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STATISTICAL-MECHANICAL DESCRIPTION OF ORIENTATIONAL ORDER TENSOR FLUCTUATION BY MEANS OF FOKKER-PLANCK EQUATION

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This article is devoted to derivation the evolution equation for the distribution function of fluctuations of tensor order parameter on bases of solving of the Liouville equation by Zubarev method.

The problem, which we pose, is an investigation of fluctuations in orientational order systems. This systems are included, for example, the liquid crystals, liquid crystalline polymers, liquid crystal elastomers, the ordered phases of DNA molecules. For description the orientation order we use the traceless second order tensor $\hat{D}_{ij}$. This tensor is defined as

$$\hat{D}_{ij}(\mathbf{x}) = \frac{1}{2}\sum_{\nu=1}^{N}(3c_i^{\nu}c_j^{\nu} - \delta_{ij})\delta(\mathbf{x}-\mathbf{x}^{\nu}), \tag{1}$$

where c_i^{ν} is projection of unit vector directed along the axis of the rigid fragment of molecule numbered ν, $\mathbf{x}^{\nu}$ is the radius vector of the center of mass of molecule fragment, N is the number of fragment.

Therefore it is important to obtain the equation which describes the time evolution of fluctuation of the tensor of orientational order.

Macromolecules in the above mentioned systems have the rigid fragments and due to this circumstance the considered materials possesses the orientation order.

We suppose that the nonequilibrium state our system can be described by the distribution function of discrete set of dynamical variables $\hat{a}_1,\dots,\hat{a}_6$. This variables represent the components of the tensor the orientational order:

$$\hat{a}_1 = \hat{D}_{11},\ \hat{a}_2 = \hat{D}_{12},\ \hat{a}_3 = \hat{D}_{13},\ \hat{a}_4 = \hat{D}_{22},$$
$$\hat{a}_5 = \hat{D}_{23},\ \hat{a}_6 = \hat{D}_{33},$$

which obeys to relation ($\hat{D}_{ii} = 0$, or $\hat{a}_1 + \hat{a}_4 + \hat{a}_6 = 0$).

The nonequilibrium distribution function $f(a,t)$ defined as

$$f(a,t) = \langle \delta(\hat{a}-a) \rangle = Tr\left[\delta(\hat{a}-a)\rho(t)\right] \tag{2}$$

where a is the vector with components

$$a_1 = D_{11},\ a_2 = D_{12},\ a_3 = D_{13},\ a_4 = D_{22},\ a_5 = D_{23},\ a_6 = D_{33}\ \ (D_{ii} = 0).$$

Here a_i are the given numerical values, but $\hat{a}_i$ are functions of phase variables, $\rho(t)$ is the nonequilibrium distribution function which obeys to the Liouville equation. The multidimensional δ-function is given by

$$\hat{n}(a) = \delta(\hat{a}-a) = \Pi\delta(\hat{a}_i - a_i). \tag{3}$$

We note this for description orientation order may be introduced 5-vector without constraint the due $D_{ii} = 0$, for example, if we use the Doi-Edvards [1] microscopic stress tensor as the tensor parameter order.

Our goal is derivation the evolution equitation for the function $f(a,t)$ on the bases of statistical-mechanical theory by Zubarev method. We start with Liouville equation for nonequilibrium phase distribution function with an infinitesimal source selecting the solution of required form,

$$\left(\frac{\partial}{\partial t}+iL\right)\rho(t)=-\varepsilon\left(\rho(t)-\rho_q(t)\right),\ \varepsilon\to+0 \tag{4}$$

where L is the Liouville operator, $\rho_q(t)$ is quasiequilibrium distribution function or the relevant distribution function. The function $\rho_q(t)$ is determined from the principle of the Shannon information entropy maximum and therefore has the form

$$\rho_q(t)=\exp\left(-\Phi(t)-\beta\hat{H}-\int daF(a,t)\hat{n}(a)\right). \tag{5}$$

Here $\beta=(k_BT)^{-1}$, $\hat{H}$ is Hamilton function for our system. The Massieu-Planck function $\Phi(t)$ is introduced for normalization function $\rho_q(t)$ to unit. The function $F(a,t)$ is the thermodynamical parameter conjugate to $\langle\hat{n}\rangle$, $da=da_1da_2...da_6$.

Taking into account the presence δ-function in the quantity $\hat{n}$ (see (3)), we can represent $\rho_q(t)$ in other forms

$$\rho_q(t)=\exp\left(-\Phi(t)-\beta H-F(\hat{a},t)\right), \tag{6}$$

$$\rho_q(t)=\int\exp\left(-\Phi(t)-\beta H-F(a,t)\right)\hat{n}(a)da. \tag{7}$$

For finding the $F(\hat{a},t)$ we will use the important self-consistency condition,

$$\langle\hat{n}\rangle_q=\langle\hat{n}\rangle, \tag{8}$$

where we keep in mind that

$$\langle\hat{n}\rangle_q=Tr\left(\rho_q\hat{n}(a)\right)=n(a,t),\ \langle\hat{n}\rangle=Tr\left(\rho,\hat{n}(a)\right). \tag{9}$$

In the classical case the symbol Tr denote the integration over are the phase variables.

After the calculation $n(a,t)$ with help (9) and (6) we obtain

$$n(a,t)=Tr\left\{\exp\left(-\Phi-\beta\hat{H}-F(a,t)\right)\hat{n}(a)\right\}, \tag{10}$$

or, taking into account the presence δ-function in $\hat{n}(a)$,

$$n(a,t)=\exp\left(-\Phi+\Phi_0-F(a,t)\right)Tr\left[\exp\left(-\Phi_0-\beta H\right)\hat{n}(a)\right], \tag{11}$$

where Φ_0 is the normalized quantity for canonical Gibbs distribution

$$\rho_0=\exp\left(-\Phi_0-\beta\hat{H}\right). \tag{12}$$

Introducing the quantity W as

$$W(a)=Tr\left(\rho_0\hat{n}(a)\right), \tag{13}$$

one rewrite (11) in the form

$$n(a,t)=\exp\left(+\Phi_0-\Phi(t)-F(\hat{a},t)\right)W(a). \tag{14}$$

Then we eliminate the Φ and F from the expresions for ρ_q. In the first place from (14) we find $\exp\left(-\Phi-F(a,t)\right)=\exp(\Phi_0)n(a,t)W^{-1}(a)$, secondly the equation (7) we represent in final form

$$\rho_q=\int\rho_0 f(a,t)\hat{n}(a)W^{-1}(a)\,da, \tag{15}$$

where $f(a,t)=n(a,t)=Tr(\rho\hat{n})$.

In obtaining the evolution equation for $f(a,t)$ we must use the Liouville equation. Following to Zubarev, we apply the Liouville equation in the form (4). For the function $\Delta\rho=\rho-\rho_q$ equation (4) may be rewritten as follow

$$\left(\frac{\partial}{\partial t}+iL+\varepsilon\right)\Delta\rho=-\left(\frac{\partial}{\partial t}+iL\right)\rho_q. \tag{16}$$

Differentiating the ρ_q (15) with respect to the time we obtain

$$\frac{\partial\rho_q}{\partial t}=-\int\rho_0\frac{\hat{n}(a)}{W(a)}Tr(\hat{n}iL\Delta\rho)\,da-\int\int\rho_0\frac{\hat{n}(a)}{W(a)}Tr\left(\hat{n}iL\rho_q\right)da. \tag{17}$$

The right-hand side of this relation may be rewritten as result of the action the projection operator P_q defined as

$$P_q\hat{A}=\int\rho_0 w^{-1}(a)Tr(\hat{A}\hat{n})\hat{n}(a)\,da. \tag{18}$$

Then the derivative $\frac{\partial\rho_q}{\partial t}$ is defined by

$$\frac{\partial\rho_q}{\partial t}=-P_q(iL\rho(t)-P_q(iL\rho_q)). \tag{19}$$

It is very important that the projection operator arises naturally as the result of the evaluation $\frac{\partial\rho_q}{\partial t}$ in contrast to many works where the such operators introduce by «hand» without the clearing up of the necessity and the sense of their introducing. Then we calculate the quantity $iL\rho_q$ with the next result

$$iL\rho_q=\int da\rho_0\hat{n}iL\hat{a}_j\frac{\partial}{\partial a_j}\left(\frac{n(a,t)}{w(a)}\right). \tag{20}$$

After above simple algebra the Liouville equation (16) is transformed into

$$\left(\frac{\partial}{\partial t}+(1-\rho_q)iL+\varepsilon\right)\Delta\rho=-\int da\rho_0 x_j(a)\frac{\partial}{\partial a_j}\left(\frac{f(a,t)}{w(r)}\right), \tag{21}$$

where

$$x_j(a)=(1-P_q)\hat{n}(a)iLa_j, \tag{22}$$

is the generalized force corresponding to the random force of the Mori theory.

By integrating the equation (21) we obtain the formal solution of the Liouville equation in the next form:

$$\rho(t) = \rho_q(t) - \int da \int dt' \exp[(t'-t)((1-P_q)iL+\varepsilon)]x_j(a)\frac{\partial}{\partial a_j}\left(\frac{f(a,t)}{w(a)}\right). \tag{23}$$

The function $\rho(t)$ depends from time via the function $f(a,t)$ in the past times. To establish the evolution equation for $f(a,t) = n(a,t)$ it is necessary to average the quantity $\dot{\hat{n}}(a) = iL\hat{n}(a)$ with help of the nonequilibrium distribution function $\rho(t)$ from equation (23).

To this end we write the mean value as

$$\frac{\partial n(a,t)}{\partial t} = <\dot{\hat{n}}(a)> = <\dot{\hat{n}}>_q + <(1-P_q)iL\hat{n})>, \tag{24}$$

or

$$\frac{\partial n(a,t)}{\partial t} = Tr(\rho_q \dot{\hat{n}}(a)) + Tr\rho((1-P_q)iL\hat{n}). \tag{25}$$

The quality $<\hat{B}> = <(1-P_q)iL\hat{n}>$ is flux for quantity $n(a,t)$. At the evaluation this flux we use expression for $iL\hat{n}(a)$ and the solution the Liouville equation (23). In result we obtain mean flux as

$$<B> = \sum_{i,j}\frac{\partial}{\partial a_j}\int da' \int_{-\infty}^{t} dt' \exp(\varepsilon(t'-t))K_{ji}(a,a',t-t')\frac{\partial}{\partial a_i'}\frac{f(a',t')}{w(a')}, \tag{26}$$

because $<B>_q = 0$.

In equation (26) the integral kernels K_{ji} defined as

$$K_{ij}(a,a',t-t') = Tr\left\{x_j(a)\exp\left[(t-t')(1-P_q)iL\right]x_i(a)\right\}. \tag{27}$$

The operator $(1-P_q)iL$ in (27) is so-called reduced evolution operator.

After evaluation the quantity $<\dot{\hat{n}}>_q = Tr(\rho_q iL\hat{n}(a))$ we find

$$<\dot{\hat{n}}>_q = -\frac{\partial}{\partial a_j}\upsilon_j(a)f(a,t), \tag{28}$$

where $\upsilon_j(a)$ are represent the average fluxes in the state with fixed values of relevant variables. They forms the drift term. Using expression for $<\dot{\hat{n}}>_q$ (28) and for $<B>$ (26) we obtain the generalized Fokker-Planck equation

$$\begin{gathered}\frac{\partial f(a,t)}{\partial t} + \sum_j \frac{\partial \upsilon_j(a)}{\partial a_j} f(a,t) = \\ = \sum_{i,j}\frac{\partial}{\partial a_j}\int da' \int_{-\infty}^{t} \exp(\varepsilon(t-t'))K_{ji}(a,a',t-t')\frac{\partial}{\partial a_i'}\frac{f(a',t')}{w(a')}dt'.\end{gathered} \tag{29}$$

The equation (28) is the integro-differential equation, which is nonlocal in space and non-Markovian in time.

If the space and the time variations of the function $f(a,t)$ are slow on the scales of microscopic processes the right-side term in equation (28) may be represented in the Markovian approximation and then we obtain the traditional form of the Fokker-Planck equation that is

$$\frac{\partial f(a,t)}{\partial t}+\sum_j \frac{\partial}{\partial a_j}\upsilon(a)f(a,t)=\sum_{j,i}\frac{\partial}{\partial a_j}D_{ji}(a)W(a)\frac{\partial}{\partial a_i}\left(\frac{f(a,t)}{W(a)}\right), \tag{29}$$

where

$$D_{ji}(a)=W^{-1}(a)\int da' \int_{-\infty}^{t}\exp\left[\varepsilon(t'-t)K_{ji}(a,a')(t-t')\right]dt' \tag{30}$$

is the kinetic coefficients.

The expression $W(a)\frac{\partial}{\partial a_i}\left(\frac{f(a,t)}{W(a)}\right)$ may be represent by next manner $W(a)\frac{\partial}{\partial a_i}\left(\frac{f(a,t)}{W(a)}\right)=\frac{f(a,t)}{\partial a_i}-f(a,t)-f(a,t)\frac{\partial \ln W(a)}{\partial a_i}$.

If $W(a)=\exp[ba_i\hat{a}_i]$ (b is some constant) the last member have the from $-f(a,t)\frac{\partial \ln W(a)}{\partial a_i}=-f(a,t)b\hat{a}_i$.

It is important that the kinetic coefficients in (31) and kernels in (27) are defined in the framework of the statistical theory of nonequilibrium processes.

In conclusion we note that description Fokker-Plank equation from Liouville equatrion is not meet with to Ito-Stratanovich problem.

REFERENCES

1. M. Doi and S.F. Edwords. Theory of Polymer dynamics. Clarendon Press-Oxford, 1986.

2. M. Warner and E.M. Terentjev. Liquid Crystal Elastomers. Clarendon Press-Oxford, 2006.

3. D. Zubarev, V. Morozov, G. Röpke. Statistical mechanics of Nonequlibrium Processes, Vol. 2, 1997. Akad. Verlag.

4. R. Zwanzig. Nonequlibrium statistical mechanics. Oxford-Univer. Press, 2001.

5. V.B. Nemtsov. Nonequlibrium statistical mechanics of system with orientational order. Minsk, Tekhnologia, 1997 (in Russian).