THE MATERIAL-POINT METHOD IN STRUCTURAL ANALYSIS OF CRYSTALS

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Abstract

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In the proposed method, the entire set of parameters to be determined from the coordinates of an absolute minimum is conventionally taken as the coordinates of a certain material point that remains on a surface described in an n-dimensional space by a chosen functional. Under the action of a conditional force of gravity, the point will be displaced, seeking to enter the region of minimum potential energy.

Let the equation of the surface be

$$\varphi(y, x_1, \dots, x_n) = y - f(x_1, \dots, x_n) = 0, \tag{1}$$

where f is the function under investigation. Then the system of differential equations describing the trajectory of a material point moving along the surface is

$$\ddot{x}_i = -\frac{g + \sum_{p=1}^{n} \sum_{q=1}^{n} \frac{\partial^2 f}{\partial x_p \, \partial x_q} \dot{x}_p \dot{x}_q}{\sum_{m=1}^{n} \left(\frac{\partial f}{\partial x_m} \right)^2 + 1} \frac{\partial f}{\partial x_i}. \tag{2}$$

We note the special features of the proposed method:

a) the motion is carried out in the direction of steepest descent at small $\dot{x}$, i.e., it incorporates gradient methods, but the rate of convergence to the local minimum is considerably higher ([1]);

b) the solution is given by a continuous function, and, consequently, in moving over the surface we are able to view the entire region of variation of the sought parameters in the corresponding direction;

c) by specifying several initial points, we obtain the possibility of surveying the region of variation of the parameters in different directions and, having obtained information on the distribution of minima in them, of judging the location of the global minimum;

d) in motion over the surface, not only the local features of the surface are used, but also all information on the geometry of the surface at "previous instants of time," at an earlier stage of the motion ("acceleration" during descent and "deceleration" during ascent);

e) since the system is characterized by inertia, if the surface being investigated is of a ravine-like form ([2]), then the motion will also proceed along the ravine.

On the other hand, a substantial negative aspect of the method may be the large volume of computational work, since it is necessary to compute the second derivatives of $f(x_1, \dots, x_n)$. This circumstance, however, is not of substantial importance for functionals usually used in structural analysis.

Turning to a difference scheme, in solving system (2) we arrive at the expression

$$x_i^{(k+1)} = x_i^{(k)} + \frac{h_{k+1}}{h_k}\left(x_i^{(k)} - x_i^{(k-1)}\right) - \frac{g_{k+1}^2 + \sum_{p=1}^{n}\sum_{q=1}^{n} \left.\frac{\partial^2 f}{\partial x_p \partial x_q}\right|_k \frac{h_{k+1}^2}{h_k^2}\left(x_p^{(k)} - x_p^{(k-1)}\right)\left(x_q^{(k)} - x_q^{(k-1)}\right)}{\sum_{m=1}^{n}\left(\left.\frac{\partial f}{\partial x_m}\right|_k\right)^2 + 1}\frac{\partial f}{\partial x_i}, \tag{3}$$

where $x_i^{(k)}$ is the value of the parameter x_i at point k and at the k-th step; h_k is the step in t (equivalent to the time of motion) from the $(k-1)$-st point to the k-th point, and $\left.\frac{\partial f}{\partial x_i}\right|_k$ and $\left.\frac{\partial^2 f}{\partial x_p \partial x_q}\right|_k$ are the corresponding partial derivatives of the functional under investigation with respect to the parameters.

The initial displacement is determined by the formula

$$x_i^{(1)} = x_i^{(0)} - h_0\left(\frac{\nu_1}{\left[\sum_{m=1}^{n}\left(\frac{\partial f}{\partial x_m}\right)^2 + 1\right]^{1/2}}\left.\frac{\partial f}{\partial x_i}\right|_0 + \nu_2 \operatorname{sign}\left.\frac{\partial f}{\partial x_i}\right|_0\right), \tag{4}$$

where

$$\operatorname{sign}\left.\frac{\partial f}{\partial x_i}\right|_0 = \begin{cases} +1, & \text{if } \left.\frac{\partial f}{\partial x_i}\right|_0 \geq 0, \\ -1, & \text{if } \left.\frac{\partial f}{\partial x_i}\right|_0 < 0, \end{cases}$$

and ν_1 and ν_2 are certain parameters of the motion.

The functionals most often used in the structural analysis of crystals have the form $\Phi_{\alpha,\beta} = \sum_{hkl} w_{hkl}\left(|F^{\mathrm{e}}_{hkl}|^{\alpha} - |F^{\mathrm{T}}_{hkl}|^{\alpha}\right)^{\beta}$, where usually α and β take the values one or two, w_{hkl} are weight functions characterizing the accuracy of measurement of $|F^{\mathrm{e}}_{hkl}|$, and $|F^{\mathrm{T}}_{hkl}|$ is the functional argument. However, the particular choice of the values of α and β can be explained only by tradition. In actuality, the solution of the system of transcendental equations $|F^{\mathrm{e}}_{hkl}| - |F^{\mathrm{T}}_{hkl}| = 0$ is equivalent to finding the common minimum of a series of functionals $\Phi_{\alpha,\beta}$ for different α and β. It should be noted that a more substantial role here is played by variation of the degree β. Nevertheless, the problem of finding the common minimum of the functionals $\Phi_{\alpha,\beta}$ is in itself very complicated. Therefore we used the following device for the solution.

We take into account that the difficulty of finding the regions of absolute minimum of the functionals $\Phi_{\alpha,\beta}$ is associated with the abundance of local minima determined by the condition

$$\beta \sum_{hkl} w_{hkl}\left(|F^{\mathrm{e}}_{hkl}|^{\alpha} - |F^{\mathrm{T}}_{hkl}|^{\alpha}\right)^{\beta-1} \frac{\partial |F^{\mathrm{T}}_{hkl}|^{\alpha}}{\partial x_i} = 0, \tag{5}$$

where $i = 1, \dots, n$. In this case each local minimum is determined by the vanishing (or near-vanishing) not of the residuals $|F|^{\alpha} - |F|^{\alpha}$, but of a linear combination of the derivatives. Thus, in moving along the surface we have the possibility of eliminating any local relative minimum by, for example, introducing correcting weight ⋯

functions

$$\nu_{hkl} = \frac{\left(|F^{\mathrm{e}}_{hkl}|^{\alpha} - |F^{\mathrm{T}}_{hkl}|^{\alpha}\right)^{\gamma}}{\sum\limits_{hkl}\left(|F^{\mathrm{e}}_{hkl}|^{\alpha} - |F^{\mathrm{T}}_{hkl}|^{\alpha}\right)^{\gamma}} \tag{6}$$

where γ is a selectable integer parameter. At the same time, this makes it possible to vary locally the degree β in $\Phi_{\alpha,\beta}$, i.e., in the neighborhood of the point of a local minimum there occurs a transition from the surface of the functional $\Phi_{\alpha,\beta}$ to $\Phi_{\alpha,\beta+\gamma}$.

The method described was applied to the determination of the crystal structure of nickel chloride nitrodiethylenediamine [Ni $\mathrm{en_2NO_2}$]Cl, the X-ray diffraction material for which was kindly provided to us by Prof. M. A. Porai-Koshits and A. E. Shvelashvili ([3]).

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REFERENCES

[1] B. G. Polyak, *Zhurn. vychisliteln. matem. i matem. fiz.*, **4**, No. 5, 791 (1964).
[2] I. M. Gelfand, M. L. Tsetlin, *DAN*, **137**, No. 2, 295 (1961).
[3] B. M. Shchedrin, N. V. Belov, N. P. Zhidkov, M. A. Porai-Koshits, A. E. Shvelashvili, *DAN*, **170**, No. 6 (1966).

Note: Figure translations are in progress. See original paper for figures.