrm{d}t} = 1 + 2\alpha(t)M_2\,. \tag{51}$$

Solution (50) and (51) is the valid macroscopic description if all other solutions of Eq. (48) are rapidly attracted to the family of Gaussian distributions (50). In other words [7], the special solution (50) and (51) is the macroscopic description if Eq. (50) is the stable invariant manifold of the kinetic equation (48). If not, then the Gaussian solution is just a member of the family of solutions, and Eq. (51) has no meaning of the macroscopic equation. Thus, the complete answer to the question of validity of Eq. (51) as the macroscopic equation requires a study of dynamics in the neighborhood of manifold (50). Because of the simplicity of model (48), this is possible to a satisfactory level even for M_2-dependent spring forces.

In Ref. [20] it was shown, that there is a possibility of "explosion" of the Gaussian manifold: with the small initial deviation from it, the solutions of Eq. (48) are very fast going far from, and then slowly coming back to the stationary point which is located on the Gaussian manifold. The distribution function Ψ is stretched fast, but loses 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 Ref. [20].

Let $M_{2n}=\int q^{2n}\Psi\,\mathrm{d}q$ denote the even moments (odd moments vanish by symmetry). We consider deviations $\mu_{2n}=M_{2n}-M_{2n}^{\mathrm{G}}$, where $M_{2n}^{\mathrm{G}}=\int q^{2n}\Psi^{\mathrm{G}}\,\mathrm{d}q$ are moments of the Gaussian distribution function (50). Let $\Psi(q,t_0)$ be the initial condition to Eq. (48) at time $t=t_0$. Introducing functions,

$$p_{2n}(t,t_0)=\exp\left[4n\int_{t_0}^{t}\alpha(t')\,\mathrm{d}t'\right] , \tag{52}$$

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

$$\mu_4(t)=p_4(t,t_0)\mu_4(t_0) , \tag{53}$$

and

$$\mu_{2n}(t)=\left[\mu_{2n}(t_0)+2n(4n-1)\int_{t_0}^{t}\mu_{2n-2}(t')p_{2n}^{-1}(t',t_0)\,\mathrm{d}t'\right]p_{2n}(t,t_0) , \tag{54}$$

for $2n\geqslant 6$. Eqs. (52), (53) and (54) describe evolution near the Gaussian solution for arbitrary initial condition $\Psi(q,t_0)$. Notice that explicit evaluation of the integral in Eq. (52) requires solution to the moment equation (51) 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

$$\lim_{t\to\infty}\int_{t_0}^{t}\alpha(t')\,\mathrm{d}t'<0 . \tag{55}$$

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. (52) is estimated as $\int_{t_0}^{t}\alpha(t')\,\mathrm{d}t'>\alpha(t-t_0)$, $\alpha>0$, $t\leqslant T$, then the Gaussian solution becomes exponentially unstable during this time interval. If this is the case, the moment equation (51) cannot be regarded as the macroscopic equation. Let us consider specific examples.

For the Hookean spring ($f\equiv 1$) under a constant elongation (κ=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 Eq. (51) 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. (51) and (53) were integrated by the fifth-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 [61]). 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

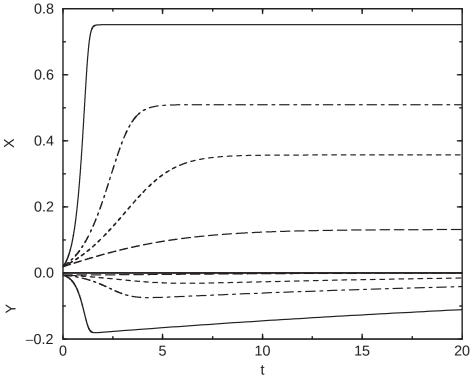


Fig. 1. Deviations of reduced moments from the Gaussian solution as a function of reduced time t in pseudo-elongation flow for the FENE-P model. Upper part: Reduced second moment $X = M_2/b$. Lower part: Reduced deviation of fourth moment from Gaussian solution $Y = -\mu_4^{1/2}/b$. Solid: $\kappa = 2$, dash-dot: $\kappa = 1$, dash: $\kappa = 0.75$, long dash: $\kappa = 0.5$. (The figure from Ref. [20], computed by Ilg.)

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. (51) approaches the steady state. However, the time constant for this exponential relaxation $|\alpha_\infty|$ is very small. Specifically, for large κ,

$$\alpha_\infty = \lim_{t\to\infty} \alpha(t) = -\frac{1}{2b} + O(\kappa^{-1}) \,. \tag{56}$$

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 (55) is met, *significant deviations from the Gaussian solution persist over the times when the solution of Eq.* (51) *is already reasonably close to the stationary state.* If we accept the usually quoted physically reasonable minimal value of parameter b of the order 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 estimation (56) 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 Ref. [62]. The statistics of FENE-P solutions with random strains was studied recently by Thiffeault [63].

In accordance with Ref. [64] the anzatz for Ψ can be suggested in the following form:

$$\Psi^{\mathrm{An}}(\{\sigma,\varsigma\},q) = \frac{1}{2\sigma\sqrt{2\pi}}\left(e^{-\frac{(q+\varsigma)^2}{2\sigma^2}} + e^{-\frac{(q-\varsigma)^2}{2\sigma^2}}\right) \,. \tag{57}$$

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 (57),

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

To build the thermodynamic projector on the manifold (57), the thermodynamic Lyapunov function is necessary. It is necessary to emphasize, that Eqs. (48) 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

$$F = U(M_2[\Psi]) - TS[\Psi] \ , \tag{58}$$

where

$$S[\Psi] = -\int \Psi(\ln\Psi - 1)\,\mathrm{d}q \ ,$$

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

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

$$\Psi^* = \exp(-U) \ ,$$

$$S_k[\Psi] = -\langle U\rangle - \int \Psi \ln\Psi\,\mathrm{d}q \ .$$

If $U(M_2[\Psi])$ in the mean field approximation is the convex function of M_2, then the free energy (58) is the convex functional too.

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

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

$$I = -B(\Psi)\nabla_q\mu \ , \tag{59}$$

where $\mu = \frac{\delta F}{\delta\Psi}$, $B \geqslant 0$. From Eq. (58) it follows that

$$\mu = \frac{\mathrm{d}U(M_2)}{\mathrm{d}M_2}\,q^2 + \ln\Psi$$

$$I = -B(\Psi)\left[2\,\frac{\mathrm{d}U}{\mathrm{d}M_2}\,q + \Psi^{-1}\nabla_q\Psi\right] \ . \tag{60}$$

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

$$I = -D\left[\frac{\mathrm{d}U}{\mathrm{d}M_2}\,q\Psi + \frac{1}{2}\,\nabla_q\Psi\right]$$

$$\frac{\partial\Psi}{\partial t} = \mathrm{div}_q I = D\,\frac{\mathrm{d}U(M_2)}{\mathrm{d}M_2}\,\partial_q(q\Psi) + \frac{D}{2}\,\partial^2 q\Psi \ , \tag{61}$$

When $D=1$ this equation coincides with (48) in the absence of the flow: due to Eq. (61) $\mathrm{d}F/\mathrm{d}t \leqslant 0$.

Let us construct the thermodynamic projector with the help of the thermodynamic Lyapunov function F (58). Corresponding entropic scalar product in the point Ψ has the form

$$\langle f|g\rangle_{\Psi} = \left.\frac{\mathrm{d}^2 U}{\mathrm{d}M_2^2}\right|_{M_2=M_2[\Psi]} \int q^2 f(q)\,\mathrm{d}q \int q^2 g(q)\,\mathrm{d}q + \int \frac{f(q)g(q)}{\Psi(q)}\,\mathrm{d}q\,. \tag{62}$$

During the investigation of anzatz (57) the scalar product (62), constructed for the corresponding point of the Gaussian manifold with $M_2=\sigma^2$, will be used. It will let us investigate the neighborhood of the Gaussian manifold (and to get all the results in the analytical form):

$$\langle f|g\rangle_{\sigma^2} = \left.\frac{\mathrm{d}^2 U}{\mathrm{d}M_2^2}\right|_{M_2=\sigma^2} \int q^2 f(q)\,\mathrm{d}q \int q^2 g(q)\,\mathrm{d}q + \sigma\sqrt{2\pi}\int \mathrm{e}^{q^2/2\sigma^2} f(q)g(q)\,\mathrm{d}q\,. \tag{63}$$

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

$$DF_{\sigma^2}(f) = \left(\left.\frac{\mathrm{d}U(M_2)}{\mathrm{d}M_2}\right|_{M_2=\sigma^2} - \frac{1}{2\sigma^2}\right)\int q^2 f(q)\,\mathrm{d}q\,, \tag{64}$$

(with the condition $\int f(q)\,\mathrm{d}q = 0$). The point

$$\left.\frac{\mathrm{d}U(M_2)}{\mathrm{d}M_2}\right|_{M_2=\sigma^2} = \frac{1}{2\sigma^2}\,,$$

corresponds to the equilibrium.

The tangent space to manifold (57) is spanned by the vectors

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

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

$$f_\varsigma = \frac{1}{4\sigma^2\varsigma\sqrt{2\pi}}\left[-\mathrm{e}^{-(q+\varsigma)^2/2\sigma^2}\,\frac{q+\varsigma}{\sigma} + \mathrm{e}^{-(q-\varsigma)^2/2\sigma^2}\,\frac{(q-\varsigma)}{\sigma}\right]; \tag{65}$$

The Gaussian entropy (free energy) production in the directions f_σ and f_ς (64) has a very simple form:

$$DF_{\sigma^2}(f_\varsigma) = DF_{\sigma^2}(f_\sigma) = \left.\frac{\mathrm{d}U(M_2)}{\mathrm{d}M_2}\right|_{M_2=\sigma^2} - \frac{1}{2\sigma^2}\,. \tag{66}$$

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 $\mathrm{d}\Psi/\mathrm{d}t = J(\Psi)$ in the point $\Psi(\{\sigma, \varsigma\})$. We need to build the projection of J onto the tangent space $T_{\sigma,\varsigma}$ in the point $\Psi(\{\sigma, \varsigma\})$:

$$P^{\mathrm{th}}_{\sigma,\varsigma}(J) = \varphi_\sigma f_\sigma + \varphi_\varsigma f_\varsigma \ . \tag{67}$$

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

$$\frac{\mathrm{d}\sigma^2}{\mathrm{d}t} = \varphi_\sigma; \quad \frac{\mathrm{d}\varsigma^2}{\mathrm{d}t} = \varphi_\varsigma \ . \tag{68}$$

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

$$\varphi_\sigma + \varphi_\varsigma = \int q^2 J(\Psi)(q)\,\mathrm{d}q \ ;$$

$$\langle \varphi_\sigma f_\sigma + \varphi_\varsigma f_\varsigma | f_\sigma - f_\varsigma \rangle_{\sigma^2} = \langle J(\Psi) | f_\sigma - f_\varsigma \rangle_{\sigma^2} \ , \tag{69}$$

where $\langle f|g \rangle_{\sigma^2} = \langle J(\Psi)| f_\sigma - f_\varsigma \rangle_{\sigma^2}$, (62). First equation of (69) means that the time derivative $\mathrm{d}M_2/\mathrm{d}t$ is the same for the initial and reduced equations. Due to the formula for the dissipation of the free energy (64), this equality is equivalent to the persistence of the dissipation in the neighborhood of the Gaussian manifold. Indeed, according to (64) $\mathrm{d}F/\mathrm{d}t = A(\sigma^2) \int q^2 J(\Psi)(q)\,\mathrm{d}q = A(\sigma^2)\,\mathrm{d}M_2/\mathrm{d}t$, where $A(\sigma^2)$ does not depend of J. On the other hand, time derivative of M_2 due to projected equation (68) is $\varphi_\sigma + \varphi_\varsigma$, because $M_2 = \sigma^2 + \varsigma^2$.

The second equation in (69) means, that J is projected orthogonally on $\ker DS \bigcap T_{\sigma,\varsigma}$. Let us use the orthogonality with respect to the entropic scalar product (63). The solution of Eqs. (69) has the form

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

$$\frac{\mathrm{d}\varsigma^2}{\mathrm{d}t} = \varphi_\varsigma = \frac{-\langle J | f_\sigma - f_\varsigma \rangle_{\sigma^2} + M_2(J)(\langle f_\sigma | f_\sigma \rangle_{\sigma^2} - \langle f_\sigma | f_\varsigma \rangle_{\sigma^2})}{\langle f_\sigma - f_\varsigma | f_\sigma - f_\varsigma \rangle_{\sigma^2}} \ , \tag{70}$$

where $J = J(\Psi)$, $M_2(J) = \int q^2 J(\Psi)\,\mathrm{d}q$.

It is easy to check that the formulas (70) are indeed defining the projector: if f_σ (or f_ς) is substituted there instead of the function J, then we will get $\varphi_\sigma = 1, \varphi_\varsigma = 0$ (or $\varphi_\sigma = 0, \varphi_\varsigma = 1$, respectively). Let us substitute the right part of the initial kinetic equations (48), calculated in the point $\Psi(q) = \Psi(\{\sigma, \varsigma\}, q)$ (see Eq. (57)) in Eq. (70) instead of J. 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 (70) are possible to calculate analytically.

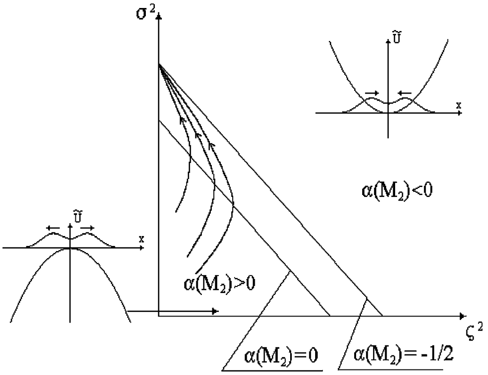


Fig. 2. Phase trajectories for the two-peak approximation, FENE-P model. The vertical axis (ς=0) corresponds to the Gaussian manifold. The triangle with $\alpha(M_2) > 0$ is the domain of exponential instability.

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 (57). 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 system (70). 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:

$$\frac{1}{\sigma^2}\frac{\mathrm{d}\varsigma^2}{\mathrm{d}t} = 2\alpha\frac{\varsigma^2}{\sigma^2} + \mathrm{o}\left(\frac{\varsigma^4}{\sigma^4}\right) , \tag{71}$$

where

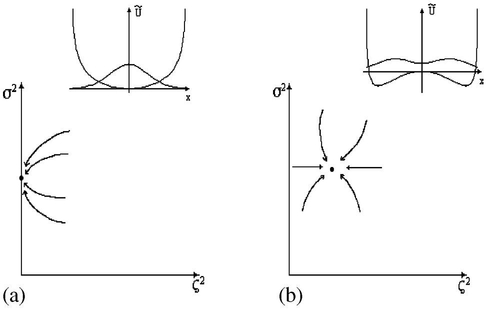
$$\alpha = \kappa - \left.\frac{\mathrm{d}U(M_2)}{\mathrm{d}M_2}\right|_{M_2=\sigma^2} .$$

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 $\mathrm{d}\sigma^2/\mathrm{d}t = 1 + 2\alpha\sigma^2$. The form of the phase trajectories is shown qualitative in Fig. 2. Note that this result completely agrees with Eq. (53).

For the real equation FPE (for example, with the FENE potential) the motion in the 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 in 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, $\tilde{U}(q) = U(q) - \frac{1}{2}\sum_{i,j}\kappa_{i,j} q_i q_j$).



(a) (b)

Fig. 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.

4.2.2. *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 had a huge amount of possible configurations. An attempt to describe this picture quantitatively meets the following obstacle: we do not know the potential U, on the other hand, the effect of molecular individualism [17–19] seems to be universal in its essence, without the dependence of the qualitative picture on details of interactions. We should find a mechanism that is as general as the effect. The simplest dumbbell model which we have discussed in the previous subsection does not explain the effect, but it gives us a hint: the flow can violate the stability of unimodal distribution. If we assume that the whole picture is hidden inside a multidimensional Fokker–Planck equation for a large molecule in a flow, then we can use this hint in such a way: when the flow strain grows there appears a sequence of bifurcations, and for each of them a new unstable direction arises. For a qualitative description of such a picture we can apply a language of normal forms [65], but with some modification.

The bifurcation in dimension one with appearance of two point of minima from one point has the simplest polynomial representation: $U(q,\alpha)=q^4+\alpha q^2$. If $\alpha \geqslant 0$, then this potential has one minimum, if $\alpha < 0$, then there are two points of minima. The normal form of degenerated singularity is $U(q)=q^4$. Such polynomial forms as $q^4+\alpha q^2$ are very simple, but they have inconvenient asymptotic at $q \to \infty$. For our goals it is more appropriate to use logarithms of convex combinations of Gaussian distributions instead of polynomials. It is the same class of jets near the bifurcation, but with given quadratic asymptotic $q \to \infty$. If one needs another class of asymptotic, it is possible just to change the choice of the basic peak. All normal forms of the critical form of functions, and families of versal deformations are well investigated and known [65].

Let us represent the deformation of the probability distribution under the strain in multidimensional case as a cascade of peak dissociation. The number of peaks will duplicate on the each step. The possible cascade of peak dissociation is presented qualitatively in Fig. 4. The important property of this qualitative picture is the linear complexity of dynamical description with exponential complexity of geometrical

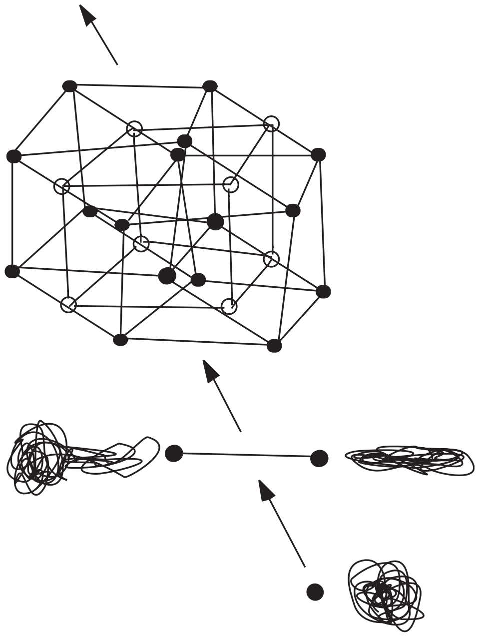


Fig. 4. Cartoon representing the steps of molecular individualism. Black dots are vertices of Gaussian parallelepiped. Zero, one, and four-dimensional polyhedrons are drawn. Presented is also the three-dimensional polyhedron used to draw the four-dimensional object. Each new dimension of the polyhedron 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.

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 and in these points the dimension of unstable direction increases.

Positions of peaks correspond to parallelepiped vertices. Different vertices in configuration space present different geometric forms. So, it seems *plausible*[6] that observed different forms (“dumbbels”, “half-dumbbels”, “kinked”, “folded” and other, not

---

[6] We cannot *prove* it now, and it is necessary to determine the status of proposed qualitative picture: it is much more general than a specific model, it is the mechanism which acts in a wide class of models. The cascade of instabilities can appear and, no doubt, it appears for the Fokker–Planck equation for a large molecule in a flow. But it is not proven yet that the effects observed in well-known experiments have exactly this mechanism. This proof requires quantitative verification of a specific model. And now we talk not about a proven, but about the plausible mechanism which typically appears for systems with instabilities.

classified forms) correspond to these vertices of parallelepiped. Each vertex is a metastable state of a molecule and has its own basin of attraction. A molecule goes to the vertex which depends strongly on details of initial conditions.

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:

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

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 $\phi(x) = (1-x)^{-1}$).

For quadratic multidimensional mean field models persist the qualitative picture of Fig. 2: there is *nonstationary molecular 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 nonperiodical fluctuations". This walk can be unexpected fast, because it can effectively be 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).

4.3. 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 Eq. (14):

$$\Psi(q) = \Psi^*(q) \prod_{i=1}^{m} \varphi_i((\varsigma_i, q)) , \tag{72}$$

where $\Psi^*(q)$ is the distribution density for one peak, for example, it may be the multidimensional Gaussian distribution $\Psi^*(q) = (1/(2\pi)^{n/2}\sqrt{\det\Sigma})\exp\left(-\frac{1}{2}(\Sigma^{-1}q,\ q)\right)$, ς_i, $(i=1,\dots,m)$ 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, $\varphi_i(x) = A_i \mathrm{ch}(\alpha_i x + \beta_i)$.

Form (72) is more flexible than 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, $\varphi_i(x) = A_i \mathrm{ch}(\alpha_i x)$ 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 nonsymmetric 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 anzatz (72).

Let us describe the tangent space T for anzatz (72) 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 (72) in a point Ψ has a form:

$$T_\Psi = \Psi \left[\sum_{i=1}^{m} L((\varsigma_i, q)) + \sum_{i=1}^{m} \left(\frac{\mathrm{d}\lambda_i(x)}{\mathrm{d}x} \right)_{x=(\varsigma_i, q)} E^* \right] , \tag{73}$$

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 $(\mathrm{d}\lambda_i(x)/\mathrm{d}x)_{x=(\varsigma_i,q)} E^*$ it is convenient to change in Eq. (73) 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):

$$T_\Psi = \Psi \left[\sum_{i=1}^{m} L((\varsigma_i, q)) + \sum_{i=1}^{m} \left(\frac{\mathrm{d}\lambda_i(x)}{\mathrm{d}x} \right)_{x=(\varsigma_i, q)} E_i^* \right] . \tag{74}$$

It means that for sufficiently rich spaces L the vectors ς_i in anzatz (72) could be chosen on the sphere, $(\varsigma_i, \varsigma_i) = 1$, to provide independence of variables.

Form (72) appears as a quasiequilibrium distribution density in the following particular case of problem (27):

$$S(\Psi) \to \max, \quad \int \delta(x - (\varsigma_i, q)) \Psi(q) \, \mathrm{d}^n q = f_i(x), \quad i = 1, \ldots, m , \tag{75}$$

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

$$S(\Psi) = -\int \Psi(q) \ln \left(\frac{\Psi(q)}{\Psi^*(q)} \right) \mathrm{d}^n q . \tag{76}$$

Hence, for fixed values of ς_i and for a space of arbitrary nonnegative smooth functions $\varphi_i(x)$ anzatz (72) is the quasiequilibrium approximation with macroscopic variables

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

Let us define the anzatz manifold (72) as a union of the quasiequilibrium manifolds (75) for all sets of values $\{\varsigma_i\}_{i=1}^m$ on the unit sphere. In this case we can apply

Proposition 4: 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

$$\langle f|g\rangle_\Psi = \int \frac{f(q)g(q)}{\Psi(q)}\,\mathrm{d}q\ , \tag{77}$$

and in the conjugated space (for example, for functions λ from space L in (73), (74))

$$\langle \mu|\lambda\rangle^c_\Psi = \int \mu(q)\lambda(q)\Psi(q)\,\mathrm{d}q\ , \tag{78}$$

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

$$\sum_{i=1}^{m} L((\varsigma_i, q)) + \sum_{i=1}^{m} \left(\frac{\mathrm{d}\lambda_i(x)}{\mathrm{d}x}\right)_{x=(\varsigma_i,q)} E_i^* \tag{79}$$

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

$$\mathrm{im}P_{\lambda_i} = L((\varsigma_i, q)), \quad \mathrm{im}P_{\varsigma_i} = \left(\frac{\mathrm{d}\lambda_i(x)}{\mathrm{d}x}\right)_{x=(\varsigma_i,q)} E_i^*\ . \tag{80}$$

Operators P_{λ_i}, $P\varsigma_i$ can be founded from the definition of their images (80) and the conditions: $P^2 = P$, $P^+ = P$, where P^+ is conjugated to P operator with respect of the scalar product $\langle\,|\,\rangle^c$ (78). 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*:

$$\langle J - P(J)|J - P(J)\rangle_\Psi \to \min \text{ for } P(J) \in T_\Psi\ . \tag{81}$$

The gradient methods for solution of problem (81) 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 a 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:

$$\mathrm{grad}_x(J - x, J - x) = 2\sum_i P_i^\perp (J - x)\ , \tag{82}$$

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 easily write the gradient method for problem (81).

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

$$\frac{\partial\Psi(q,t)}{\partial t}=\nabla_q\{D(q)[\Psi(q,t)(\nabla_q U(q)-F_{\mathrm{ex}}(q,t))+\nabla_q\Psi(q,t)]\}\ . \tag{83}$$

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 ($(r,D(q)r)\geqslant 0$) symmetric diffusion matrix, and $F_{\mathrm{ex}}(q,t)$ is an external force (we omit here such multipliers as $k_{\mathrm{B}}T$, friction coefficients, etc). Another form of Eq. (83) is

$$\frac{\partial\Psi(q,t)}{\partial t}=\nabla_q\left\{D(q)\Psi^*(q)(\nabla_q-F_{\mathrm{ex}}(q,t))\left(\frac{\Psi(q,t)}{\Psi^*(q)}\right)\right\}\ , \tag{84}$$

where $\Psi^*(q)$ is the equilibrium density: $\Psi^*(q,t)=\exp(-U(q))/\int\exp(-U(p))\,\mathrm{d}p$. For anzatz (72) $\Psi(q,t)=\Psi^*(q)\exp\sum_i\lambda_i((\varsigma_i,q),t)$. For this anzatz the left-hand side of Eq. (84) has the form

$$\begin{aligned}
J(\Psi)=\Psi\Bigg[&\sum_i(\varsigma_i,D(q)\varsigma_i)\left(\frac{\partial^2\lambda_i}{\partial x^2}\right)_{x=(\varsigma_i,q)}\\
&+\sum_{i,j}(\varsigma_j,D(q)\varsigma_i)\left(\frac{\partial\lambda_i}{\partial x}\right)_{x=(\varsigma_i,q)}\left(\frac{\partial\lambda_j}{\partial x}\right)_{x=(\varsigma_j,q)}\\
&-\sum_i\left(\frac{\partial\lambda_i}{\partial x}\right)_{x=(\varsigma_i,q)}((\varsigma_i,D(q)(\nabla_q U(q)+F_{\mathrm{ex}}(q,t)))-(\nabla_q,D(q)\varsigma_i))\\
&+(\nabla_q U(q),D(q)F_{\mathrm{ex}}(q,t))-(\nabla_q,D(q)F_{\mathrm{ex}}(q,t))\Bigg]\ ,
\end{aligned} \tag{85}$$

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

The projected equations have the form:

$$\frac{\partial\lambda_i}{\partial t}=P_{\lambda_i}J(\Psi),\qquad \frac{\mathrm{d}\varsigma_i}{\mathrm{d}t}=P_{\varsigma_i}J(\Psi)\ , \tag{86}$$

where the vector field $J(\Psi)$ is calculated by formula (85), and the projectors, P_{λ_i} and P_{ς_i}, are defined by Eqs. (80). For adaptive methods the right-hand parts of Eqs. (86) are solutions of auxiliary equations.

We can return from anzatz (72) to the polymodal polyhedron: It corresponds to a finite-dimensional multimodal approximation for each of Eqs. (86). 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 further development of approximation (72) it is possible to add some usual moments to system (75). 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 (72) will be replaced to a more general nonconstant quasiequilibrium density.

Ansatz (72) can be discussed and studied from different points of view:

(1) It is an *uncorrelated particle* representation of kinetics: The distribution density function (72) 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 [66]. There are three significant differences between anzatz (73) and usual uncorrelated anzatz: First, anzatz (72) is not symmetric with respect to particle permutation, second, the configuration spaces of particles for this anzatz are dynamic variables. The third difference is: Ansatz (72) 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* [67]. 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 [68–70]. Nevertheless, neural networks with relatively rich spaces of activation functions are in use too [71,72].

5. 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 thermodynamic properties in model reduction is solved. POET is an *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 the open system as well: 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 impacts of POET on the model reduction technology is the new possibility of constructing thermodynamically consistent reduced model with almost arbitrary anzatz. On the other hand, it gives the possibility to create thermodynamically consistent discretization of the problem of model reduction [73].

The short memory approximation gives the coarse-grained equations. Entropy production for these equations is larger than for initial equations. This approach allows us to produce systems with dissipation from conservative systems, for example.

It should be stressed that all the constructions, equations and statements are valid for arbitrary (linear or nonlinear) vector fields, classical or quantum, mechanical, or not. The only requirement is: the projector field preserves the sign of dissipation, and such a field was constructed.

In this paper we discussed the important example of anzatz: the multipeak models. Two examples of these type of models demonstrated high efficiency during decades: the Tamm–Mott-Smith bimodal anzatz for shock waves, and the Langer–Bar-on–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. Distributions of this type are expected to appear in each kinetic model with multidimensional instability as universally, as Gaussian distribution appears for stable systems. This statement needs a clarification: everybody knows that the Gaussian distribution is stable with respect to convolutions and the appearance of this distribution is supported by central limit theorem. Gaussian polyhedra form a stable class: convolution of two Gaussian polyhedra is a Gaussian polyhedron and convolution of a Gaussian polyhedron with a Gaussian distribution is a Gaussian polyhedron with the same number of vertices. On the other hand, a Gaussian distribution in a potential well appears as an exponent of a quadratic form which represents the simplest stable potential (a normal form of a nondegenerated critical point). Families of Gaussian parallelepipeds appear as versal deformations with given asymptotic for systems with cascade of simplest bifurcations.

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 Refs. [20,64]. 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. Each vertex has its own basin of attraction. A molecule goes to the vertex which depends strongly on details of initial conditions.

These models pretend to be the kinetic basis for the theory of molecular individualism. The detailed computations will be presented in following works, but some of the qualitative features of the models are in agreement with some of qualitative features of the picture observed in experiment [17–19]: effect has the threshold character, different observed conformations depend significantly on the initial conformation and orientation.

Some general 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 an 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 a picture other than the relaxation of unknoted molecules)?
- The analysis of random walk of molecules from peak to peak should be carried out, and results of this analysis should be compared with observed large fluctuations.

The systematic discussion of a difference between the Gaussian elipsoid (and its generalizations) and the Gaussian multipeak polyhedron (and its generalizations) seems necessary. This polyhedron appears generically as the effective anzatz for kinetic systems with instabilities.

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