

PARAMETERS OF SPATIAL HETEROGENEITY OF NON-EQUILIBRIUM SYSTEMS

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The parameters characterising a deviation of system as whole from spatially homogeneous state are offered

The thermodynamic description of any processes demands, as is known, a finding of their coordinates – parameters, with necessity changing at their course and remaining invariable in their absence. It concerns and the processes of carrying over studied by non-equilibrium thermodynamics. Such processes have the ordered (directed) character and are generated by spatial heterogeneity of system. Therefore they demand introduction of specific vector parameters of the spatial heterogeneities reflecting the reason of occurrence in system of such processes and characterising their direction and speed. For a finding of extensive parameters of spatial heterogeneity it is necessary to find a way of transition from functions of distribution (fields) of density $\rho_i = d\Theta_i/dV$ any thermodynamic variable Θ_i (the mass M of the system and all its k^{th} components M_k , their entropy S and electric charge Θ_e , component P_α of the system impulse \mathbf{P} etc.) to the parameters of the system in a whole, which thermodynamics operates with.

This transfer may be provided in the same way as used in mechanics to change over from motion of separate points to system center-of-mass motion. To better understand such a transfer, let us consider an arbitrary continuum featuring non-uniform density distribution $\rho_i = \rho_i(\mathbf{r}, t)$ of particular extensive physical values Θ_i characterizing continuum properties, over the system volume V . Fig.1 illustrates the arbitrary density distribution $\rho_i(\mathbf{r}, t)$ as a function of spatial coordinates (the radius vector of a field point \mathbf{r}) and time t .

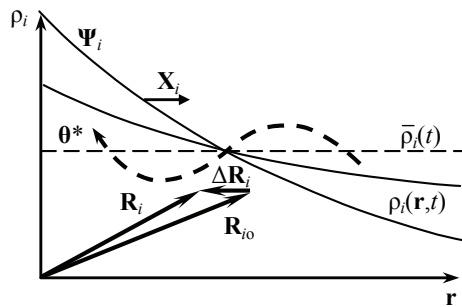


Fig.1. To Generation of Distribution Moment

As may be seen from the figure, when the distribution Θ_i deviates from that uniform (horizontal line), some amount of this value (asterisked) migrates from one part of the system to other, which displaces the center of this value from the initial \mathbf{R}_{i0} to a current position \mathbf{R}_i . Position of the center of a particular extensive value Θ_i defined by the radius vector \mathbf{R}_i is given by a known expression:

$$\mathbf{R}_i = \Theta_i^{-1} \int \rho_i(\mathbf{r}, t) \mathbf{r} dV, \quad (i = 1, 2, \dots, n) \quad (1)$$

For the same system, but in a homogeneous state, the Θ_i center position \mathbf{R}_{i0} may be derived if factoring $\rho_i = \bar{\rho}_i(t)$ in equation (1) outside the integral sign:

$$\mathbf{R}_{i0} = \Theta_i^{-1} \int \bar{\rho}_i(t) \mathbf{r} dV = V^{-1} \int \mathbf{r} dV. \quad (2)$$

Thus the state of a spatially heterogeneous system features emergence of a specific “distribution moments” \mathbf{Z}_i of the parameter Θ_i :

$$\mathbf{Z}_i = \Theta_i(\mathbf{R}_i - \mathbf{R}_{i0}) = \int [\rho_i(\mathbf{r}, t) - \bar{\rho}_i(t)] \mathbf{r} dV. \quad (3)$$

This expression most evidently manifests that the parameters \mathbf{Z}_i of spatial heterogeneity are additive values and summed up providing the $\bar{\rho}_i(t)$ value remains the same in various parts of a heterogeneous system. This follows from the conservation of integral (3) at its partition into parts with a volume $V' < V$. However, these parameters become zero at «contraction» of the system to a material point, when $\rho_i(\mathbf{r}, t) \rightarrow \bar{\rho}_i(t)$. It is natural, because the processes of density

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redistribution $\rho_i(\mathbf{r},t)$ are absent in material points. And once again this confirms the fact that an entity of continuum elements considered as a system, non-equilibrium in whole, possesses additional degrees of freedom.

For any part of a homogeneous isolated system the \mathbf{R}_{io} value remains unvaried since running of any processes is herein impossible¹⁾. Therefore the \mathbf{R}_{io} may be accepted for such systems as a reference point \mathbf{r} or \mathbf{r}_i and set equal zero ($\mathbf{R}_{io} = 0$). In this case the vector \mathbf{R}_i will define a displacement of the Θ_i center from its position for the system being in internal equilibrium state, and the moment of distribution of a particular value Θ_i in it will become:

$$\mathbf{Z}_i = \Theta_i \mathbf{R}_i \quad (4)$$

Herein the moment \mathbf{Z}_i becomes an absolute extensive measure of the system heterogeneity with respect to one of the system properties – like such absolute parameters of classic thermodynamics as mass, volume, entropy, etc.

In case of discrete systems the integration over system volume will be substituted for the summation with respect to elements $d\Theta_i$ of the Θ_i value:

$$\mathbf{Z}_i = \Theta_i \mathbf{R}_i = \sum_i \mathbf{r}_i d\Theta_i, \quad (5)$$

where \mathbf{r}_i – radius vector of the element $d\Theta_i$ center. Therefore expression (4) remain valid for also the systems with discrete distribution of charges, poles, elementary particles, etc.

As follows from expressions (2,3), the distribution moment \mathbf{Z}_i emerges due to exclusively the displacement of the Θ_i center and has nothing to do with the variation of the Θ_i value itself. Thus the expression for the complete differential of the function $\mathbf{Z}_i = \mathbf{Z}_i(\Theta_i, \mathbf{R}_i)$ becomes:

$$d\mathbf{Z}_i = (\partial \mathbf{Z}_i / \partial \Theta_i) d\Theta_i + (\partial \mathbf{Z}_i / \partial \mathbf{R}_i) d\mathbf{R}_i. \quad (6)$$

Expression (6) indicates there are two categories of processes running in spatially heterogeneous media, each having its own group of independent variables. The first categories of processes running at $\mathbf{R}_i = \text{const}$ involves the uniform variation of the physical value Θ_i in all parts of the system. Such processes resemble the uniform fall onto an irregular (in the general case) surface. Therefore these processes will hereafter be named the *uniform* processes. In particular such case comprise quasi-static processes of heat exchange, mass exchange and cubic strain, which do not break spatial uniformity of system.

Processes described by the addend in (6) run with the Θ_i parameters being constant and consist in redistribution of their density $\rho_i = d\Theta_i/dV$ among the parts (zones) of a heterogeneous system. They are accompanied by, e.g., decreasing the entropy S , concentrations c_k of the k^{th} substances, their momentums \mathbf{P}_k , etc., in some parts of the system and by increasing the same in other parts. Such processes are caused by transfer of a part of the Θ_i value within the system and resemble the migration of liquid in a vessel. Such processes are always non-equilibrium even if they run infinitely slowly (quasi-statically) since the system is now withdrawing from internal equilibrium or approaching it. State modifications of such a kind are caused by, e.g., work done by external force fields. The similar state variations are caused by also the relaxation vector processes accompanied by equalization of temperatures, pressures, chemical and other potentials of the system. The processes of such a kind feature a directional (ordered) character, which distinguishes the useful work from the work of uniform (quasi-static) introduction of substance, charge, etc., or expansion work. Such processes will hereafter be named the *redistribution* processes. According to (1) the coordinate of the processes pertaining to this category is understood as the vectors $d\mathbf{R}_i$ of the Θ_i center displacement. Derivatives on time from coordinates define the generalised speed of such processes

¹⁾ Systems, where homogeneous chemical reactions run, are not exception since they are actually accompanied by changing the spatial arrangement of atoms.

$$\mathbf{v}_i \equiv d\mathbf{R}_i/dt, \quad (7)$$

and product $\Theta_i \mathbf{v}_i$ – specific streams of displacement of i^{th} energy carrier Θ_i :

$$\mathbf{J}_i \equiv \Theta_i \mathbf{v}_i. \quad (8)$$

In that case motive forces \mathbf{X}_i causing occurrence of stream \mathbf{J}_i , can be found without drawing up of the bulky equations of balance of entropy [3] as derivative of energy E on the moments of distribution \mathbf{Z}_i :

$$\mathbf{X}_i \equiv -(\partial E/\partial \mathbf{Z}_i). \quad (9)$$

Since at $\Theta_i = \text{const}$, $(\partial E/\partial \mathbf{Z}_i) = \Theta_i^{-1}(\partial E/\partial \mathbf{R}_i) = \mathbf{F}_i/\Theta_i$, then the \mathbf{X}_i thermodynamic forces thus introduced are actually the forces \mathbf{F}_i in their usual (Newtonian) meaning $\mathbf{F}_i \equiv -(\partial E/\partial \mathbf{R}_i)$, per unit of the value Θ_i they transfer. Such are, in particular, the specific mass, volume and surface forces, for which the Θ_i value is construed as, respectively, mass M , volume V and surface F of the body. This category also includes the electromotive force \mathbf{X}_e that is Lorenz's force \mathbf{F}_e related to the value of the electric charge Θ_e being transferred. In the theory of irreversible processes such forces are named "thermodynamic forces in their energy representation" (Gyarmati, 1974). Further we will show, that introduction of the missing co-ordinates \mathbf{Z}_i interfaced to thermodynamic forces \mathbf{X}_i , allows to give consistently thermodynamic substantiation of the theory of irreversible processes major positions [5], not resorting to any hypotheses and postulates.

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