

Diffusion of hydrogen in metals with substitutional defects

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ABSTRACT

It is known that substitutional defects in metals can create bound states with migrating hydrogen atoms. For example, an increased concentration of electron density near a defect forces hydrogen to move near the defect together with its own electron cloud. This state of the hydrogen atom (a proton) is usually considered as a deep potential well (a trap) in the set of more shallow interstitial positions for protons between matrix atoms. Diffusion in such a lattice with traps was considered earlier in the range of the model of continuous time random walking (CTRW). In the present report we modeled random walks of an impurity particle along the chain of potential wells with two depths which are distributed randomly along the chain. Calculations of effective diffusion coefficient D we compared with the CTRW theory. Then we calculated D for such a system taking into account the flux of the hydrogen into places with stretched crystal lattice near defects.

Analytical solution of the problem by the CTRW method*

*B. A. Merisov et al., Metallofizika 8, 63-67 (1986).

If the particle jumps in the chain of equidistant potential wells consisted of wells with the averaged time of life λ_1^{-1} and randomly distributed (with the concentration c) deep wells with the averaged time of life λ_2^{-1} , the mean square displacement $\overline{X^2}(t)$ of jumping particle is equal to:

$$\overline{X^2}(t) = \frac{l^2}{\bar{t}} t + \frac{c(1-c)(\lambda_2 - \lambda_1)^2 l^2}{[(1-c)\lambda_2 + c\lambda_1]^2} \{1 - e^{-[(1-c)\lambda_2 + c\lambda_1]t}\}, \quad \bar{t} = \frac{c}{\lambda_2} + \frac{(1-c)}{\lambda_1},$$

where l is the distance between wells.

Limiting cases relatively the time $\tau = [(1-c)\lambda_2 + c\lambda_1]^{-1}$:

Small times ($t \ll \tau$): $D_{t \ll \tau} = \frac{\lambda_1 l^2}{2}$;

Large times ($t \gg \tau, c \ll 1$): $D_{t \gg \tau} \approx \frac{\lambda_2 l^2}{2 \cdot c}$.

The method of random walk

1. Positions of deep potential wells are randomly chosen.
2. A particle can leave the well if the "energy fluctuation" (a random number) exceeds the depth of the well. The direction of the jump is chosen randomly. For nearest neighbors of deep wells probabilities of jumping into the deep well are larger than in the opposite directions on the value of $\Delta p^* = \frac{a}{2k_B T} P \nabla \varepsilon_{ii}$.
3. After a chosen number of jumps (unsuccessful jumps are also counted), the coordinate of the particle is recorded.

Actions 1-3 are considered as one "experiment". The "experiment" was repeated $10^5 - 10^6$ times. For each potential well, the sum of "experiments" in which the particle ends up in this well after a chosen number of jumps is collected.

After the entire cycle of "experiments" is carried out, the relative frequencies of the number of stops in each well are calculated. This distribution of relative frequencies along the chain of wells is the probability $G(x, t)$ that the particle is located at time t at the position x .

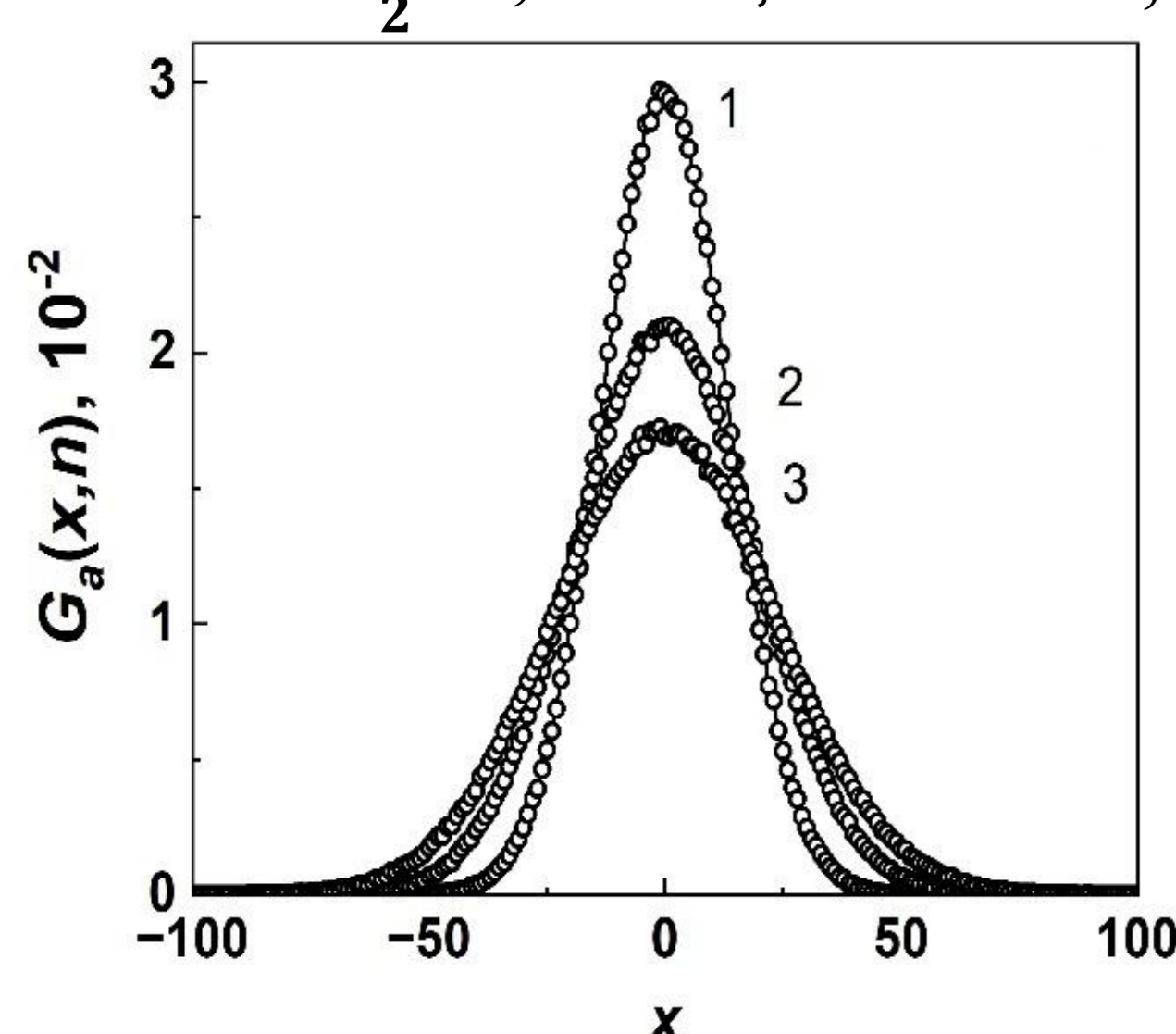
$$\overline{X^2}(t) = \frac{\int_{-L/2}^{L/2} x^2 G(x, t) dx}{\int_{-L/2}^{L/2} G(x, t) dx}$$

The aim of the work is to compare dependences $\overline{X^2}(t)$ obtained by these two methods and to extend the method of random walking to calculate $\overline{X^2}(t)$ for fluxes corresponding to the Gorsky effect.

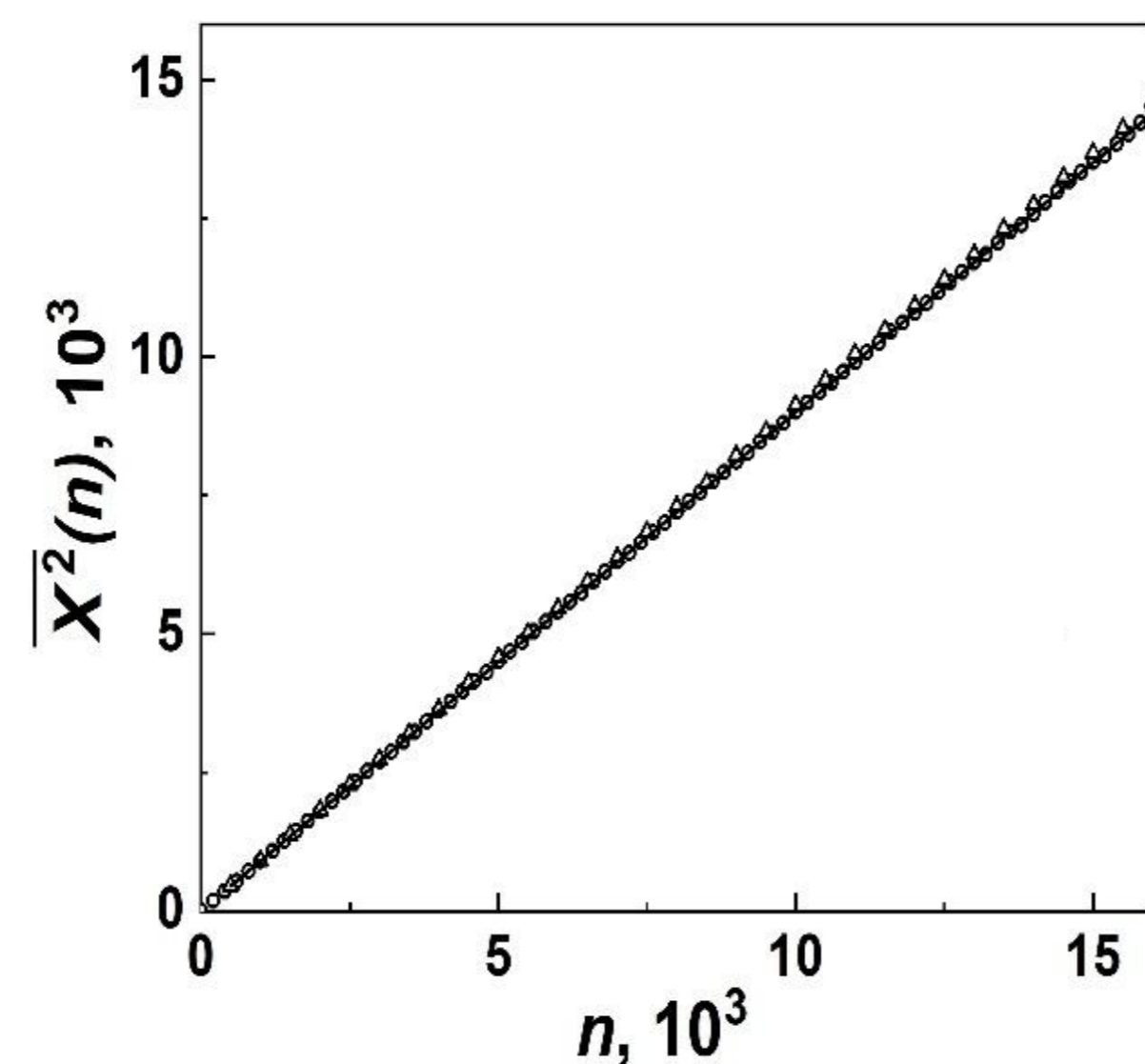
Test calculations for $\lambda_1 = 0.9, \lambda_2 = 0, \Delta p^* = 0$.

$$D = \frac{\lambda_1 l^2}{2}; \quad l^2 = 1; \quad D = 0.45;$$

$$\overline{X^2} = 2Dn$$



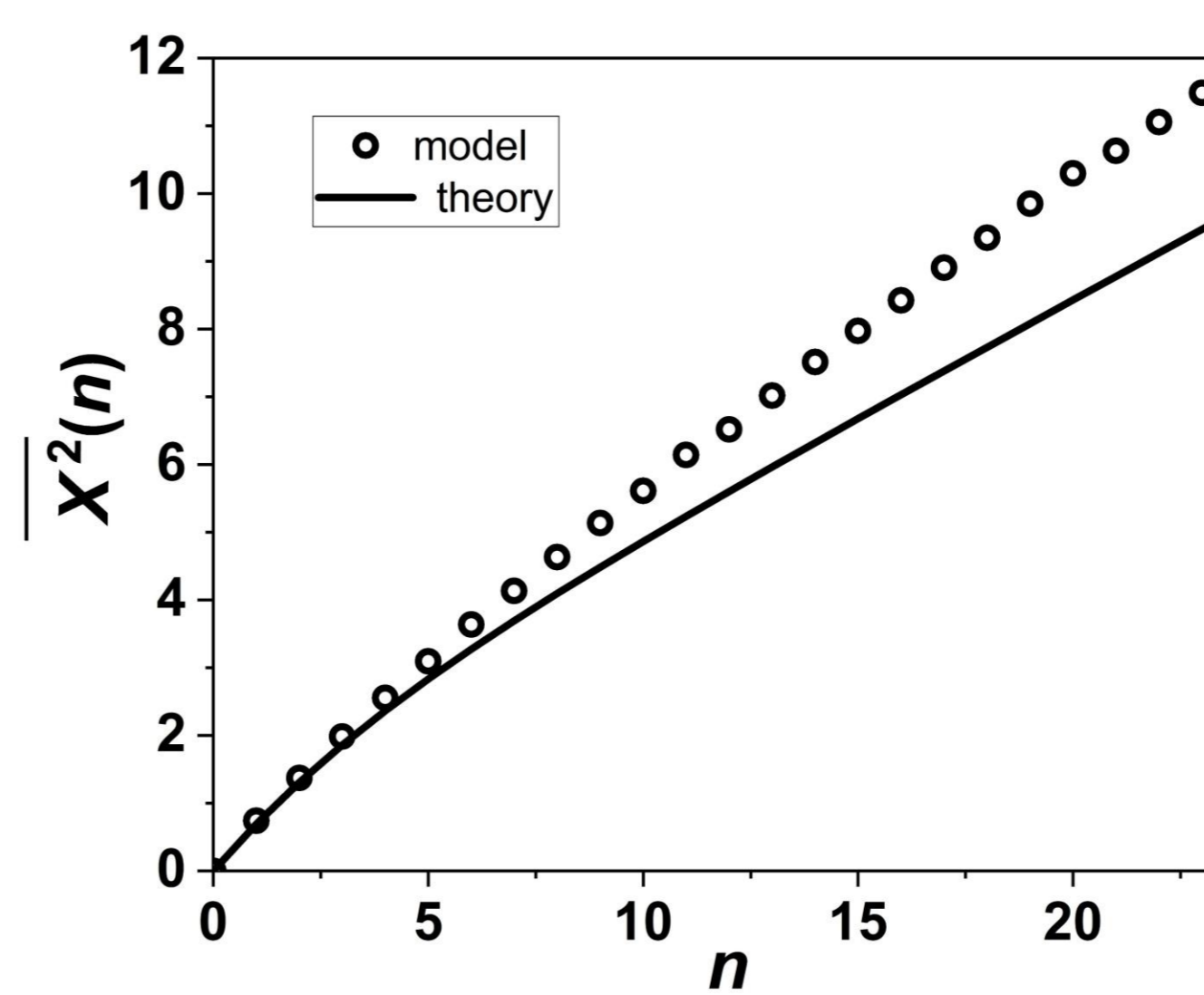
$G_a(x, n)$ for $n=200$ jumps (1), $n=400$ (2) та $n=600$ (3).



$$D = 0.451 \pm 0.001$$

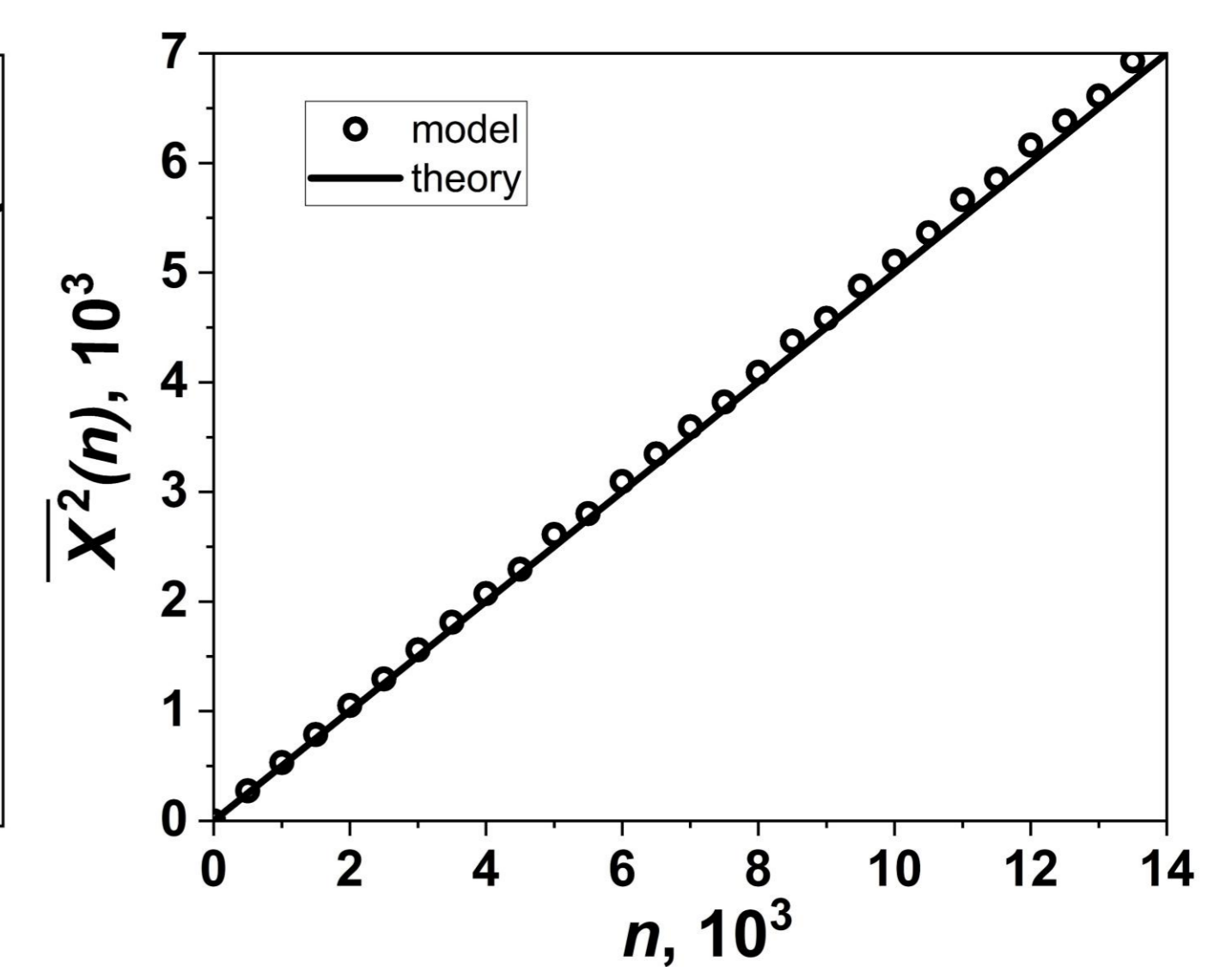
Results of calculations for $\lambda_1 = 0.9, \lambda_2 = 0.1, \Delta p^* = 0, c = 0.1$:

Small times ($t \sim \tau, \tau \approx 4$):



$$D_{n < 4} = \frac{\lambda_1 l^2}{2} = 0.45;$$

Large times ($t \gg \tau$):

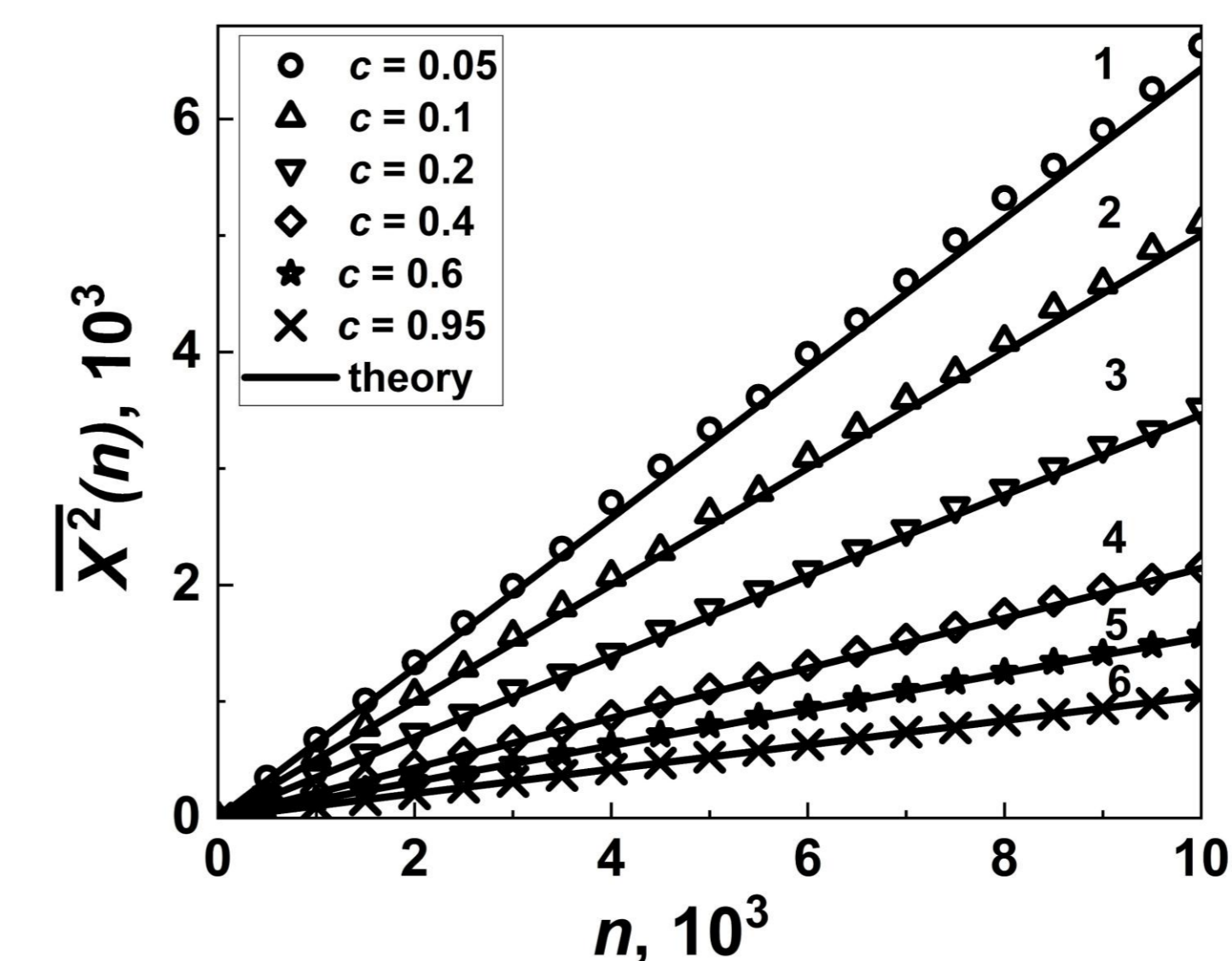


$$D_{n \gg \tau} \approx \frac{\lambda_2 l^2}{2 \cdot c} = 0.25.$$

$$D = 0.254 \pm 0.001.$$

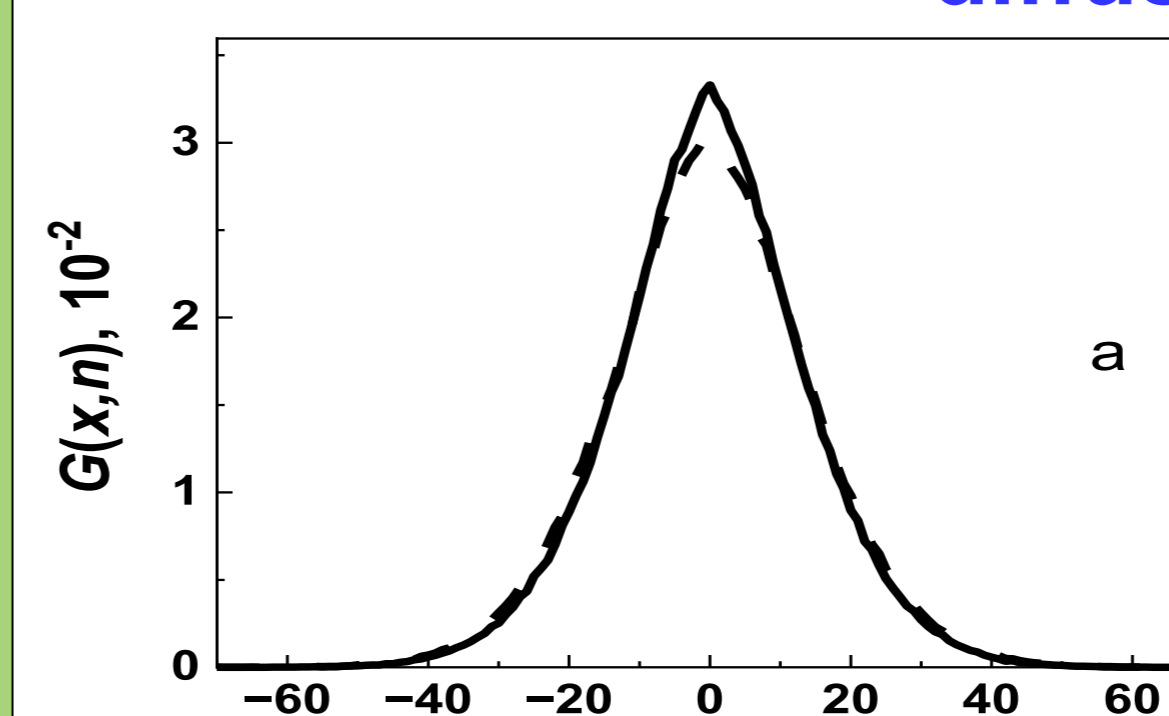
The deviation of calculations from the theory occurred because the CTRW theory was developed for the fixed concentration of traps in the unit of volume, whereas in our model this condition is violated.

Results of calculations for different c with $\lambda_1 = 0.9, \lambda_2 = 0.1, \Delta p^* = 0$:

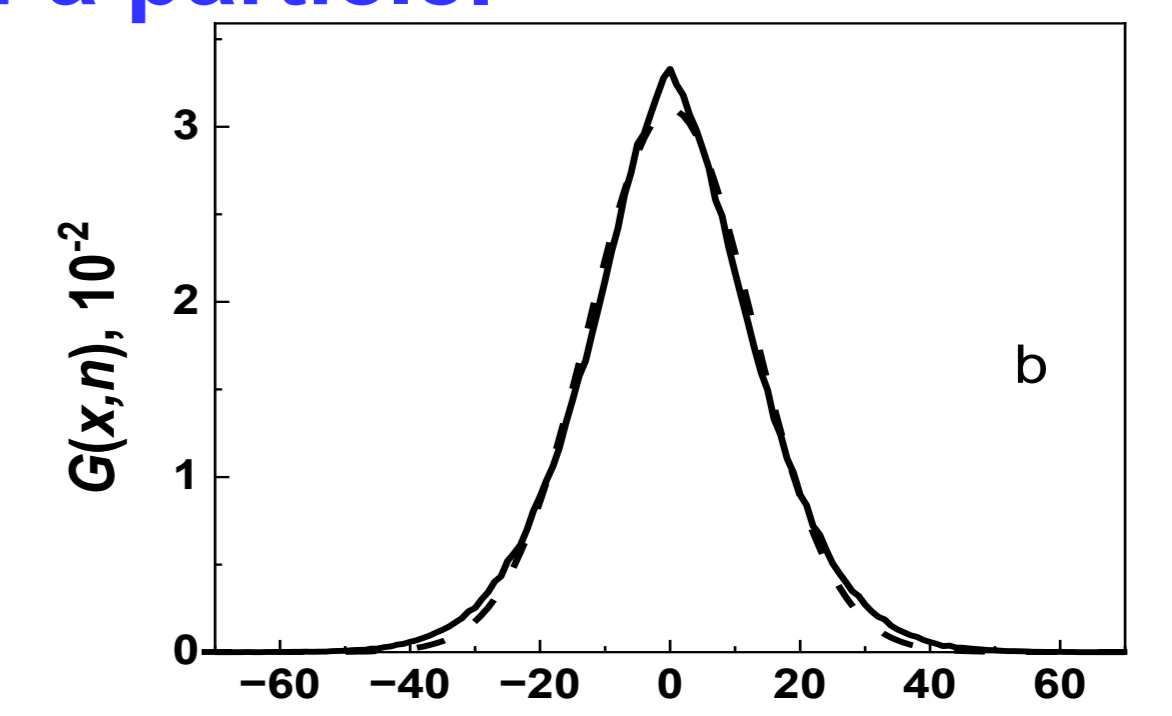


The CTRW theory describes satisfactory dependences $\overline{X^2} = f(n)$ at large times.

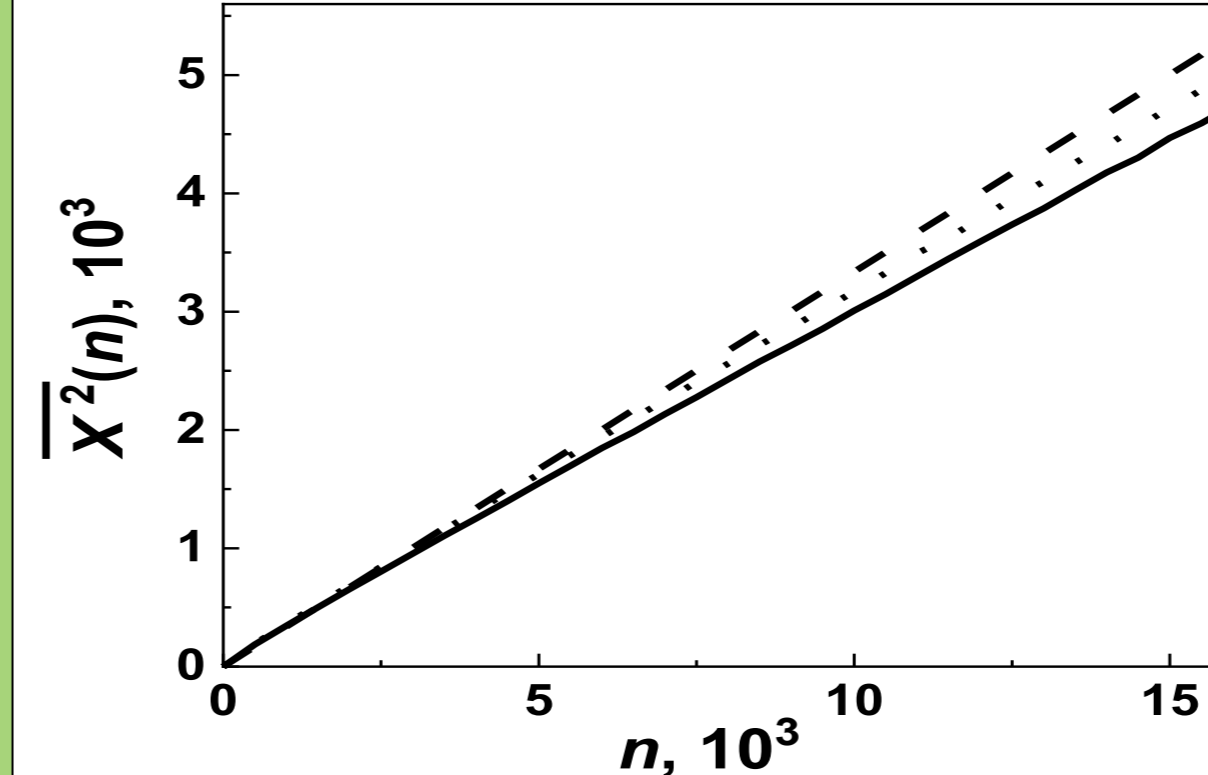
The influence of the lattice strain gradient near defects on diffusion of a particle.



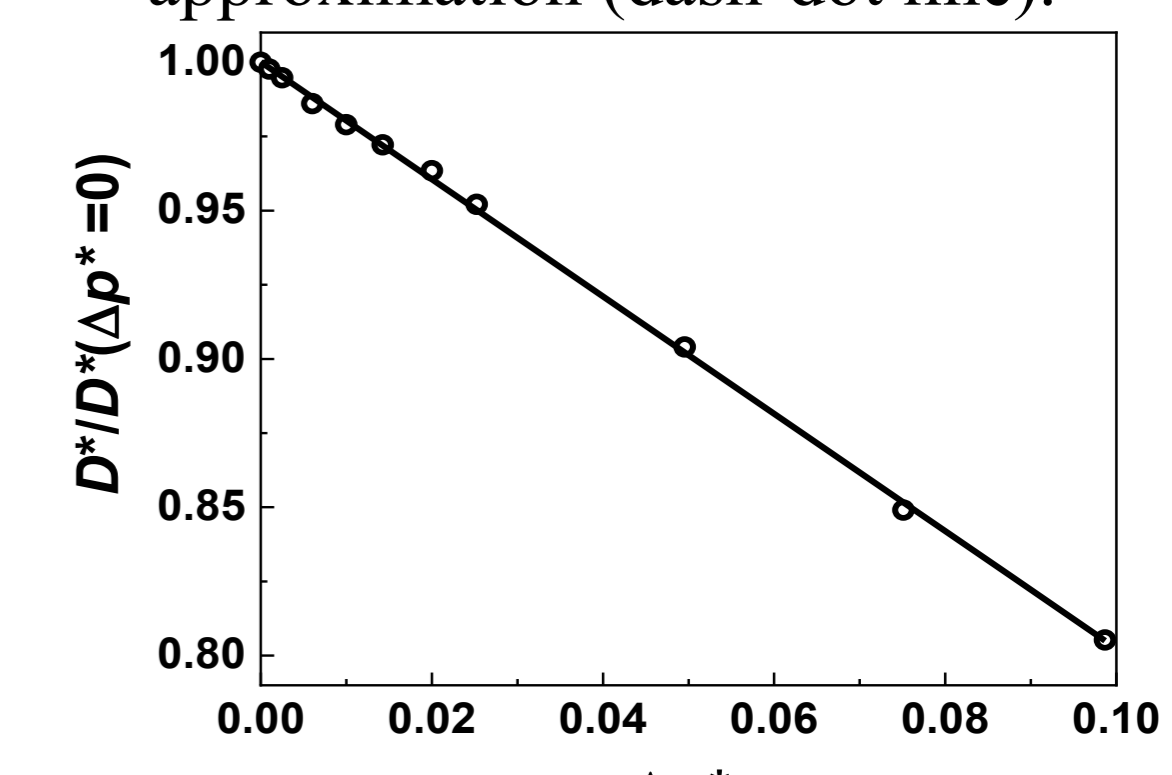
$\lambda_1 = 0.9, \lambda_2 = 0.05, c = 0.1.$
 $\Delta p^* = 0$ (dashed line), $\Delta p^* = 0,075$ (solid line)



$\Delta p^* = 0,075$ (solid line), Gaussian approximation (dash-dot line).



$\Delta p^* = 0$ (dashed line), $\Delta p^* = 0.05$ (dots), $\Delta p^* = 0.075, \Delta p = 0.04$ (solid line).



$$\frac{D^*}{D(\Delta p^* = 0)} = 1 - b \cdot \Delta p^*, \quad b = 1,98 \pm 0.02$$

CONCLUSIONS

1. We developed the model of random jumps of the particle along the chain of potential well with two different depths. We compared calculated dependences of the mean square displacement as a function of the number of jumps of the particle n with those calculated in ranges of the theory of continuous time random walking (CTRW).
2. We found that at small n dependences $\overline{X^2} = f(n)$ calculated in the model of random walk deviate from those predicted by the CTRW theory. This deviation occurred because the CTRW theory was developed for the fixed concentration of traps in the unit of volume, whereas in our model this condition is violated.
3. In the ranges of the developed model we investigated the flux into places with stretched crystal lattice near defects. We found that such a flux slows down diffusion process. The effective diffusion coefficient of the particle linearly decreases with increasing of the gradient of crystal lattice deformation near structural defects.