Extension of the variational formulation of the Onsager-Machlup theory of fluctuations

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We considered spontaneous fluctuations of thermodynamic variables in an adiabatically insulated system where nonlinear irreversible processes can take place. We introduced an extended definition of the Onsager-Machlup functional. In terms of this functional, a conditional probability density function was constructed, which describes, generally, non-Gaussian fluctuations. A sufficiently common form of phenomenological laws governing irreversible processes was found. In the case of linear laws, the proposed extention leads to the Onsager-Machlup results.

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I. INTRODUCTION

The formalism of the linear irreversible thermodynamics, which describes irreversible processes and related spontaneous fluctuations of the thermodynamic variables characterizing the deviations of a fluctuating system from the equilibrium state, has been developed in the classical Onsager works [1,2]. The central part of this formalism is the reciprocity relations, which express the symmetry of the matrix of the coefficients of the phenomenological equations for the thermodynamic variables. The reciprocity relations, which are proved on the basis of the microscopic reversibility assumption, are limitations for the linear phenomenological equations.

Using the variational approach, Onsager and Machlup have established a more profound connection between the theory of irreversible processes and fluctuations of the thermodynamic variables [3,4]. For this purpose, on the basis of the stochastic model, the so-called Onsager-Machlup (OM) function and the corresponding functional have been introduced. The minimum value of this functional determines the transition probability of the system from one state to another. As a result, the conditional probability density function of fluctuations of the thermodynamic variables has been obtained.

However, all these results have been obtained in the cases of linear irreversible processes and Gaussian fluctuations of the thermodynamic variables. In this work, we propose an extension of the variational aspects of the Onsager-Machlup theory of fluctuations. We consider nonlinear irreversible processes and related non-Gaussian fluctuations. Using the definition of dissipative function in the case where the phenomenological equations are generally nonlinear [5], we introduce an extended OM function and the corresponding functional. We obtain the extended conditional probability density function of fluctuations of the thermodynamic variables and show that, in the linear regime, this function is reduced to that obtained earlier by Onsager and Machlup.

In this work, we consider an extension only of the variational formulation of the OM theory. The other aspects, for example, the consistency of this extended version with the description of fluctuations in terms of the Fokker-Planck equation or stochastic differential equations [6], require special investigations.

Following the work of [4], we represent the entropy as a function of the thermodynamic variables and their time derivatives. As a result, we take the inertial effects into account. We consider the thermodynamic variables that are even functions of the molecular variables (in the absence of a magnetic field). Based on the microscopic reversibility assumption, we establish the limitations for nonlinear phenomenological equations. We show that, in the specific case of linear irreversible processes, these limitations are reduced to the Onsager reciprocity relations.

II. LINEAR THEORY

Let us consider an adiabatically insulated system, displaced from the equilibrium state, that returns to the state of thermodynamic equilibrium. Following Onsager and Machlup, we introduce N variables φ_i, that express the deviation of the system from the equilibrium state and vanish in this state. We consider that the entropy of the system S depends on the variables φ_i and their time derivatives $\dot{\varphi}_i$. In the equilibrium state at $\varphi_i = 0$ and $\dot{\varphi}_i = 0$, the entropy attains the maximum value S_0. Let us introduce an entropy change $z = S_0 - S$. Then, we can write

$$z = z(\varphi_1, \ldots, \varphi_N; \dot{\varphi}_1, \ldots, \dot{\varphi}_N) \geq 0;$$

$z = 0$ in the equilibrium state.

In the linear Onsager-Machlup theory, the entropy change is a sum of the positive definite quadratic forms of the variables φ_i and $\dot{\varphi}_i$,

$$z = \frac{1}{2}\sum_{i,j} s_{ij}\varphi_i\varphi_j + \frac{1}{2}\sum_{i,j} m_{ij}\dot{\varphi}_i\dot{\varphi}_j. \tag{1}$$

Thermodynamic forces are linear functions of φ_i and $\ddot{\varphi}_i$,

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$$\chi_i = \frac{\partial z}{\partial \varphi_i} + \frac{d}{dt}\frac{\partial z}{\partial \dot{\varphi}_i} = \sum_j s_{ij}\varphi_j + \sum_j m_{ij}\ddot{\varphi}_j, \quad i = 1, \ldots, N. \quad (2)$$

In this case, the time derivative of entropy change can be represented by the bilinear form

$$\dot{z} = \sum_i \chi_i \dot{\varphi}_i \leq 0. \quad (3)$$

Irreversible processes in the neighborhood of the equilibrium state are described by the linear phenomenological equations

$$-\dot{\varphi}_i = \sum_j L_{ij}\chi_j \quad \text{or} \quad -\sum_j R_{ij}\dot{\varphi}_j = \chi_i, \quad i = 1, \ldots, N, \quad (4)$$

where the phenomenological coefficients form reciprocal matrices and obey the Onsager reciprocity relations

$$L_{ij} = L_{ji} \quad \text{or} \quad R_{ij} = R_{ji}. \quad (5)$$

The evidence of reciprocity relations is based on the Boltzmann-Planck postulate, the microscopic reversibility assumption, and the hypothesis that the fluctuating variables $\varphi_i(t)$ obey, on the average, the same phenomenological equations (4).

According to the Boltzmann-Planck postulate, the function z determines the probability density $p(\varphi_1, \ldots, \varphi_N; \dot{\varphi}_1, \ldots, \dot{\varphi}_N)$ of that, at some instant, the variables take the values from φ_i to $\varphi_i + d\varphi_i$ and from $\dot{\varphi}_i$ to $\dot{\varphi}_i + d\dot{\varphi}_i$, namely,

$$p(\varphi_1, \ldots, \varphi_N, \dot{\varphi}_1, \ldots, \dot{\varphi}_N) \propto \exp\left(-\frac{z}{k_B}\right), \quad (6)$$

where k_B is the Boltzmann constant.

Based on this linear formalism, Onsager and Machlup have constructed the conditional probability density function $p(\Gamma^{(1)}, t_1; \Gamma^{(2)}, t_2)$ of the transition of the system from the state $\Gamma^{(1)} = (\varphi_1^{(1)}, \ldots, \varphi_N^{(1)}; \dot{\varphi}_1^{(1)}, \ldots, \dot{\varphi}_N^{(1)})$ at the instant t_1 to the state $\Gamma^{(2)} = (\varphi_1^{(2)}, \ldots, \varphi_N^{(2)}; \dot{\varphi}_1^{(2)}, \ldots, \dot{\varphi}_N^{(2)})$ at the instant t_2. For this purpose, on the basis of the dissipative function

$$\psi = \sum_{i,j} R_{ij}\dot{\varphi}_i\dot{\varphi}_j, \quad (7)$$

the OM function

$$\mathcal{L}(\dot{\varphi}_1, \ldots, \dot{\varphi}_N; \chi_1, \ldots, \chi_N) = \sum_{i,j} R_{ij}\dot{\varphi}_i\dot{\varphi}_j + \sum_{i,j} L_{ij}\chi_i\chi_j + 2\sum_i \chi_i\dot{\varphi}_i \quad (8)$$

and the corresponding functional

$$\phi[\varphi_1, \ldots, \varphi_N; \dot{\varphi}_1, \ldots, \dot{\varphi}_N] = \int_{t_1}^{t_2}\left(\sum_{i,j} R_{ij}\dot{\varphi}_i\dot{\varphi}_j + \sum_{i,j} L_{ij}\chi_i\chi_j + 2\sum_i \chi_i\dot{\varphi}_i\right) dt \quad (9)$$

have been constructed.

As Onsager and Machlup have shown, the conditional probability density function $p(\Gamma^{(1)}, t_1; \Gamma^{(2)}, t_2)$ is determined by the minimum value of functional (9) $\phi_{\min}$ and has the form

$$p(\Gamma^{(1)}, t_1; \Gamma^{(2)}, t_2) \propto \exp\left(-\frac{1}{4}\frac{\phi_{\min}}{k_B}\right). \quad (10)$$

The minimum value of (9) is found from the equation

$$\delta\phi = \int_{t_1}^{t_2} \delta\mathcal{L} dt = 0$$

under the assumption that the variations of the variables $\varphi_i, \dot{\varphi}_i$ and their time derivatives are equal to zero in the initial and final states $\Gamma^{(1)}$ and $\Gamma^{(2)}$, which are equivalent to the set of the generalized Euler-Lagrange equations

$$\frac{d^2}{dt^2}\frac{\partial \mathcal{L}}{\partial \ddot{\varphi}_i} - \frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \dot{\varphi}_i} + \frac{\partial \mathcal{L}}{\partial \varphi_i} = 0, \qquad i = 1, \ldots, N. \quad (11)$$

One can show [3,4] that, in a specific case, when the system passes from the equilibrium state $\Gamma^{(1)} = 0$ at $t_1 = -\infty$ to some state $\Gamma^{(2)} = \Gamma$ at $t_2 = t$, the value $\phi_{\min}$ is related to the entropy change in the following manner:

$$\frac{1}{4}\phi_{\min} = \frac{1}{4}\left(\int_{-\infty}^{t} \mathcal{L} dt\right)_{\min} = z;$$

therefore, (10) is reduced to (6). This transition is described, on the average, by

$$\dot{\varphi}_i = \sum_j L_{ij}\chi_j \quad \text{or} \quad \sum_j R_{ij}\dot{\varphi}_j = \chi_i, \qquad i = 1, \ldots, N,$$

which are obtained from (4) by changing the sign of t. We extend these results for the system in which, in a general case, nonlinear irreversible processes and a nonlinear connection between the thermodynamic forces and the state variables take place.

III. EXTENSION OF THE ONSAGER-MACHLUP FUNCTION

Let us consider a general case in which the entropy change has the form

$$z = z_0(\varphi_1, \ldots, \varphi_N) + \frac{1}{2}\sum_{i,j} m_{ij}\dot{\varphi}_i\dot{\varphi}_j, \quad (12)$$

where $z_0(\varphi_1, \ldots, \varphi_N) \geq 0$; $z_0(\varphi_1, \ldots, \varphi_N) = 0$ only at $\varphi_1 = \cdots = \varphi_N = 0$. The second term on the right-hand side of (12) is a positive definite quadratic form of $\dot{\varphi}_i$. The thermodynamic forces are determined similarly to (2)

$$\chi_i = \frac{\partial z}{\partial \varphi_i} + \frac{d}{dt}\frac{\partial z}{\partial \dot{\varphi}_i} = \frac{\partial z_0}{\partial \varphi_i} + \sum_j m_{ij}\ddot{\varphi}_j, \qquad i = 1, \ldots, N. \quad (13)$$

The phenomenological equations describing irreversible processes have the form

$$-\dot{\varphi}_i = f_i(\bar{\chi}) \quad \text{or} \quad -g_i(\dot{\bar{\varphi}}) = \chi_i, \qquad i = 1, \ldots, N, \quad (14)$$

where $\bar{\varphi} = (\varphi_1, \ldots, \varphi_N)$; $\dot{\bar{\varphi}} = (\dot{\varphi}_1, \ldots, \dot{\varphi}_N)$; $\bar{\chi} = (\chi_1, \ldots, \chi_N)$; $\bar{f} = (f_1, \ldots, f_N)$ and $\bar{g} = (g_1, \ldots, g_N)$ are reciprocal vector functions. We assume that these functions are odd functions of their variables in the aggregate.

Let us introduce a dissipative function [5]

$$\psi(\dot{\bar{\varphi}}) = \sum_i \dot{\varphi}_i g_i(\dot{\bar{\varphi}}), \quad (15)$$

which coincides with (7) in the linear case. To determine the OM function in the general case, let us consider first the linear one-dimensional case. Then, $f(\chi) = L\chi$, $g(\dot{\varphi}) = R\dot{\varphi}$, $\psi(\dot{\varphi}) = R\dot{\varphi}^2$, and

$$\mathcal{L} = R\dot{\varphi}^2 + L\chi^2 + 2\chi\dot{\varphi} = \psi - \eta,$$

where $\eta = -L\chi^2 - 2\chi\dot{\varphi}$. The function η, as a function of $\dot{\varphi}$, coincides with the equation of a tangent to the graph of the function $\psi = R\dot{\varphi}^2$ at the point $\dot{\varphi} = -L\chi$. Therefore, we define an extended OM function also as a difference between the dissipative function $\psi = \dot{\varphi}g(\dot{\varphi})$ and the linear function η of $\dot{\varphi}$, which is an equation of a tangent to the graph of the function ψ at the point $\dot{\varphi} = -f(\chi)$:

$$\begin{aligned}\mathcal{L}(\dot{\varphi}, \chi) &= \psi - \eta \\ &= \psi - \psi\Big|_{\dot{\varphi}=-f(\chi)} - [\dot{\varphi} + f(\chi)]\frac{\partial \psi}{\partial \dot{\varphi}}\Big|_{\dot{\varphi}=-f(\chi)} \\ &= \dot{\varphi}g(\dot{\varphi}) + \lambda(\chi)f(\chi) + [\lambda(\chi) + \chi]\dot{\varphi},\end{aligned}$$

where

$$\lambda(\chi) = f(\chi)\,\frac{\partial g}{\partial \dot{\varphi}}\Big|_{\dot{\varphi}=-f(\chi)}.$$

The similar definition in the multidimensional case leads to the extended OM function in the form

$$\mathcal{L}(\dot{\bar{\varphi}}, \bar{\chi}) = \psi - \eta = \sum_i \Big\{ \dot{\varphi}_i g_i(\dot{\bar{\varphi}}) + \lambda_i(\bar{\chi}) f_i(\bar{\chi}) + [\lambda_i(\bar{\chi}) + \chi_i]\dot{\varphi}_i \Big\}, \quad (16)$$

where

$$\lambda_i(\bar{\chi}) = \sum_j f_j(\bar{\chi})\,\frac{\partial g_j}{\partial \dot{\varphi}_i}\Big|_{\dot{\bar{\varphi}}=-\bar{f}(\bar{\chi})}, \quad i = 1, \ldots, N. \quad (17)$$

In the multidimensional case, $\eta = \eta(\dot{\bar{\varphi}})$ is an equation of the tangent plane to the graph of the dissipative function (15) at the point $\dot{\bar{\varphi}} = -\bar{f}(\bar{\chi})$. In the specific case, when the phenomenological equations are linear, the well-known definition of the OM function (8) follows from (16) and (17), in which

$$\lambda_i(\bar{\chi}) = \chi_i, \qquad i = 1, \ldots, N. \quad (18)$$

It immediately follows from the definition of the extended Onsager-Machlup function that the solutions of phenomenological equations (14) make this function vanish identically. It follows from (17) that, at any $k = 1, \ldots, N$,

$$\begin{aligned}\sum_i \lambda_i(\bar{\chi})\frac{\partial f_i(\bar{\chi})}{\partial \chi_k} &= \sum_{i,j}\left[f_j(\bar{\chi})\,\frac{\partial g_j}{\partial \dot{\varphi}_i}\Big|_{\dot{\bar{\varphi}}=-\bar{f}(\bar{\chi})}\,\frac{\partial f_i(\bar{\chi})}{\partial \chi_k}\right] \\ &= \sum_j \left\{ f_j(\bar{\chi}) \sum_i \left[\frac{\partial g_j}{\partial \dot{\varphi}_i}\Big|_{\dot{\bar{\varphi}}=-\bar{f}(\bar{\chi})}\,\frac{\partial f_i(\bar{\chi})}{\partial \chi_k}\right]\right\} \\ &= \sum_j f_j(\bar{\chi})\delta_{jk} = f_k(\bar{\chi}), \end{aligned} \quad (19)$$

as $\bar{f}$ and $\bar{g}$ are reciprocal vector functions (δ_{jk} is the Kronecker delta). One can show that, in the nondegenerated case, (17) follows from equality (19); i.e., these equalities are characteristic for defining the functions $\lambda_i(\bar{\chi})$, if the Jacobian $\left(\frac{\partial f_i}{\partial \chi_k}\right)$ is not equal to zero. Using the extended OM function, let us consider a conditional probability density function.

IV. CONDITIONAL PROBABILITY DENSITY FUNCTION

Let us define a conditional probability density function similarly to the linear case. Let us introduce a functional

$$\phi[\varphi_1, \ldots, \varphi_N; \dot{\varphi}_1, \ldots, \dot{\varphi}_N] = \int_{t_1}^{t_2} \mathcal{L}dt, \quad (20)$$

where $\mathcal{L}$ is an extended OM function (16). We consider that, in the nonlinear case, the probability density function has the form (6) and the conditional probability density function $p(\Gamma^{(1)}, t_1; \Gamma^{(2)}, t_2)$ is also determined by the minimum value $\phi_{\min}$ of functional (20):

$$p(\Gamma^{(1)}, t_1; \Gamma^{(2)}, t_2) \propto \exp\left(-\frac{F(\phi_{\min})}{k_B}\right), \quad (21)$$

where $F = F(\phi_{\min})$ is an increasing function of $\phi_{\min}$. In the linear case, according to (10), $F(\phi_{\min}) = \frac{1}{4}\phi_{\min}$. Finding the minimum value $\phi_{\min}$ is reduced to solving the set of the generalized Euler-Lagrange equations (11).

In the specific case, when an adiabatically insulated system passes from the equilibrium state $\Gamma^{(1)} = 0$ at $t_1 = -\infty$ to some state $\Gamma^{(2)} = \Gamma$ at $t_2 = t$, the function $p(\Gamma^{(1)}, t_1; \Gamma^{(2)}, t_2)$ must be reduced to the density function $p(\Gamma(t))$ of the form (6). It follows from this that the solutions of the equations, which are obtained from (14) by changing t for $-t$

$$\dot{\varphi}_i = f_i(\bar{\chi}), \qquad g_i(\dot{\bar{\varphi}}) = \chi_i, \qquad i = 1, \ldots, N, \quad (22)$$

must satisfy the set of the generalized Euler-Lagrange equations (11).

It follows directly from the definition of the extended OM function and relation (19) that the set of the Euler-Lagrange equations (11) can be written in the form

$$\frac{d^2}{dt^2}\sum_{j,k}\left[[\dot{\varphi}_j + f_j(\bar{\chi})]\frac{\partial[\lambda_j(\bar{\chi})+\chi_j]}{\partial\chi_k}\frac{\partial\chi_k}{\partial\ddot{\varphi}_i}\right] - \frac{d}{dt}\left(\lambda_i(\bar{\chi}) + \chi_i + g_i(\dot{\bar{\varphi}}) + \sum_j \dot{\varphi}_j\frac{\partial g_j}{\partial\dot{\varphi}_i}\right) + \sum_{j,k}\left[[\dot{\varphi}_j + f_j(\bar{\chi})]\frac{\partial[\lambda_j(\bar{\chi})+\chi_j]}{\partial\chi_k}\frac{\partial\chi_k}{\partial\varphi_i}\right] = 0, \quad i = 1,\ldots,N. \tag{23}$$

Let us determine when the solutions of Eqs. (22) are solutions of the set (23). For this purpose, we substitute $\dot{\varphi}_i = f_i(\bar{\chi})$ for Eqs. (23). As a result, we obtain the set of equations

$$\frac{d^2}{dt^2}\sum_{j,k}\left[f_j(\bar{\chi})\frac{\partial[\lambda_j(\bar{\chi})+\chi_j]}{\partial\chi_k}\frac{\partial\chi_k}{\partial\ddot{\varphi}_i}\right] - \frac{d}{dt}[\lambda_i(\bar{\chi}) + \chi_i] + \sum_{j,k}\left[f_j(\bar{\chi})\frac{\partial[\lambda_j(\bar{\chi})+\chi_j]}{\partial\chi_k}\frac{\partial\chi_k}{\partial\varphi_i}\right] = 0, \quad i = 1,\ldots,N. \tag{24}$$

Let us show that the relations

$$\frac{d^2}{dt^2}\sum_j f_j(\bar{\chi})\frac{\partial\chi_j}{\partial\ddot{\varphi}_i} - \frac{d\chi_i}{dt} + \sum_j f_j(\bar{\chi})\frac{\partial\chi_j}{\partial\varphi_i} = 0, \quad i = 1,\ldots,N \tag{25}$$

take place under the assumption of the validity of (22). Using (13) and (22), we have

$$\frac{d^2}{dt^2}\sum_j f_j(\bar{\chi})\frac{\partial\chi_j}{\partial\ddot{\varphi}_i} = \sum_j\left[\frac{\partial\chi_j}{\partial\ddot{\varphi}_i}\frac{d^2 f_j(\bar{\chi})}{dt^2} + 2\frac{df_j(\bar{\chi})}{dt}\frac{d}{dt}\frac{\partial\chi_j}{\partial\ddot{\varphi}_i} + f_j(\bar{\chi})\frac{d^2}{dt^2}\frac{\partial\chi_j}{\partial\ddot{\varphi}_i}\right] = \sum_j m_{ij}\frac{d^2 f_j(\bar{\chi})}{dt^2}, \tag{26}$$

$$\frac{d\chi_i}{dt} = \sum_j\left[\frac{\partial\chi_i}{\partial\ddot{\varphi}_j}\frac{d\ddot{\varphi}_i}{dt} + \frac{\partial\chi_i}{\partial\varphi_j}\frac{d\varphi_i}{dt}\right] = \sum_j\left[m_{ij}\frac{d^2 f_j(\bar{\chi})}{dt^2} + f_j(\bar{\chi})\frac{\partial\chi_i}{\partial\varphi_j}\right]. \tag{27}$$

As $m_{ij} = m_{ji}$ and $\frac{\partial\chi_i}{\partial\varphi_j} = \frac{\partial^2 z}{\partial\varphi_j\partial\varphi_i} = \frac{\partial\chi_j}{\partial\varphi_i}$, $i,j = 1,\ldots,N$, then, (25) follows from (26) and (27).

It follows from (24) and (25) that the functions $\lambda_j(\bar{\chi})$ satisfy the equations

$$\frac{d^2}{dt^2}\sum_{j,k}\left[f_j(\bar{\chi})\frac{\partial\lambda_j(\bar{\chi})}{\partial\chi_k}\frac{\partial\chi_k}{\partial\ddot{\varphi}_i}\right] - \frac{d\lambda_i(\bar{\chi})}{dt} + \sum_{j,k}\left[f_j(\bar{\chi})\frac{\partial\lambda_j(\bar{\chi})}{\partial\chi_k}\frac{\partial\chi_k}{\partial\varphi_i}\right] = 0, \quad i = 1,\ldots,N, \tag{28}$$

when the solutions of Eqs. (22) are solutions of (23). It follows from (18) and (25) that Eqs. (28) hold when the phenomenological laws are linear.

Set (28) is only a necessary condition for the existence of the transition from the conditional probability density function $p(\Gamma^{(1)}, t_1; \Gamma^{(2)}, t_2)$ to the probability density function $p(\Gamma(t))$. It follows from (6) and (21) that the equality

$$F(\phi_{\min}) = z \tag{29}$$

must hold under the assumption of the validity of (22).

We need to know the specific form of the function $F = F(\phi_{\min})$ for further calculations. In this work, we consider the case of the linear function

$$F(\phi_{\min}) = \frac{1}{\beta}\phi_{\min}, \tag{30}$$

where β is some coefficient. It follows from (21) that $\beta > 0$. In the linear case, according to (10), $\beta = 4$.

V. DEFINING THE FORM OF THE PHENOMENOLOGICAL EQUATIONS

Under the assumption of the validity of Eqs. (22), it follows from (29) and (30) that

$$\frac{1}{\beta}\phi_{\min} = z \tag{31}$$

or, if the definition of $\phi_{\min}$ is taken into consideration,

$$\frac{1}{\beta}\int_{-\infty}^{t}\mathcal{L}dt = \int_{-\infty}^{t}\dot{z}dt. \tag{32}$$

Differentiating both sides of (32) and using (12), (13), (16), and (22), we obtain

$$\beta = \left.\frac{\mathcal{L}}{\dot{z}}\right|_{\dot{\bar{\varphi}}=\bar{f}(\bar{\chi})} = \frac{2\sum_i[\lambda_i(\bar{\chi}) + \chi_i]f_i(\bar{\chi})}{\sum_i \chi_i f_i(\bar{\chi})}. \tag{33}$$

For relations (28) and (33) to hold we need to make some assumptions of the forms of the functions $\lambda_i(\bar{\chi})$, $i = 1,\ldots,N$. Our analysis shows that the simpliest and sufficiently general assumption is that these functions satisfy the relations generalizing (18):

$$\lambda_i(\bar{\chi}) = \alpha\chi_i, \qquad i = 1,\ldots,N, \tag{34}$$

where $\alpha \neq 0$ is a constant that does not depend on i. The validity of (28) follows directly from (34) and (25). We obtain from (34) and (33) that

$$\beta = 2(\alpha + 1). \tag{35}$$

In the case of the linear phenomenological equations, $\alpha = 1$ and hence $\beta = 4$, which coincides with the Onsager-Machlup result.

Substituting (34) in (16), we obtain the extended OM function in the form

$$\mathcal{L}(\dot{\bar{\varphi}}, \bar{\chi}) = \sum_i[\dot{\varphi}_i g_i(\dot{\bar{\varphi}}) + \alpha\chi_i f_i(\bar{\chi}) + (\alpha+1)\chi_i\dot{\varphi}_i]. \tag{36}$$

By a similar substitution in (19), we obtain the following equations for $f_i(\bar{\chi})$:

$$\sum_i \chi_i \frac{\partial f_i(\bar{\chi})}{\partial \chi_k} = \frac{1}{\alpha} f_k(\bar{\chi}), \qquad k = 1, \dots, N. \tag{37}$$

It follows from the definition of dissipative function (15) and relations (17) and (34) that

$$\left.\frac{\partial \psi(\dot{\bar{\varphi}})}{\partial \dot{\varphi}_i}\right|_{\dot{\bar{\varphi}}=\bar{f}(\bar{\chi})} = \left.\left[g_i(\dot{\bar{\varphi}}) + \sum_j \dot{\varphi}_j \frac{\partial g_j(\dot{\bar{\varphi}})}{\partial \dot{\varphi}_i} \right]\right|_{\dot{\bar{\varphi}}=\bar{f}(\bar{\chi})}$$
$$= \chi_i + \lambda_i(\bar{\chi}) = (\alpha + 1)\chi_i.$$

Then, using (36), we have

$$\mathcal{L}(\dot{\bar{\varphi}}, \bar{\chi})|_{\dot{\bar{\varphi}}=\bar{f}(\bar{\chi})} = 2(\alpha + 1) \sum_i \chi_i f_i(\bar{\chi})$$
$$= 2 \sum_i f_i(\bar{\chi}) \left.\frac{\partial \psi(\dot{\bar{\varphi}})}{\partial \dot{\varphi}_i}\right|_{\dot{\bar{\varphi}}=\bar{f}(\bar{\chi})}. \tag{38}$$

Equalities (34) and (38) allow us to write relation (33) in the form

$$\sum_i \dot{\varphi}_i \left.\frac{\partial \psi(\dot{\bar{\varphi}})}{\partial \dot{\varphi}_i}\right|_{\dot{\bar{\varphi}}=\bar{f}(\bar{\chi})} = \left.\frac{\beta}{2}\psi(\dot{\bar{\varphi}})\right|_{\dot{\bar{\varphi}}=\bar{f}(\bar{\chi})}. \tag{39}$$

Let us assume that the function $\psi(\dot{\bar{\varphi}})$ satisfies the equation

$$\sum_i \dot{\varphi}_i \frac{\partial \psi(\dot{\bar{\varphi}})}{\partial \dot{\varphi}_i} = \frac{\beta}{2}\psi(\dot{\bar{\varphi}}) \tag{40}$$

at all values of $\dot{\bar{\varphi}}$ and not only at $\dot{\bar{\varphi}} = \bar{f}(\bar{\chi})$, as in (39). Equation (40) is the Euler equation for the homogeneous function $\psi(\dot{\bar{\varphi}})$ of degree $\frac{\beta}{2}$. By virtue of (15), for the function $\psi(\dot{\bar{\varphi}})$ to be homogeneous, it is sufficient to require that $\beta > 2$ and all functions $g_i(\dot{\bar{\varphi}})$ are homogeneous functions of degree $\frac{(\beta-2)}{2}$. It follows from this that all functions $f_i(\bar{\chi})$ are homogeneous functions of degree $\frac{2}{(\beta-2)}$, i.e., they satisfy the Euler equation

$$\sum_i \chi_i \frac{\partial f_k(\bar{\chi})}{\partial \chi_i} = \frac{2}{\beta - 2} f_k(\bar{\chi}), \qquad k = 1, \dots, N. \tag{41}$$

The right-hand sides of Eqs. (41) and (37) are equal. We equate the left-hand sides and obtain

$$\sum_i \chi_i \left(\frac{\partial f_i(\bar{\chi})}{\partial \chi_k} - \frac{\partial f_k(\bar{\chi})}{\partial \chi_i} \right) = 0, \quad k = 1, \dots, N. \tag{42}$$

Thus the homogeneous functions $f_i(\bar{\chi})$ must satisfy relations (42).

Let us consider then a class of the homogeneous functions $f_i(\bar{\chi})$ satisfying the conditions that are stronger than (42):

$$\frac{\partial f_i(\bar{\chi})}{\partial \chi_k} = \frac{\partial f_k(\bar{\chi})}{\partial \chi_i}, \quad i, k = 1, \dots, N. \tag{43}$$

Conditions (43) are equivalent to the fact that there exists a potential of the thermodynamic forces $V = V(\bar{\chi})$ such as

$$f_i(\bar{\chi}) = \frac{\partial V(\bar{\chi})}{\partial \chi_i}, \qquad i = 1, \dots, N. \tag{44}$$

Let us consider the case, which is most important for practical applications, when all functions $f_i(\bar{\chi})$ are homogeneous polynomials of odd degree. In this case, there necessarily exists a potential $V(\bar{\chi})$ that is a homogeneous polynomial of even degree, accurate to a constant.

For example, at $N = 2$, the functions $f_i(\chi_1, \chi_2)$ are homogeneous polynomials of χ_1 and χ_2 of odd degree and

$$\frac{2}{\beta - 2} = 2n - 1 \ \text{ or } \ \beta = \frac{4n}{2n - 1}, \quad n = 1, 2, \dots \ . \tag{45}$$

Then $V(\chi_1, \chi_2)$ can be written in the form

$$V(\chi_1, \chi_2) = \frac{1}{2n} L_{11} \chi_1^{2n} + \sum_{i=1}^{2n-1} L_{i\,2n} \chi_1^{2n-i} \chi_2^i$$
$$+ \frac{1}{2n} L_{2n\,2n} \chi_2^{2n}, \tag{46}$$

where $L_{i\,2n}$ are constant coefficients. It follows from (44) that

$$f_1(\chi_1, \chi_2) = L_{11} \chi_1^{2n-1} + \sum_{i=1}^{2n-1} (2n - i) L_{i\,2n} \chi_1^{2n-i-1} \chi_2^i,$$
$$f_2(\chi_1, \chi_2) = \sum_{i=1}^{2n-1} (2n - i) L_{i\,2n} \chi_1^{2n-i} \chi_2^{i-1} + L_{2n\,2n} \chi_2^{2n-1}.$$

In particular, when $n = 1$,

$$V(\chi_1, \chi_2) = \frac{1}{2} L_{11} \chi_1^2 + L_{12} \chi_1 \chi_2 + \frac{1}{2} L_{22} \chi_2^2, \tag{47}$$

we have linear phenomenological equations, and

$$f_1(\chi_1, \chi_2) = L_{11} \chi_1 + L_{12} \chi_2,$$
$$f_2(\chi_1, \chi_2) = L_{12} \chi_1 + L_{22} \chi_2,$$

where the Onsager reciprocity relations have already been taken into account.

VI. CONCLUSION AND SUMMARY

We showed that the variational aspects of the Onsager-Machlup theory can be extended to systems in which non-Gaussian fluctuations take place and irreversible processes are described by nonlinear phenomenological equations. We used a geometric approach and constructed the extended OM function as a difference between the dissipative function and the function whose graph is a tangent to the graph of the dissipative function at the point $\dot{\bar{\varphi}} = -\bar{f}(\bar{\chi})$.

Using the extended OM function, we constructed the functional, the minimum value of which determines the probability of fluctuations of the thermodynamic variables in the neighborhood of the equilibrium state. The generalized Euler-Lagrange equations follow from the condition of the minimum of this functional. The solutions of these equations determine the conditional probability density function of fluctuations of the thermodynamic variables. As the conditional probability density function must conform to formula (6), then the solutions of the equations $\dot{\bar{\varphi}} = \bar{f}(\bar{\chi})$ must also be solutions of the generalized Euler-Lagrange equations. This condition leads to Eqs. (28) for the functions $\lambda_i = \lambda_i(\bar{\chi})$.

We considered the conditional probability density function, which depends on the parameter $\beta > 2$, and the functions $\lambda_i(\bar{\chi})$ (34), which depend on the parameter $\alpha > 0$, where β and α are connected by the relation $\beta = 2(\alpha + 1)$. In this case, the functions $f_i(\bar{\chi})$ are of a class of homogeneous functions of degree $\frac{2}{(\beta-2)}$ and obey relation (42). Then, we considered a more restricted class of the potential functions $f_i(\bar{\chi})$, which are connected by relations (43). The specific case of the potential functions are homogeneous polynomials of odd degree. In this case, the coefficient β takes the discrete values (45): 4, $\frac{8}{3}$, $\frac{12}{5}$, ... In particular, if we consider homogeneous polynomials of the first degree, i.e., linear functions $f_i(\bar{\chi})$, then $\beta = 4$, which leads us to conditional probability density function (10), obtained by Onsager and Machlup.

[1] L. Onsager, Phys. Rev. **37**, 405 (1931).
[2] L. Onsager, Phys. Rev. **38**, 2265 (1931).
[3] L. Onsager and S. Machlup, Phys. Rev. **91**, 1505 (1953).
[4] S. Machlup and L. Onsager, Phys. Rev. **91**, 1512 (1953).
[5] S. I. Serdyukov, Zh. Fiz. Khim. **67**, 879 (1993) [Russ. J. Phys. Chem. **67**, 790 (1993)].
[6] J. Keizer, *Statistical Thermodynamics of Nonequilibrium Processes* (Springer, New York, 1987).