

LETTER TO THE EDITOR

Nanoparticles as dislocation sources in nanocomposites

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Online at stacks.iop.org/JPhysCM/18/L225**Abstract**

A new mechanism for nucleation of dislocation dipoles at nanoparticles (nanoinclusions) in nanocomposite solids is suggested and theoretically described. The mechanism represents the nucleation of a nanoscale dipole of 'non-crystallographic' partial dislocations whose Burgers vector magnitudes continuously grow during the nucleation process. It is shown that the dislocations nucleated at nanoparticles can be emitted into a matrix in nanocomposites deformed at high mechanical stresses.

(Some figures in this article are in colour only in the electronic version)

Nanocomposite solids consisting of at least two phases, with at least one phase having characteristic sizes less than 100 nm, represent the subject of intensive research efforts motivated by their diverse technological applications and interest in fundamentals of nanoscale effects in solids; see, e.g., [1–7]. Both the structure and properties of crystalline nanocomposites such as 'nanoparticle–matrix' and 'nanoscale film–substrate' composites are strongly influenced by misfit stresses arising due to a misfit between the crystal lattices of the adjacent component phases at interphase boundaries. A partial relaxation of misfit stresses often occurs by nucleation and evolution of misfit dislocations (MDs) at interphase boundaries in thin-film and bulk nanocomposites; see, e.g., [8–20]. Commonly misfit stress relaxation is realized through the nucleation of MD semiloops at the free surface, their subsequent glide to the interphase boundary and further expansion [8, 9]. This scenario requires that the dislocations overcome a rather high energetic barrier, which appears due to the attraction of dislocations to the free surface. However, in general, misfit stress relaxation in nanocomposites may occur by alternative mechanisms. In particular, we think that there exists a new alternative relaxation mechanism in nanoparticle–matrix nanocomposites. This mechanism involves the non-local nucleation of a nanoscale dipole of 'non-crystallographic' partial dislocations (located at and near the nanoparticle–matrix interface) with a Burgers vector magnitude s growing from zero to the Burgers vector magnitude b of a perfect lattice dislocation (figures 1(a)–(d)). The new mechanism effectively operates under the action of

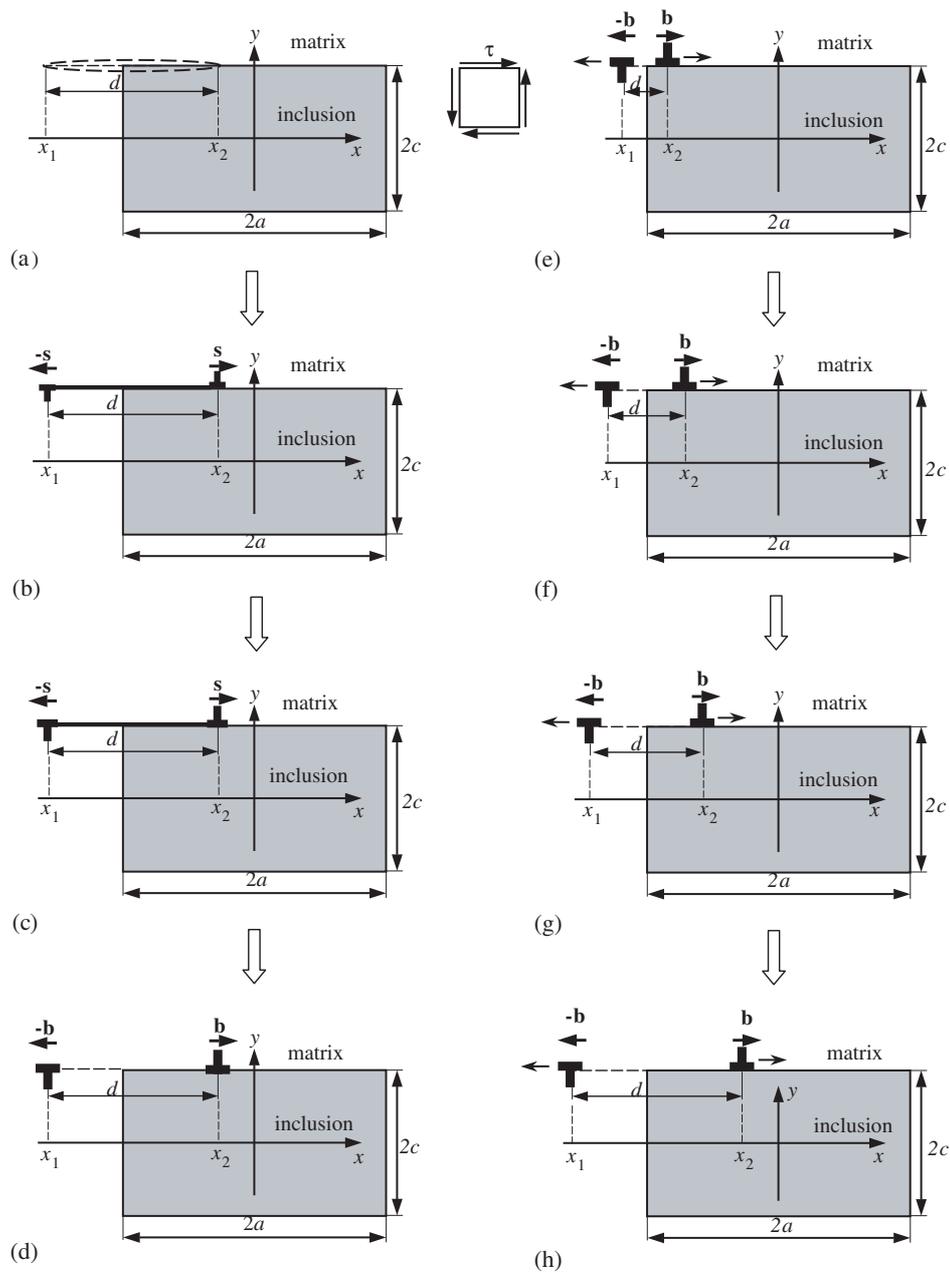


Figure 1. Mechanisms for formation of a dislocation dipole at a nanoparticle (rectangular inclusion) in a nanocomposite solid. (a)–(d) The new mechanism involves a nanoscale ideal shear. (a), (b) A nanoscale ideal shear occurs along a fragment of nanoparticle–matrix interface plane and results in the formation of dipole of non-crystallographic partial dislocations with very small Burgers vector magnitude s , connected by a stacking fault. (c) The Burgers vector magnitude s continuously increases and (d) reaches the Burgers vector magnitude b of perfect misfit dislocations. (e)–(h) The standard mechanism is realized by (e) generation of a dipole of misfit dislocations at the nanoparticle–matrix interface followed by (f)–(h) their glide in opposite directions along the interface plane.

external mechanical stresses that can induce emission of lattice dislocations from nanoparticles in a mechanically loaded nanocomposite. The main aim of this letter is to theoretically describe both the new mechanism of dislocation nucleation at nanoparticles and the dislocation emission by nanoparticles in deformed nanoparticle–matrix nanocomposites.

Let us consider a model nanocomposite solid that consists of a matrix and a rectangular inclusion (nanoparticle) with an infinite length, nanoscale width and height (figure 1). The nanocomposite is subjected to the action of an external shear stress τ . Within the model, the matrix and nanoparticle are elastically isotropic solids having the same values of the shear modulus G and the same values of Poisson's ratio ν . In the coordinate system shown in figure 1, the nanoparticle occupies the region $(-a < x < a, -c < y < c)$ and is characterized by a uniform three-axis dilatational eigenstrain $\varepsilon_{ij}^* = f\delta_{ij}$, where $i, j = x, y, z$, and δ_{ij} is the Kronecker delta. In the case of cubic crystal lattices of the matrix and nanoparticle, the magnitude f of the nanoparticle eigenstrain determines the misfit of the crystal lattice parameters a_m and a_i of the matrix and nanoparticle, respectively. The misfit f is defined as $f = (a_m - a_i)/a_i$. For convenience, in the following we put $f > 0$.

If the values of the misfit f and external shear stress τ are high enough, the external stress and misfit stresses can induce the generation of a dislocation dipole at one of the nanoparticle facets (figure 1(e)). The dislocation dipole can form by the standard mechanism involving the nucleation of a dipole of perfect dislocations with an extremely small interspacing (equal to one interatomic distance; see figure 1(e)) and subsequent glide of the generated dislocations in opposite directions (figures 1(f)–(h)). Also, we think that the dislocation dipole can form by a new mechanism, namely via the non-local formation of a nanoscale dipole of non-crystallographic partial dislocations whose Burgers vector magnitude s continuously grows from 0 to the magnitude b of the Burgers vector of lattice dislocations (figures 1(a)–(d)). In doing so, at the first stage of the dipole formation, the partial dislocations have the Burgers vectors of a very small magnitude s and are distant from each other by several nanometres (figures 1(a) and (b)). Such a dislocation dipole (hereinafter called a nanodisturbance) forms due to a nanoscale plastic shear by value of s in the region between the dislocations, where a nanoscale stacking fault is generated. At the second stage, due to the action of both the misfit stresses and external shear stress τ , the magnitude s of the dislocation Burgers vectors increases (figure 1(c)). Finally, if the stresses are high enough, the magnitude s of the dislocation Burgers vectors reaches the magnitude b of the Burgers vector of a perfect dislocation, in which case the nanodisturbance transforms into a dipole of conventional perfect dislocations (figure 1(d)).

Thus, the standard mechanism for dislocation dipole formation comprises the formation of two perfect dislocations at a very small distance from each other and growth of the dislocation interspacing (figures 1(e)–(h)), while the new mechanism includes the non-local formation of two dislocations (with very small Burgers vector magnitudes) at a comparatively large, nanoscale distance from each other and further growth of their Burgers vectors (figures 1(a)–(d)). To judge the opportunities for the formation of a dislocation dipole by the two mechanisms described, we compare the equilibrium conditions for dipole formation with the aid of the new and the standard mechanism.

First, consider the generation of a nanodisturbance at the nanoparticle–matrix interface (figures 1(a)–(d)). The nanodisturbance represents a dipole of partial dislocations with the Burgers vectors $\pm \mathbf{s} = \pm s\mathbf{e}_x$, with s ranging from 0 to b . The positions of the dislocations with the Burgers vectors $-\mathbf{s}$ and \mathbf{s} are denoted as $x = x_1$ and $x = x_2$, respectively (see figures 1(a)–(d)).

The energy change ΔW_{nd} associated with the formation of a nanodisturbance is defined as the difference between the energy of the matrix–nanoparticle composite with the nanodisturbance and the energy of the composite without a nanodisturbance. It can be written

as

$$\Delta W_{\text{nd}} = W_{\text{nd}}^{\text{self}} + W_{\text{nd-f}} + W_{\text{nd-}\tau} + W_{\gamma}. \quad (1)$$

Here $W_{\text{nd}}^{\text{self}}$ denotes the partial dislocation dipole self-energy (including dislocation core energies), $W_{\text{nd-f}}$ the energy of the interaction between the dislocation dipole and the misfit stress field, $W_{\text{nd-}\tau}$ the energy of the interaction of the dislocation dipole and external shear stress τ and W_{γ} the stacking fault energy.

The self-energy $W_{\text{nd}}^{\text{self}}$ of the dislocation dipole is calculated as [21]

$$W_{\text{nd}}^{\text{self}} = Ds^2 \left[-\ln \frac{d}{s} + 1 \right], \quad (2)$$

where $d = x_2 - x_1$ and $D = G/[2\pi(1 - \nu)]$. The energy $W_{\text{nd-f}}$ of the elastic interaction of the partial dislocation dipole with the misfit stress field is calculated using the expressions (see, e.g. [22]) for the stress field of a rectangular inclusion with a dilatational eigenstrain. In doing so, we find $W_{\text{nd-f}} = Dsf(1 + \nu)K(a, c, x_1, x_2)$, where

$$K(a, c, x_1, x_2) = \left\{ (x - x') \ln \frac{(x - x')^2 + 4c^2}{(x - x')^2} + 4c \arctan \frac{x - x'}{2c} \right\} \Big|_{x'=-a}^{x'=a} \Big|_{x=x_1}^{x=x_2}. \quad (3)$$

The energy $W_{\text{nd-}\tau}$ of the interaction between the dislocation dipole and the external shear stress τ follows as

$$W_{\text{nd-}\tau} = -\tau s d. \quad (4)$$

Finally, the stacking fault energy can be represented as $W_{\gamma} = \gamma(s)d$, where $\gamma(s)$ is the specific energy of the stacking fault connecting partial dislocations with the Burgers vectors $\pm s$. In a first approximation, the expression for the specific energy of the stacking fault $\gamma(s)$ can be chosen as

$$\gamma(s) = \kappa D b \sin(\pi s/b), \quad (5)$$

where $\kappa \ll 1$ is a dimensionless parameter. This expression reflects evolution of the stacking fault energy with a change in s characterizing the nanoscale ideal shear along the stacking fault.

With the expressions for the energies $W_{\text{nd}}^{\text{self}}$, $W_{\text{nd-f}}$, $W_{\text{nd-}\tau}$ and W_{γ} substituted into formula (1), we obtain the following expression for the energy change ΔW_{nd} :

$$\Delta W_{\text{nd}} = D b^2 \left[p^2 \left(-\ln \frac{d}{s} + 1 \right) + p(1 + \nu) f \frac{K(a, c, x_1, x_2)}{b} - p \frac{\tau d}{D b} + \kappa \frac{d}{b} \sin(\pi p) \right], \quad (6)$$

where $p = s/b$. With the analysis of formula (6) in the examined case of $d \ll (2a, 2c)$, we find that the nanodisturbance is most favourable to nucleate near the left nanoparticle corner $x = -a$. Therefore, in the following calculation of ΔW_{nd} , we put $x_1 = -a - d/2$ and $x_2 = -a + d/2$.

The dependences $\Delta W_{\text{nd}}(s/b)$ are presented in figure 2, for $a = c = 50b$, $d = 20b$, $\nu = 0.3$, $\kappa = 0.01$, $x_1 = -a - d/2$, $x_2 = -a + d/2$ and different values of f and τ . Figure 2 shows that the dependences $\Delta W_{\text{nd}}(s/b)$ either monotonically increase or have a minimum. In the former case, the formation of the nanodisturbance at the matrix–nanoparticle interface is energetically unfavourable. In the latter case, the formation of a nanodisturbance with a not too large Burgers vector diminishes the energy of the matrix–nanoparticle composite. The growth of the magnitude s of the Burgers vectors of the non-crystallographic partial dislocations (figures 1(a)–(d)) is energetically beneficial as long as it results in a decrease in the energy ΔW_{nd} . In other words, the formation of the dipole of perfect dislocations with the Burgers vectors $\pm \mathbf{b}$ is energetically favoured, if $(\partial \Delta W_{\text{nd}}/\partial s)|_{s=b} \leq 0$. Moreover, the formation of the dipole of perfect dislocations by the new mechanism (figures 1(a)–(d)) is characterized by the

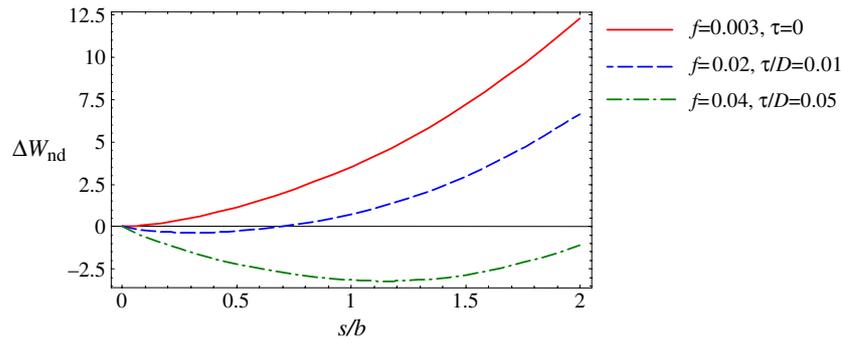


Figure 2. Dependences of the energy change ΔW_{nd} (in units of Db^2) associated with the formation of a nanodisturbance at the interface of a matrix and a rectangular nanoparticle on the normalized magnitude s/b of the partial dislocation Burgers vectors.

absence of an energetic barrier, if $(\partial \Delta W_{nd} / \partial s) \leq 0$ during growth of s from zero to b . In particular, the latter relation is satisfied at the parameter values $f = 0.04$ and $\tau = 0.05D$, for which the bottom curve in figure 2 is plotted. In general, as follows from figure 2, the formation of the dipole of perfect dislocations at the matrix–nanoparticle interface due to the nucleation of a nanodisturbance can occur as a non-barrier process at high values of misfit f or shear stress τ . Furthermore, our analysis shows that for high enough misfit f ($f > 0.041$) the non-barrier formation of a perfect dislocation dipole by this mechanism can occur even in the absence of an external shear stress (at $\tau = 0$).

Now consider the generation of a dipole of perfect dislocations with the Burgers vectors $\pm \mathbf{b} = \pm b \mathbf{e}_x$ at the nanoparticle–matrix interface (figures 1(e)–(h)). Let the dislocations $-\mathbf{b}$ and \mathbf{b} (that compose the dipole) nucleate and glide in the plane $y = c$ and have the coordinates $x = x_1$ and $x = x_2$, respectively (see figures 1(e)–(h)). The variation ΔW_d of the system energy associated with the formation of a dipole of perfect dislocations is defined as the difference between the energy of the composite with the dislocation dipole and the energy of the composite without the dipole. The energy variation ΔW_d is calculated in the same way as the energy change ΔW_{nd} . In doing so, we find

$$\Delta W_d = Db^2 \left[-\ln \frac{d}{b} + 1 + (1 + \nu) f \frac{K(a, c, x_1, x_2)}{b} - \frac{\tau d}{Db} \right], \quad (7)$$

where $d = x_2 - x_1$, as above. In the examined case of $d \ll (2a, 2c)$, the dislocation dipole is easiest to nucleate near the left nanoparticle corner $x = -a$, as with nanodisturbances. Therefore, for the analysis of dipole nucleation we assume that $x_1 = -a - d/2$ and $x_2 = -a + d/2$.

With formula (7), we have calculated the dependences $\Delta W_d(d/b)$, for the case $a = c = 50b$, $\nu = 0.3$, $x_1 = -a - d/2$, $x_2 = -a + d/2$ and different values of f and τ . These calculations show that ΔW_d first increases and then decreases. In the region of small values of d , where ΔW_d grows with d , the dipole dislocations are attracted to each other and tend to annihilate. In the area of large values of d , where ΔW_d reduces with an increase in d , the dislocations repulse. Thus, to move apart, the dislocations have to overcome an attraction region. The maximum value of ΔW_d represents the energetic barrier that the nanocomposite has to overcome to form a stable dislocation dipole. Following our estimates, the magnitude of this energetic barrier is high; it is several times larger than the dislocation core energy. As a consequence, even at very high values of external shear stress τ ($\tau = 0.05D \approx G/90$) and a sufficiently high value of misfit f ($f = 0.02$), the standard mechanism (figures 1(e)–(h))

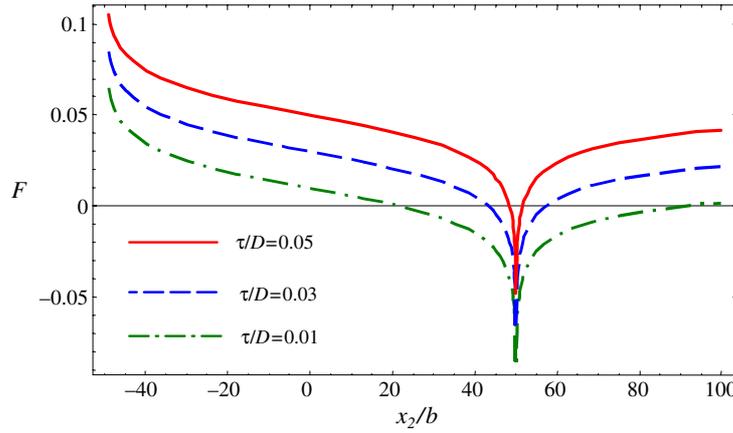


Figure 3. Dependences of the force F (in units of Db) acting on a dislocation, that glides along the nanoparticle boundary, on the normalized dislocation coordinate x_2/b .

for the formation of a dislocation dipole is unfavoured compared to the new mechanism (figures 1(a)–(d)).

It should be noted that, if the lattice dislocations nucleating at a nanoparticle–matrix interface (figure 1(d)) glide in opposite directions far enough, then the nanoparticle serves as a source of lattice dislocations. While the dislocation $-\mathbf{b}$ can move far away after it has left the attraction zone of the other dislocation, the dislocation with the Burgers vector \mathbf{b} may be stopped near the nanoparticle corner $x = a$ due to the nanoparticle misfit stress effect. To estimate the possibility that the dislocation \mathbf{b} moves far from the nanoparticle, we calculate the force $\mathbf{F} = F\mathbf{e}_x$ acting on this dislocation. The force F is calculated from the relation $F = -\partial\Delta W_d/\partial x_2$ as

$$F = Db \left\{ \frac{\tau}{D} - (1 + \nu) f \ln \frac{(x_2 + a)^2[(x_2 - a)^2 + 4c^2]}{(x_2 - a)^2[(x_2 + a)^2 + 4c^2]} - \frac{b}{x_2 - x_1} \right\}. \quad (8)$$

For simplicity, in the following, we mainly focus on the case where the dislocation \mathbf{b} is close to the nanoparticle corner $x = a$ and slows down in this region while the other dislocation $-\mathbf{b}$ rapidly glides away from the dislocation \mathbf{b} . In this case, we neglect the relatively weak interaction between the dislocations and put $x_1 \rightarrow -\infty$.

The dependence of the force F (in units of Db) on the coordinate x_2 is shown in figure 3 for $a = c = 50b$, $\nu = 0.3$, $f = 0.005$, $x_1 = -\infty$ and different values of shear stress τ . The dislocation \mathbf{b} is repelled from the dislocation $-\mathbf{b}$ if $F > 0$, and is attracted to it if $F < 0$. As is seen from figure 3 and formula (8), the force F has a logarithmic singularity at the nanoparticle corner $x = a$. This results in the existence of an equilibrium position for the dislocation \mathbf{b} near the nanoparticle corner. The singularity of the force F at the nanoparticle corner is the consequence of the singularity of the shear stress created by the nanoparticle in the linear elasticity theory applied here. To estimate the values of shear stress τ at which the dislocation \mathbf{b} may move far away from the nanoparticle, we suppose that this dislocation may overcome the attraction region near the nanoparticle corner $x = a$ (where the force F is negative), if the width δ of this region does not exceed $5b$. The latter condition is met if $\tau > \tau_c$, where τ_c is a critical stress. In this case, taking into account that $\delta^2/16 \ll (a^2, c^2)$, from formula (8) and the condition $x_1 \rightarrow -\infty$ we obtain the following expression for τ_c :

$$\tau_c = (1 + \nu) D f \ln \frac{16a^2c^2}{25(a^2 + c^2)b^2}. \quad (9)$$

As follows from formula (9), the critical stress τ_c is proportional to misfit f and grows with nanoparticle sizes a and c . If misfit f is not very small (more than several thousands), τ_c reaches very high values. For example, for $\nu = 0.3$ and $f = 0.01$, we have $\tau_c \approx 0.087D \approx G/50$ at $a = c = 50b$, and $\tau_c \approx 0.045D \approx G/100$ at $a = c = 10b$. For $\nu = 0.3$ and $f = 0.05$, we obtain $\tau_c \approx G/10$ at $a = c = 50b$ and $\tau_c \approx G/20$ at $a = c = 10b$. These values of local shear stress can be reached in shock-loaded nanocomposites and near local stress concentrators in nanocomposites under quasi-static deformation.

Thus, in this paper a new mechanism for dislocation nucleation in deformed nanoparticle–matrix nanocomposites—the nucleation of nanoscale dipoles of non-crystallographic partial dislocations with continuously growing Burgers vector magnitude (figures 1(a)–(d))—has been suggested. According to our analysis of the energy characteristics of this mechanism, it effectively competes with the standard mechanism (figures 1(e)–(h)) in wide ranges of applied stress and misfit values. Also, it is theoretically shown that nanoparticles can serve as sources of dislocations in nanoparticle–matrix nanocomposites deformed at high mechanical stresses. The discussed phenomena of dislocation nucleation and emission at nanoparticles are worth being experimentally examined and theoretically described in detail in the future. Of special importance will be experimental ‘*in situ*’ observation of the dislocation nucleation events at nanoparticles in deformed nanocomposites with various compositions and geometric parameters. Besides, the discussed new mechanism for dislocation nucleation is of general fundamental interest, because it can effectively operate in various solid structures, in particular film–substrate composites, Gum Metal structures [23] and nanocrystalline solids deformed by unusual deformation modes [24, 25].

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