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Dynamics of thermal motion of liquid lead nanoinclusions attached to fixed dislocations coupled in a dislocation node in the aluminum-based matrix

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ABSTRACT
Thermal motion of four liquid lead nanoinclusions attached to fixed dislocation segments joining in a dislocation node in aluminum-based alloy at 485°C is studied in-situ using TEM. The mutual interaction of the inclusions in all pairs is detected demonstrating the collective interaction of the all inclusions. The time-correlated thermal motion of each of the inclusions, and time-correlated thermal motion of the inclusions in all the pairs are indicated. Phase spectra of the time dependencies of the positions of the inclusions on the dislocations obtained using FFT reveal an existence of a common harmonic in their thermal oscillations at low frequencies demonstrating synchronous oscillations of the inclusions. The transition between synchronous and asynchronous dynamics of the thermal oscillations of the inclusions with increasing frequency is observed. The external vibrations introduced by the inclusion attached to the dislocation node are probably the reason for this transition.

1. Introduction
In-situ observations using transmission electron microscopy (TEM) have shown that nanosized inert gas bubbles [1–6] and liquid inclusions [7–13] in a solid matrix are in thermal motion at elevated temperatures. It has been quantitatively proven that free inert gas bubbles and liquid inclusions exhibit a threedimensional random walk when there is no external driving force [2,5–9,13]. The movement of bubbles and inclusions in the crystalline matrix is necessarily associated with local destruction and formation of the surrounding crystalline lattice near the interface between them and the surrounding matrix. The theoretical consideration of the random motion of spherical pores controlled by surface diffusion along the pore-matrix interface, diffusion through matrix

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and the gas phase of the pore was presented in [14,15]. It was also shown that the diffusion of faceted bubbles and pores is controlled by the nucleation and motion of steps at the interface [3]. Note that the equations obtained in [3,14,15] are easily adapted to describe the thermal motion of liquid inclusions in a crystalline matrix. It is remarkable that the diffusion coefficients of liquid Pb inclusions in the Al matrix are several orders of magnitude higher than those of He bubbles in solid pure Al. For example, the diffusion coefficient of a liquid Pb inclusion with a size of 15 nm at 720 K is about $2 \times 10^{-16} \text{ m}^2/\text{s}$ [8], and the diffusion coefficient of a He bubble with a size of 3.5 nm at the same temperature, which is calculated from the Arrhenius equation, is about $5 \times 10^{-22} \text{ m}^2/\text{s}$ [6]. This fact and the very good TEM contrast of the Pb inclusions in the solid aluminum matrix allow in situ TEM studies of the thermal motion of the Pb liquid inclusions with a much higher spatial and temporal resolution than in the case of inert gas bubbles.

TEM-observations show that a significant part of inert gas bubbles [1,16] and liquid Pb inclusions [8–12] are attached to dislocation segments fixed at their ends, which are efficient traps for bubbles and inclusions. Unlike the thermal motion of free inert gas bubbles, pores, and liquid inclusions, the thermal motion of an inert gas bubble [16,17] or a liquid Pb inclusion [8–12] attached to a fixed dislocation segment manifests itself in the form of chaotic oscillations near the dislocation line that is due to the elastic action of the fixed dislocation segment. The corresponding mathematical analysis was presented in [9]. Using in-situ TEM observations of the thermal oscillations of liquid Pb inclusions attached to fixed dislocation segments in an Al matrix, the dependency of their diffusion coefficients on their size and temperature were obtained [11,12]. It was found that the motion mechanism of the inclusions below the temperature of roughening of their \{111\} faces is consistent with the model of motion of interfacial steps [3]. This finding was later confirmed using the thermal motion of free liquid Pb inclusions in an Al matrix [13]. At the higher temperatures, the thermal motion of liquid Pb inclusions in solid Al is controlled by diffusion along the Pb inclusion/Al matrix interface [8]. Several liquid Pb inclusions attached to a one fixed dislocation segment in the Al matrix also oscillate in its close vicinity [18–21]. The study of thermal motion of two liquid Pb inclusions attached to a fixed dislocation segment in Al matrix had shown their repulsion at small distances and their attraction at larger distances that prevented them from merging [18,21]. Furthermore, their spatially correlated and on average spatially synchronised thermal motion was discovered in [21].

In the present paper, results of the analysis of in-situ TEM study of thermal motion of four liquid Pb inclusions attached to fixed dislocation segments joining in a dislocation node in an Al-based matrix are reported. It is shown that this system can be considered as an ensemble of coupled chaotic oscillators. The dynamics of the thermal motion of the inclusions was studied in details.
Specifically, the spatial and time correlations of the thermal motion of the inclusions and in all pairs of inclusions were examined. In addition, using the FFT (Fast Fourier transformation), the frequency spectra were obtained from the dependencies of the positions of the inclusions on the dislocation segments on time and from the time dependencies of the distances between the inclusions in all their pairs. Thereafter, the spectra obtained were analyzed to consider the temporal dynamics of the system of the inclusions.

We should point out that the same system of the liquid Pb nanoinclusions attached to the fixed dislocation segments was used by us earlier to examine the size dependence of their diffusion coefficients [19].

2. Experiment

A ribbon of high-purity Al with 0.65 at. % Pb was obtained by rapid solidification using the melt spinning technique from a temperature above the Al-Pb liquid miscibility gap [22,23]. A 3 mm diameter specimen was punched out from the ribbon. Its stabilised microstructure consisting of Pb-rich nanoinclusions embedded in the polycrystalline matrix of almost pure aluminum [22,23] was obtained by a subsequent annealing in a high purity Ar atmosphere at 280°C for 2 h. To prepare a thin foil for the TEM study, the annealed specimen was electropolished to perforation in a Struers Tenupol twin-jet immersion polisher.

In-situ TEM observations of thermal motion of the inclusions were carried out at a temperature of 485°C in a 200 kV Philips CM 20 microscope using a single tilt heating stage (Gatan). The accuracy of the sample temperature control was around 1°C and the estimated error in the absolute temperature determination was 5–10°C. The observations were recorded on video at a rate of 25 frames per second, which was digitised and split into individual video-frames. Coordinates of the sequential positions of the centres of the individual inclusions were obtained from measurements on the video-frames using a 30 s video sequence containing 751 frames. Projections of the points of trajectories of the individual inclusions onto the image plane were obtained by subsequent correction for sample drift during the observations using fixed points in the images. The sizes of the inclusions were measured as well.

3. Results and analysis

3.1. Character of thermal motion of the inclusions attached to dislocation

Figure 1(a) presents a TEM image (an enlarged part of a video frame) showing a set of four liquid Pb inclusions attached apparently to one fixed dislocation in the almost pure Al matrix at the temperature 485°C. The TEM video demonstrating thermal motion of the inclusions in real time can be found in [24].
The dislocation line is out of contrast in Figure 1(a). It goes approximately through the centres of the rounded inclusions. The diameters of the inclusions numbered in Figure 1(a) as 1, 2, 3, and 4 are about 15, 20, 39 and 22 nm, respectively. Figure 1(b) shows the 30-seconds trajectories of thermal motion of the inclusions. Each of them is presented by 751 points. The trajectories are elongated along the dislocation line showing approximately its direction. They suggest that the dislocation line is slightly curved. Then, the dislocation line was linearly approximated using all points of the trajectories of all the inclusions. The straight line thus obtained is presented in Figure 1(b) as z-axis. The direction perpendicular to the z-axis is taken as x-axis. The dependences of z- and x-coordinates of the inclusions on time (t) are presented in Figure 2(a) and (b), respectively. Visually, they indicate an apparently chaotic oscillatory motion of the inclusions.

### 3.2. Longitudinal motion of the inclusions

Figure 3(a) shows the normalised histograms presenting the distributions of z-coordinates of positions of the inclusions. They are constructed using all 751 points of the trajectories. The bin width is 2 nm. The histograms are separated from each other along the dislocation line indicating that the inclusions move in isolated regions. The histograms have pronounced maxima. The three peaks
The dependences of (a) $z$- and (b) $x$-coordinates of the inclusions on time. The trajectories are marked by the numbers of the inclusions, see Figure 1(a) for reference. In (b) the trajectories in the $x$-direction are offset along the $x$-axis to visually avoid overlaps.

(from left to right) of the histogram of the 3rd inclusion correspond to the parts of the dependence $z(t)$ of the 3rd inclusion in Figure 2(a), which are sequential in time. These peaks display a jerky motion of the 3rd inclusion that indicates its attachment to a dislocation node. The latter is also suggested by the much larger size of the 3rd inclusion in Figure 1(a) and by the apparent curvature of the dislocation line suggested by the trajectories of the inclusions in Figure 1(b). The jerky motion can be caused by displacements of the dislocations joined in the node. Thus, Figure 1(a) actually shows the 3rd inclusion attached to the dislocation node. Then the 1st and 2nd inclusions and the 4th inclusion are attached to the different dislocations segments connected at this node. The positions of these two assumed dislocation segments were estimated by linear approximations of points of the trajectories of the inclusions 1, 2, 3 and 3, 4, respectively, shown in Figure 1(b). It was found that the dislocation lines were misoriented in the dislocation node by the angle about 2.5°. Then, their...
positions are close to the position of the $z$-axis in Figure 1(b). Therefore, the $z$-axis determines $z$-coordinates of the trajectories points of the inclusions with a good accuracy.

In fact, Figure 1(a) and (b) present the projection of the 3D arrangement of the dislocations joining in the node onto the image plane. Since it is needed for their mechanical equilibrium in the node, four dislocations must be joined in a dislocation node in the case of their 3D arrangement (three dislocations can be joined in a node only in the case of their planar arrangement). One of the possible 3D arrangements of the dislocations joined in the node and the inclusions attached to them is displayed schematically in Figure 3(b). For example, such a configuration can be created by two intersected dislocations. Then, the jerky motion of the 3rd inclusion can be related to the displacements of one of them. Since the misorientation angle of the dislocation segments in Figure 1(b) is small, then the directions of the two other dislocation segments connected in this node should be approximately perpendicular to the image plane of Figure 1(b) and also misoriented by a small angle, see Figure 3(b). The above is necessary to ensure the mechanical balance in the image plane. These two dislocations may be invisible in Figure 1(a) since they may be out of TEM contrast or be masked by the large 3rd inclusion. Then, the projection of the 3D arrangement onto the image plane of Figure 3(b) is similar to the image in Figure 1(a).

To avoid a possible influence of the jerky motion of the 3rd inclusion, the 560 trajectory points (at $t < 22.4$ s), which corresponded to the highest peak of the histogram of the 3rd inclusion, were used for the further analysis of thermal motion of the inclusions. To separate the trajectory points belonging to the highest peak, the point of transition (at $t = 22.4$ s) to the adjacent peak was determined using the dependence $z(t)$ of the 3rd inclusion in Figure 2(a).

Let’s note that the direction of $z$-axis obtained by a linear approximation using the 560 points of trajectories of all the inclusions is only changed by $0.04^\circ$ relatively $z$-axis shown in Figure 1(b), which was obtained by the linear approximation using all points of all the trajectories. Then, the $z$-coordinates of points of the trajectories change negligibly. The histograms obtained using the 560 points are shown in Figure 4(a). The effective potentials $U_z(z)$, in which the inclusions move, are derived from these histograms using the equation

$$U_z = -kT \ln \left[ \frac{N}{N_0} \right]$$

following from the Boltzmann distribution law, as it was done in [21]. Here $N_0 = 560$ is the total number of points of the trajectory, $N$ is the number of points of the trajectory in the bin of coordinate $z$, $T$ is the absolute temperature, and $k$ is the Boltzmann constant. The effective potentials obtained are presented in Figure 4(b). They have a potential well shape that suggests interaction of the inclusions with their nearest neighbours (inclusions or fixed ends of the
dislocation). The potential related to the 3rd inclusion is notably deeper than others suggesting its probable attachment to the dislocation node.

Inter-inclusions distances $\Delta z$ along the dislocation line were determined for all possible pairs of the inclusions to consider their mutual interaction. Figure 5 presents the dependences of $\Delta z$ on time for all pairs of the inclusions. Visually, they demonstrate an apparently random oscillatory behaviour. The normalised histograms of the distributions of $\Delta z$ for all pairs of the inclusions are presented in Figure 6. Effective potentials of pair interaction of the inclusions $U_{\text{int}}(\Delta z)$ were obtained from them using the equation

$$U_{\text{int}}(\Delta z) = -kT \ln \left[ \frac{N}{N_o} \right]$$

(2)

following from the Boltzmann distribution law, as it was done above to obtain the effective potentials $U_z(z)$. Here $N$ is the number of $\Delta z$-points in the bin of

**Figure 4.** (a) The histograms obtained using the 560 points ($N_o = 560$) of the trajectories corresponding to the ones belonging to the highest peak of the histogram of the 3rd inclusion in Figure 3(a). (b) Effective potentials $U_z(\Delta z)$ obtained from the histograms in Figure 4(a). The lines are guides for eyes only. The numbers identify the inclusions.

**Figure 5.** Time dependences of inter-inclusions distances along the dislocation line for all pairs of the inclusions. The numbers identify the inclusions forming the pair, see Figure 1(a) for reference. The tick labels of $\Delta z$-axis show only the scale as the dependences are vertically shifted to avoid overlaps.
coordinate $\Delta z$. They are shown in Figure 6(g). The interaction potentials demonstrate a repulsion of inclusions at smaller distances and their attraction at larger distances as in the case of two inclusions attached to one dislocation.
[19, 20]. One can see that the pair potentials of the inclusions being nearest neighbours (12, 23, 34) have closely similar shapes. It is also true for the pair potentials of the inclusions being next nearest neighbours (13, 24). The further the paired inclusions are apart (nearest neighbours (12, 23, 34), next nearest neighbours (13, 24), most separated inclusions (14)) the shallower and wider are the potentials. The interaction of the inclusions in all pairs manifests the collective interaction of all the inclusions and suggests that their thermal motion along the dislocation line is spatially correlated. Figure 7 shows the dependences of z-positions of paired inclusions on their separation.

**Figure 7.** (a–f). Dependences of z-coordinates of the inclusions on their separation Δz for all the pairs. They were obtained using the 560 points of each of the trajectories. The numbers identify the inclusions.
$\Delta z$ for all the pairs. All dependences in Figure 7 form the compact approximately linear regions that confirm the collective interaction of the inclusions.

Figure 7 shows also that the ranges of $z$-displacements of inclusions in all pairs are different. This is due to different inertia of the inclusions that is due to their unequal masses. It is seen in Figure 7 that, the inertia of the inclusions increases in the following order of their numbers: 1, 2, 4, and 3. This order coincides with the order of increasing inclusion size. In particular, Figure 7 (b–d) shows that the $z$-displacements of the 3rd inclusion in all its pairs are very small, and the change in $\Delta z$ is related mainly to the $z$-displacements of the inclusions being paired with the 3rd inclusion. This is due to the larger mass of the 3rd inclusion, and its attachment to a dislocation node.

3.3. Thermal motion of the inclusions in the transverse direction

Figure 8 shows the averaged trajectories of the inclusions. To obtain them the dislocation segment was divided into 2 nm $z$-intervals for the 1st and the 2nd inclusions, and 1 nm $z$-intervals for the 3rd and the 4th inclusions. The different $z$-intervals are used as the trajectories of the 1st and the 2nd inclusions are notably longer than those of the 3rd and the 4th inclusions. The average value, of the $x$-coordinates, $\langle x \rangle$, and the average value, $\langle z \rangle$, of the $z$-coordinates of the points of the trajectories of the inclusions were found for each of the $z$-intervals. The values of $\langle x \rangle$ and $\langle z \rangle$ define points of the averaged trajectories of the inclusions, which are shown in Figure 8. Note that the averaged trajectories of the inclusions present the average positions of the dislocation line, to which they are attached. Figure 8 shows that the averaged trajectories are inclined to the dashed straight line presenting the average position of the dislocation line, which was obtained earlier by linear approximation using all the trajectories, each of which contained 560 points. The observed inclination is probably due to the interaction of the inclusions. A similar inclination of the averaged trajectories of the inclusions was also observed in [21], where thermal motion of two liquid Pb inclusions attached to a fixed dislocation in Al matrix was studied.

![Figure 8](image-url). The averaged trajectories of the inclusions. The $x$- and $z$-coordinates of the inclusions are averaged over 2 nm (the 1st and the 2nd inclusions) and 1 nm (the 3rd and the 4th inclusions) $z$-intervals. The dashed straight line presents the average dislocation position. The numbers identify the inclusions.
Thereafter, for each of the z-intervals, transverse displacements of the inclusions from their average positions \( \langle x \rangle \), i.e. \( \Delta x = x - \langle x \rangle \), were determined for all points lying in each of the z-intervals. Normalised \( \Delta x \)-histograms obtained for all the inclusions are shown in Figure 9(a). The effective potentials \( U_x \) in which the inclusions move in the transverse direction were obtained from these histograms using the Boltzmann distribution law, Figure 9(b). All the potentials are described well by a single parabolic dependence

\[
U_x = \frac{f_d}{2} \Delta x^2 + U_o
\]

with the effective force constant \( f_d = (4.0 \pm 0.2) \times 10^{-2} \) eV/nm\(^2\) and \( U_o = 0.12 \) eV introduced because of the uncertainty in the energy level. Note, it was theoretically shown that the effective potential for the transverse thermal motion of a single inclusion attached to a fixed dislocation segment had a parabolic shape [9]. Besides, the transverse motions of two inclusions attached to a fixed dislocation segment were also described by the single parabolic effective potential [21].

3.4. Effect of elasticity of the dislocation on thermal motion of the inclusions

It was shown in [8,9], that the elasticity of a fixed dislocation segment leads to thermal motion of an attached inclusion performing random oscillations of the inclusion along the dislocation line. These chaotic oscillations of the inclusion can be regarded as its thermal motion in a potential well, whose ends are related to the fixed points of the segment [20,21].

The line of fixed dislocation segment with several inclusions attached to it always stretches between them under the action of its line tension as its mobility
is much higher, and its inertia is much lower than those of the inclusions. Then, the motion of each inclusion between its neighbours is reduced to the single inclusion case considered above. The neighbours can be two inclusions or one inclusion and a fixed end of the dislocation. This explains the appearance of the potential wells, in which the inclusions move, and the interaction of neighbouring inclusions. Figure 10 shows schematically a fixed dislocation OL with four attached inclusions (P₁ to P₄). We can consider the thermal motion of the inclusions (P₁ to P₄) along the segments OP₂, P₁P₃, P₂P₄, and P₃L as it was done for a single inclusion on a fixed dislocation in [8,9]. They oscillate in the potential wells, whose ends are related to the ends of the dislocation (O and L) or with the inclusions (P₁ to P₄). Chaotic oscillations of each inclusion lead to oscillatory shifts of the edges of the potential wells, which are related to it. At the same time, the oscillations of each potential well contribute to the motion of the inclusion oscillating inside it. Thus, the oscillations of neighbouring inclusions display some degree of coupling. This can explain the observed collective interaction of the inclusions, which can result in their collective spatially-correlated thermal oscillations in the steady-state regime. Also, one can expect an appearance of time correlations, and the common harmonics in the steady-state thermal oscillations of the all inclusions attached to the dislocation. It is reasonably to assume, the common harmonics are related to the natural vibrations of the fixed dislocation segment, which dominate in its steady-state thermal vibrations [25].

4. Spatial correlations in thermal motion of the inclusions

To quantify the correlation of thermal motion of the inclusions, the mutual correlation coefficients of the z- and x-coordinates of paired inclusions, Rz and Rx,
respectively, as functions of $\Delta z$ were determined for all the pairs. To determine $R_z$, $\Delta z$-axis was divided into 2 nm $\Delta z$-intervals. Then, the linear correlation coefficient in the form

$$R_{ij,k} = \frac{\sum_{n=1}^{N_k} (z_{in} - \bar{z}_i)(z_{jn} - \bar{z}_j)}{\left[ \sum_{n=1}^{N_k} (z_{in} - \bar{z}_i)^2 \sum_{n=1}^{N_k} (z_{jn} - \bar{z}_j)^2 \right]^{-1/2}} \tag{4}$$

was calculated for each (kth in Equation (4)) of the 2 nm $\Delta z$-intervals. In Equation (4), $i$ and $j$ are the number of the inclusions forming the pair, $k$ is the number of the 2 nm interval, $N_k$ is the number of $\Delta z$-points belonging to the kth 2 nm $\Delta z$-interval, $n$ is the order number of the $\Delta z$-point in the 2 nm $\Delta z$-interval, $z_{in}$ and $z_{jn}$ are the z-coordinates corresponding to nth $\Delta z$-point of ith and jth inclusions, respectively, and $\bar{z}_i$ and $\bar{z}_j$ are the z-coordinates of the centres of weight of the trajectories of ith and jth inclusions, respectively.

The form of the equation used for calculation of the linear correlation coefficients of x-coordinates of the inclusions in a pair is similar to Equation (4), if $x_i = 0$ and $x_j = 0$ are taken into account. The correlation coefficients $R_z$ and $R_x$ as a function of $\Delta z$ are shown, respectively, in Figures 11 and 12 for all the pairs of the inclusions. The correlation coefficients $R_z$ and $R_x$ depend strongly on $\Delta z$ that is they depend on the inclusions pair potential, see Figure 6(g). The coefficients $R_z$ are close to unity near the minima of the pair potentials, and strong anti-correlation is observed near the ends of the $\Delta z$-ranges, Figure 11. The correlation coefficients $R_x$ exhibit a similar behaviour, Figure 12. Lower maxima of the dependences of $R_x$ on $\Delta z$ are probably due to the larger relative contribution of the errors of the measurements of much smaller x-displacements of the inclusions. The interesting feature of the dependences of $R_z$ and $R_x$ on $\Delta z$ is that of some of them, at least, look as consisting of few more or less overlapping bell-shaped distributions. In contrast, analogous dependences for the two inclusions on a one dislocation were of smooth bell-shaped form [21]. Then, the observing behaviour the dependences of $R_z$ and $R_x$ on $\Delta z$ is probably related to the effect of other inclusions. Some overlapping bell-shaped distributions may be unresolved due to their smaller size, and the strong data-points scatter related to the poor statistics in the distributions tails.

Since the averaged trajectories of the inclusions in Figure 8 are approximately parallel, then, on average collective correlated transverse motion of all the inclusions follows necessarily from their on average collective correlated motion along the dislocation that is proved by the dependences in Figures 11 and 12. This substantiates on average collective correlated 3D oscillations of all the inclusions.
It is noted in Section 3.4 that the mutual interaction of all the inclusions can lead to appearance of time correlations in their thermal motions (oscillations). To detect them the dependences of the coefficients of autocorrelation $R_i$ for all the inclusions, and the coefficients of cross-correlation $R_{ij}$ for all pairs of the inclusions on a lag (time delay) $\tau$ were obtained. These dependences are known as autocorrelograms and cross-correlograms, respectively [26]. The x-displacements of the inclusions are usually much smaller than their z-displacements then the relative errors of the measurements of the x-displacements are much larger than those of the measurements of the z-displacements. Therefore, the autocorrelation and cross-correlation for the longitudinal thermal motion of the inclusions are much smaller than those for the vertical motion.

**Figure 11.** (a–f) The dependences of the correlation coefficients for z-coordinates of the inclusions on $\Delta z$ for all the pairs. The numbers identify the inclusions forming the pairs. The lines are guides for eyes only. The arrows show the positions of the minima of the interaction potentials shown in Figure 6(g).

5. Time correlations in the thermal motion of the inclusions

It is noted in Section 3.4 that the mutual interaction of all the inclusions can lead to appearance of time correlations in their thermal motions (oscillations). To detect them the dependences of the coefficients of autocorrelation $R_i$ for all the inclusions, and the coefficients of cross-correlation $R_{ij}$ for all pairs of the inclusions on a lag (time delay) $\tau$ were obtained. These dependences are known as autocorrelograms and cross-correlograms, respectively [26]. The x-displacements of the inclusions are usually much smaller than their z-displacements then the relative errors of the measurements of the x-displacements are much larger than those of the measurements of the z-displacements. Therefore, the autocorrelation and cross-correlation for the longitudinal thermal motion of the inclusions are much smaller than those for the vertical motion.
oscillations of the inclusions are considered only. Furthermore, since the thermal motions of the inclusion in x- and z directions are coupled then their similarity is expected. The equation

\[ R_{ij}(\tau_m) = \frac{\sum_{n=1}^{N_0-m} (z_{i,n} - \bar{z}_{i,n})(z_{j,n+m} - \bar{z}_{j,n+m})}{\left[ \sum_{n=1}^{N_0-m} (z_{i,n} - \bar{z}_{i,n})^2 \sum_{n=1}^{N_0-m} (z_{j,n+m} - \bar{z}_{j,n+m})^2 \right]^{1/2}}, \]  

(5)

is used to obtain the autocorrelograms and cross-correlograms. Here \( \bar{z}_{i,n} = \sum_{n=1}^{N_0-m} z_{i,n} / (N_0 - m) \), \( \bar{z}_{j,n+m} = \sum_{n=1}^{N_0-m} z_{j,n+m} / (N_0 - m) \), \( \tau_m = \Delta t \cdot m \) is

Figure 12. (a–f) The dependences of the correlation coefficients for x-coordinates of the inclusions on \( \Delta z \) for all the pairs. The lines are guides for eyes only. The arrows show the positions of the minima of the interaction potentials shown in Figure 6(g).
the lag, $\Delta t = 0.04$ s, and the integer $m$ lies in the interval $[0, 500]$. The coefficients of autocorrelation $R_i(\tau_m)$ and cross-correlation $R_{ij}(\tau_m)$ are calculated taking in Equation (5) at $i = j$ and $i \neq j$, respectively.

Figure 13 demonstrates the oscillatory-like behaviour of the correlation coefficients in the autocorrelograms of all the inclusions, indicating the presence of strong positive and negative temporal correlations in thermal motion of the inclusions. The correlograms of 1st, the 2nd, and the 3rd inclusions show 5 or 6 irregular oscillations of large-amplitude with average periods of 3–4 s. The correlogram of the 4th inclusion demonstrates the notably smaller amplitude and average period of oscillations.

The cross-correlograms for all pairs of the inclusions are shown in Figure 14. The behaviour of the dependences $R_{ij}(\tau)$ is qualitatively similar to that of $R_i(\tau)$ in Figure 13. However, the amplitudes in $R_{ij}(\tau)$ are much smaller than those in $R_i(\tau)$.

The dependence $R_{12}(\tau)$ demonstrates the oscillations of largest amplitude, which are close to regular. The dependences $R_{13}(\tau)$ and $R_{23}(\tau)$ demonstrate about twice as small amplitudes, suggesting weaker temporal correlations. Even smaller amplitudes of the dependences $R_{4i}(\tau)$ indicate most weak temporal correlations. The cross-correlograms of this family have common features. At this time, they are notably different from other cross-correlograms. The comparison of Figure 13(d) and Figure 14(c, e, f) indicates the strong contribution of the 4th inclusion to the dependences $R_{4i}(\tau)$ at $\tau > 13.5$ s. The above
indicates that the 3rd inclusion significantly reduces the correlation between the thermal motion of the 4th inclusion and the thermal motion of the 1st and the 2nd inclusions. Moreover, Figure 14 shows the temporally correlated longitudinal thermal motion of the inclusions in all pairs. This indicates on the presence of common harmonics in thermal oscillations of all the inclusions. Conditions for the appearance of common harmonics are likely controlled by the 3rd inclusion, attached to the dislocation node, making transmit of own thermal oscillations and those of other inclusions. Unfortunately, the strong overlap of the peaks and the presence of numerous small narrow peaks make it difficult to fully analyze the correlograms shown in Figures 13 and 14.

Figure 14. The cross-correlograms for all pairs of the inclusions. The numbers identify the inclusions forming the pairs.
6. Analysis of the phase spectra of thermal oscillations of the inclusions

The frequency spectra of the phase $\Phi(\nu) = \arctan[\text{Im}(\nu)/\text{Re}(\nu)]$ for all the inclusions and for all pairs of the inclusions are obtained using FFT (Fast Fourier Transformation) from the arrays $z_i(t_n)$ and $\Delta z_{ij}(t_n)$, respectively. Here $\text{Re}(\nu)$ and $\text{Im}(\nu)$ denote the real and imaginary parts of the Fourier series, respectively, $\nu$ is the frequency, and $t_n = \Delta t(n - 1)$ is the time of motion corresponding to the $n$th successive trajectory point. The total number of the points $N_s = 1024$ were used in the each FFT procedure. The number $N_s$ included $N_o = 560$ of the significant data-points and zero value points added up to $N_s$. Then, the $\nu$-step between successive $\Phi$-points of the spectra was $\Delta \nu = (\Delta t N_s)^{-1} \approx 0.0244 \text{ Hz}$, and the Nyquist frequency of the spectra was equal to 12.5 Hz. The Hamming window [27] was used in the FFT procedure.

For convenience of their comparison, all the spectra in Figure 15 were shifted along $\Phi/2\pi$-axis so that the equality $\Phi(0) = 0$ was fulfilled for all them. In Figure 15(a), the $\Phi(\nu)$ spectra for all the inclusions are presented by upward curves, which are non-monotonic at a higher magnification. Note the minima in the spectra 1 and 2. The shapes of the $\Phi(\nu)$ spectra for all pairs of the inclusions in Figure 15(b) are also presented by upward curves with minima, excepting the spectrum 12 presented by the almost straight line. All the spectra shown in Figure 15 have the same slopes in the low-frequency range that is demonstrated in Figure 15(a) by the spectrum 12 (the dashed line) taken from Figure 15(b). The enlarged parts of the low-frequency ranges of the spectra shown in Figure 15(a) and (b) are presented in Figure 16(a) and (b), respectively. Here the spectra are presented by the $\Phi$-points. These figures show that the $\Phi$-points of all spectra lie on the same straight line at $\nu < 0.85 \text{ Hz}$ in Figure 16(a) and at $\nu < 0.6 \text{ Hz}$ in Figure 16(b). The spectra in Figure 16

![Figure 15](image)

**Figure 15.** The $\Phi(\nu)$ spectra for (a) all the inclusions and (b) their pairs, respectively. The numbers indicate the inclusions and the inclusions forming the pairs. The spectrum 12 of (b) shown in (a) by the dashed line demonstrates the all spectra in (a) and (b) have the same slope near zero frequency. The numbers identify the inclusions in (a) and the inclusions forming the pairs in (b).
demonstrate a stepwise behaviour at the higher frequencies. The linear segments of the spectra lie on near-parallel straight lines. It is remarkably that the averaged $\Phi$-distances between all the parallel lines are multiples of $2\pi$ radians with the standard errors less than 0.6% that was found using the $\Phi$-points shown in Figure 16(a). The data displayed in Figure 16(b) give a similar result. Consequently, $\Phi$-steps in all the $\Phi(v)$ spectra in Figure 16 are multiples of $2\pi$ radians. These $2\pi$-steps in the $\Phi(v)$-spectra associate with a '2\pi (radians) phase slip' appearing near a boundary with the synchronous oscillations region [28]. Then, $2\pi$-steps separate the intervals of $\Phi(v)$-spectra in which oscillations of the inclusions are synchronous.

The $\Phi(v)$ spectra displayed in Figure 15(a) are shown in Figure 17 as wrapped in the $\Phi$-interval of $[-\pi, \pi]$ radians. Here the spectra are presented by their $\Phi$-points. The difference between the wrapped and unwrapped spectra shown in Figure 15 is that the multiples of $2\pi$ radians parts of $\Phi$-steps in the unwrapped spectra don’t contribute to the wrapped $\Phi(v)$ spectra. Therefore, the regions of synchronous oscillations regions separated by steps, which are the multiples of $2\pi$ radians, are displayed as the single region in wrapped $\Phi(v)$ spectra, which is associates with synchronous oscillations. In all the spectra, $\Phi$-points form the regular patterns of generally identical geometry at low frequencies.

**Figure 16.** The enlarged parts of the low-frequency ranges of the $\Phi(v)$ spectra shown (a) in Figure 15(a) and (b) in Figure 15(b). The spectra are presented by the $F$-points. The numbers identify the inclusions in (a) and the inclusions forming pairs in (b).

**Figure 17.** (a–d) The wrapped $\Phi(v)$ spectra for all the inclusions. The numbers identify the inclusions.
suggests coherent oscillations of the inclusions at low frequencies. In spectra 1 and 2 of Figure 17, the abrupt randomisation of \( \Phi \)-points arrangement occurs, when \( \nu \) reaches 4.5–5 Hz. The spectra 3 and 4 in Figure 17 demonstrate the development of randomisation of the patterns with the frequency increasing, but a complete disorder is not reached here. Note that, in contrast to the spectra 1 and 2, the spectra 3 and 4 do not have minima in Figure 15(a).

The \( \Phi(\nu) \) spectra displayed in Figure 15(b) are shown in Figure 18 as the ones wrapped in the \( \Phi \)-interval of \([-\pi, \pi]\) radians. They characterise relative oscillations in all pairs of the inclusions. The spectra in Figure 18 also show the regular patterns in the low- frequency ranges, the basic geometry of which coincides with that of the spectra in Figure 17. The randomisation of the regular patterns occurs abruptly in the frequency range, which is specific for each of pairs of the inclusions. The exception is the spectrum 12 forming the almost perfect pattern in the entire frequency range, Figure 18(a). Note the spectrum 12 in Figure 15(b) is the almost straight line, in contrast to the other spectra in this figure, which are curved. This seems to indicate that the \( \nu \)-range of the transitions from the regular pattern to the random arrangement of \( \Phi \)-points in spectra in Figure 17(a, b) and Figure 18(b–f) correlate with the positions of the minima in the spectra in Figure 15.

The \( \Phi(\nu) \) spectra shown in Figures 17 and 18 strongly indicate that they are based on the same basic regular pattern, which is distorted to varying degrees by chaotic contributions, which are probably due to the influence of other inclusions. The same slope of all the spectra at low frequency in Figures 15 and 16 confirms the above conclusion. The spectrum 12 represented by the almost straight line and the near perfect two-dimensional lattice of \( \Phi \)-points in Figure 15 and Figure 18(a), respectively, seems be very close to the basis perfect pattern. Then, the \( \Phi \)-points forming the unwrapped spectrum 12
shown in Figure 15(b) were linearly approximated. Next, \( \Phi_p \)-points, which lay on the fit straight line obtained and had the same \( v \)-coordinates as the \( \Phi \)-points, were found. The unwrapped \( \Phi_p(v) \) spectrum obtained was converted to the wrapped one representing the perfect basic pattern. Thereafter, the phase shifts \( \Delta \Phi = \Phi - \Phi_p \) were determined for all the spectra of the inclusions and their pairs. The \( \Delta \Phi \)-values thus obtained were used to quantify a disorder in the arrangement of \( \Phi \)-points in all spectra shown in Figures 17 and 18. All \( \Delta \Phi \)-values were divided into groups of 15 of \( \Delta \Phi \) in ascending order of frequency. Each group occupied \( v \)-interval of 0.342 Hz width. The standard deviation \( \sigma_{\Delta \Phi} \) was then determined using \( \Delta \Phi \) values of each group. The \( v \)-position of \( \sigma_{\Delta \Phi} \) was characterised by the mean \( v \)-coordinate of the \( \Delta \Phi \)-points forming the group. The standard error of determination of \( \sigma_{\Delta \Phi} \) was about 26%. Using the \( \sigma_{\Delta \Phi} \) obtained, the values of the expression \( \lambda = 1 - \sigma_{\Delta \Phi}/(\sigma_{\Delta \Phi})_{\text{max}} \), which estimated the order parameter, were calculated. Here \( (\sigma_{\Delta \Phi})_{\text{max}} = 1.98 \) radians is the maximum value of all the \( \sigma_{\Delta \Phi} \) values determined for all the spectra shown in Figures 17 and 18. It was assumed that the value of \( (\sigma_{\Delta \Phi})_{\text{max}} \) was close to the value of \( \sigma_{\Delta \Phi} \) characterising the disordered completely pattern. So, \( \lambda = 1 \) for perfect regular pattern associated with synchronous oscillations, and \( \lambda = 0 \) for completely disordered pattern, where oscillations are not synchronous.

Figure 19. (a–d) The dependences \( \lambda(v) \) for all the inclusions. The arrows indicate the positions of the boundaries between the ordered and disordered regions in the corresponding \( \Phi(v) \) spectra in Figure 17. The numbers are the same as those of the corresponding \( \Phi(v) \) spectra.
In Figures 19 and 20, the dependences of $\lambda(\nu)$ are shown for all the inclusions and all their pairs, respectively. The dependences 1 and 2 presented in Figure 19(a) and (b) show the sharp jumps of $\lambda$, which are accompanied by the abrupt increase in the scatter of $\lambda$-points. The $\nu$-ranges, where the $\lambda$-jumps occur, are close to those, where the order–disorder transitions are observed in Figure 17(a) and (b), the latter are shown by the arrows in Figure 19(a) and (b). In contrast, the $\lambda(\nu)$ of the inclusions 3 and 4 in Figure 19(c) and (d) display a monotonous decreasing in $\lambda$ over the entire frequency range. Their behaviour correlates with a monotonic increase in the disorder in the spectra 3 and 4 in Figure 17(c) and (d). Excluding

Figure 20. The dependences $\lambda(\nu)$ for all pairs of the inclusions. The arrows indicate the positions of the boundaries between the ordered and disordered regions in the corresponding $\Phi(\nu)$ spectra in Figure 18. The numbers are the same as those of the corresponding spectra.
the \( \lambda(\nu) \) dependence 12, which is expectably close to unity over the entire frequency range, the behaviour of the dependences \( \lambda(\nu) \) in Figure 20 is similar to that of the \( \lambda(\nu) \) dependences 1 and 2 in Figure 19(a) and (b). The \( \lambda \)-jumps occur at the frequencies close to those (shown by the arrows in Figure 20), where the order–disorder transitions are observed in the respective \( \Phi(\nu) \) spectra in Figure 18. Excluding the \( \lambda(\nu) \) dependence 12, all \( \lambda(\nu) \) decrease as in the ordered so as in the disordered regions, Figures 19 and 20, that shows their defectiveness rise with the frequency increasing.

The disordering of the regular patterns in the spectra in Figures 17 and 18 accompanied by the abrupt decrease in \( \lambda \)-values in Figures 19 and 20 allows to consider the transition from the regular pattern to the disordered arrangement of \( \Phi \)-points in the spectra in Figures 17 and 18 as the manifestation of the transition from synchronous regime to asynchronous regime of thermal oscillations of the inclusions. That looks like a first order phase transition. Note that complete destruction of the synchronization was not occurred in any of the cases.

7. Discussion

It is shown in the present study the thermal motion of all the inclusions is spatially and temporally correlated. Moreover, the identity of the basic pattern of all the wrapped \( \Phi(\nu) \) spectra in Figures 17 and 18 indicates a common harmonic in thermal oscillations of all the inclusions in the frequency ranges, where the regular pattern is observed in the \( \Phi(\nu) \) spectra. The above are the signs of some degree of synchronisation of thermal oscillations of the inclusions that is due to their interaction through the elasticity of the fixed dislocation segments. Then, the order–disorder transitions in the arrangement of \( \Phi \)-points observed in Figures 17 and 18 can be considered as the transition between synchronous and asynchronous dynamics of the thermal oscillations of the inclusions [28]. The system of the inclusions investigated can be considered as an ensemble of coupled chaotic oscillators in the terms of [28]. The phase synchronisation is possible in such types of systems. Note the amplitude of the oscillations remains chaotic in this case [28].

The \( \Phi \)-steps of the multiple \( 2\pi \) radians values in the unwrapped \( \Phi(\nu) \) spectra, which are observed in Figure 16, are associated with a ‘phase slip’ [28]. They separate neighbouring regions, where thermal oscillations of the inclusions are synchronised. These \( \Phi \)-steps are absent in the unwrapped \( \Phi(\nu) \) spectra at \( \nu < 0.85 \) Hz in Figure 16(a) and at \( \nu < 0.6 \) Hz in Figure 16(b). In these \( \nu \)-ranges, thermal oscillations of all the inclusions and the inclusions in all their pairs, respectively, are synchronised. A further increase in \( \nu \) is accompanied by an increase in a density of the \( \Phi \)-steps, their interaction, and appearance of \( \Phi \)-steps of arbitrary values. This process is the reason for the appearance of the minima on the unwrapped \( \Phi(\nu) \) spectra in Figure 15 those correlate
with the order–disorder transition in the arrangement of $\Phi$-points in the spectra in Figures 17 and 18.

As it was noted above, Figure 1(b) and Figure 3(a) present the strong indications the 3rd inclusion is attached to a dislocation node. Then, we are actually considering the system consisting of the 3rd inclusion attached to the dislocation node, the 1st and the 2nd inclusions attached to a one fixed dislocation segment, and the 4th inclusion attached to another fixed dislocation segment. The large 3rd inclusion, separating the 1st and the 2nd inclusions from the 4th inclusion, weakens their interaction. Indeed, all the spectra in Figure 18, excluding the spectrum 12, demonstrate the regular patterns in the low-frequency ranges only. In contrast, the spectrum 12 of the pair of the 1st and the 2nd inclusions, which are not separated by the 3rd inclusion, demonstrates the almost perfect regular pattern in the entire frequency range that indicates their synchronised thermal oscillations at these frequencies. It can then be expected that thermal oscillations of inclusions attached to a fixed single dislocation segment will be well synchronised if their interaction is strong enough. In addition, the influence of the large 3rd inclusion can be the reason for the destruction of synchronisation of thermal oscillations of the inclusions with increasing in the frequency observed visually in Figures 17 and 18. This degradation of synchronisation is quantified by the dependences $\lambda(\nu)$ in Figures 19 and 20.

The jumps of $\lambda$ in Figures 19 and 20, which are related with the transition between the ordered and disordered regions observed in Figures 17 and 18, suggests the first order phase transition between synchronous and asynchronous states in the ensemble of the inclusions studied, which can consider as an ensemble of coupled chaotic oscillators.

8. Summary

(1) Thermal motion of four liquid lead nanoinclusions attached to fixed dislocation segments joining in a dislocation node in aluminum at 485°C is studied in-situ using TEM.

(2) The inclusions demonstrate visually chaotic oscillatory thermal motion in the vicinity of the dislocation lines that is due to their elastic interaction with the neighbouring inclusions and/or the dislocations ends.

(3) The effective longitudinal and transverse potentials, in which the inclusions move, are obtained from the experimental data. The effective potentials of interaction of the inclusions in all pairs are also found that indicates on the collective interaction of the all inclusions.

(4) The observed correlation of the positions of the inclusions in all pairs proves their collective spatially-correlated motion.

(5) The auto- and cross-correlograms obtained for the longitudinal thermal oscillations of all the inclusions and all the pairs of the inclusions, respectively, indicate the time-correlated thermal motion of each of the inclusions, and the time-correlated relative thermal motion of the inclusions in all their pairs.
(6) The phase spectra of the time dependencies of the inclusions positions on the dislocation segments show that common harmonic presents in their longitudinal thermal oscillations at sufficiently low frequencies. This suggests synchronisation in their thermal oscillations. The former is likely the ‘phase synchronization’ in the terms of [28].

(7) The degradation of synchronisation of thermal oscillations of the inclusions on the fixed dislocation segments is due to the influence of the large inclusion separating them, which is attached to a dislocation node.

(8) The abrupt transition between synchronous and asynchronous regimes of the thermal oscillations of the inclusions is found using the wrapped phase spectra.

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References


[24] URL to access the video file in on-line paper


