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NONLINEAR DYNAMICS OF INTERSTITIAL ATOM

B. KOZARZEWSKI

Institute of Physics, Cracow University of Technology
Podchorążych 1, 30-084 Kraków, Poland

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Interstitial impurity atom in an sc lattice driven by lattice vibrations is considered. The equation of motion derived is suitable for the study of an oscillator driven by modulated longitudinal wave and deterministic diffusion as well.

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1. Introduction

Diffusive motion is normally considered as a result of stochastic driven forces. Therefore in standard approach to diffusion one starts from the Langevin equation [1]

$$m\ddot{x} + \gamma\dot{x} = \xi(t), \tag{1}$$

where m is the mass of the particle and γ is the friction constant, $\xi(t)$ is the random force with zero mean and a nonzero variance. As an example let us mention a generalized Langevin equation describing dynamics of atoms interacting with thermal vibrations of the crystal lattice derived in Ref. [2]. Both the friction and the random force are very crude phenomenological substitutes of the real coupling of the particle to a heat bath. We hope that in a lattice system one can formulate a Fokker–Planck equation which describes diffusive motion and is free of that shortcoming. The first step is done in the present paper. It consists in derivation of the equation of motion in periodic potential for interstitial atom driven by phonons of wave vector q and frequency $\omega(q)$. In recent years, following the paper of Chirikov [3], studies on diffusion in deterministic systems get increasing interest. The deterministic diffusion is thought to be an interesting manifestation of classical chaos. In the present paper we consider a particular case of deterministic equation related to diffusion of an impurity atom. Many important processes occurring in solids are the result of interaction of the lattice vibrations with other subsystems. The one we are interested in is the phonons driven transport of interstitial atom

through the lattice. Generally, the dynamics of such a process constitutes a mechanical problem which, neglecting quantum effects, can be described by means of the classical mechanics. The phonon dynamics will be described in the harmonic approximation. The remainder of the paper can be outlined as follows. In Sec. 2 we set up a general model. A simplified model of motion along one of the square lattice directions is considered in Sec. 3 In Sec. 4 stationary points are shortly discussed. Section 5 contains a preliminary study of periodic orbits and their symmetry. In the end some concluding remarks are given.

2. Model

Let us consider the Bravais simple cubic lattice and one interstitial atom of radius vector r. Potential energy of the atom, when expanded with respect to deviation δr_l of the lattice atoms from their equilibrium positions r_l , becomes

$$\sum_l v(r - r_l - \delta r_l) = V(r) + \delta V(r).$$

Here

$$V(r) = \sum_l v(r - r_l) \tag{2}$$

means the periodic potential of the static lattice and

$$\delta V(r) = -\sum_l \mathrm{grad} v(r - r_l) \cdot \delta r_l \tag{3}$$

is the contribution to the potential coming from nonperiodic deviation δr_l. Within the nearest neighbour and harmonic approximation for the perfect lattice the displacement of atom at l-th lattice site due to a single normal mode of vibration is

$$\delta r_l = e \exp[\mathrm{i}(r \cdot q - \omega(q)t], \tag{4}$$

where $\omega(q)$ represents the frequency of longitudinal or transversal phonons, and e depends on polarization of the lattice wave. With Eq. (4) the nonperiodic contribution to the $\delta V(r)$ which we call potential in spite of its time dependence, can be rewritten as follows

$$\delta V(r) = -W(r) \exp[\mathrm{i}(r \cdot q - \omega(q)t].$$

The periodic function of radius vector

$$W(r) = \sum_l \mathrm{grad} v(r - r_l) \cdot e \exp(\mathrm{i}(r - r_l) \cdot q) \tag{5}$$

can be Fourier transformed

$$W(r) = \sum_Q W_Q \exp(\mathrm{i} Q \cdot r),$$

where Q is the reciprocal lattice vector and

$$W_Q(r) = \frac{1}{\Omega} \int W(r) \exp(-\mathrm{i} Q \cdot r) \mathrm{d}^3 r. \tag{6}$$

Finally, the contribution of a single lattice wave of wave vector q and frequency $\omega(q)$ to the interstitial atom potential becomes

$$\delta V(r) = -\sum_Q W_Q \exp\{\mathrm{i}[(Q + q) \cdot r - \omega(q)t]\}. \tag{7}$$

The force on the interstitial atom consists therefore of two terms, the first coming from the static lattice

$$F(r) = -\mathrm{grad}V(r), \tag{8}$$

and the second one due to the lattice vibrations

$$\delta F(r) = -\mathrm{grad}\delta V(r). \tag{9}$$

Neglecting other forces like the one coming from friction, the Newton equation of motion of an interstitial atom reads

$$m\frac{d^2r}{dt^2} = F(r) + \delta F(r). \tag{10}$$

3. Model potential

A reasonable and at the same time very simple form of periodic potential experienced by an interstitial atom in a simple cubic lattice having a lattice constant a can be taken, for example, as

$$V(r) = V_0\left[\cos\left(\frac{2\pi x}{a}\right) + \cos\left(\frac{2\pi y}{a}\right) + \cos\left(\frac{2\pi z}{a}\right)\right]. \tag{11}$$

Therefore the single lattice wave of wave vector q contributes to the interstitial atom potential as follows

$$\delta V(r) = \frac{2\pi V_0}{a}\left[e_x \sin\left(\frac{2\pi x}{a}\right) + e_y \sin\left(\frac{2\pi y}{a}\right) + e_z \sin\left(\frac{2\pi z}{a}\right)\right]$$

$$\times \cos[laq_x + maq_y + naq_z - \omega(q)t]$$

for

$$(l - 1/2)a \leq x \leq (l + 1/2)a, \quad (m - 1/2)a \leq y \leq (m + 1/2)a$$

and

$$(n - 1/2)a \leq z \leq (n + 1/2)a,$$

where l, m and n are integers. The problem of solution of Eq. (10) becomes much more tractable if we allow the interstitial atom to move only along the $y = a/2$, $z = a/2$ line. The quantities q, F and e mean from now on x-components of the corresponding vectors. We also neglect the contribution to the right hand side of Eq. (9) coming from transversal phonons. The forces in the present case of one-dimensional motion read

$$F(x) = \frac{2\pi V_0}{a}\sin\left(\frac{2\pi x}{a}\right) \tag{12}$$

and

$$\delta F(x) = V_0 e\left(\frac{2\pi}{a}\right)^2 \cos\left(\frac{2\pi x}{a}\right)\cos(alq - \omega(q)t) \tag{13}$$

for $(l - 1/2)a \leq x \leq (l + 1/2)a$, l being an integer. Conventional dimensionless coordinate is $\xi = 2\pi(x/a + 1/2)$ and time $\tau = 2\pi t/T_0$, where $T_0 = a\sqrt{m/V_0}$ and $\omega = 2\pi/T_0$ are natural period and frequency of small oscillations of the interstitial

atom, respectively. Introducing dimensionless force constant $F = 2\pi e/a$ Eq. (10) for one-dimensional motion becomes

$$\ddot{\xi} = -\sin\xi + F\cos\xi\cos(kp(\xi) - w\tau), \tag{14}$$

where $k = qa$ and $w = \omega/\omega_0$ are dimensionless wave vector and frequency of phonons, respectively, and $p(x) = [\xi/(2\pi)]$, where $[x]$ denotes the integer part of x. It has the form of the equation of motion for a particle moving in the field of modulated lattice plane wave.

In principle all phonons of the wave vector $-\pi/a \leq q \leq \pi/a$ or $-\pi \leq k \leq \pi$ contribute to the force δF. It is instructive, however, to consider first the motion due to force from phonon of single wave vector q or a pair of phonons having opposite wave vectors. In the latter case instead of (14) we get

$$\ddot{\xi} = -\sin\xi + F\cos\xi\ \cos(kp(\xi))\cos(w\tau). \tag{15}$$

Equation (14) or (15) is suitable for the study of an oscillator driven by longitudinal running or standing lattice wave of wave vector q and deterministic diffusion as well. If the second term on the right hand side of Eq. (14) is replaced by $F\cos(k\xi - \omega\tau)$ (with arbitrary k) we get the equation of motion for a particle moving in the field of plane wave analyzed by Zaslawsky et al. [4]. If a gradient of temperature along the x-axis is applied to the crystal the prevalent number of phonons move from the warmer end of the crystal to the cooler one. We suggest that under above circumstances the diffusive motion of the interstitial atom follows the equation of motion (14) with parallel to the gradient of temperature. On the other hand if the lattice is in thermal equilibrium there are equal numbers of phonons moving to the right as well as to the left. In that case suitable is the equation of motion of the particle in a modulated standing lattice wave, i.e. Eq. (15). The results presented constitute a starting point to analytical and numerical study of deterministic diffusion in the simple, nevertheless physically relevant system. In the following we restrict our attention to Eq. (15). Let us, however note that $p(x)$ is a discontinuous function of coordinate x which presents a serious difficulty in numerical study of the equation. Therefore we approximate $p(x)$ by $x/(2\pi)$. Thus instead of e.g. Eq. (15) we get

$$\ddot{x} = -\cos x + F\cos x\cos(kx)\cos(wt), \tag{16}$$

where from now on the k denotes dimensionless wave vector, $-1/2 \leq k \leq 1/2$ and t means dimensionless time.

4. Stationary points

The autonomous system equivalent to Eq. (16) reads

$$\frac{dx}{dt} = y,$$

$$\frac{dy}{dt} = -\sin x + F\cos x\cos(kx)\cos z,$$

$$\frac{dz}{dt} = w. \tag{17}$$

A solution of the set $\sin x - F\cos x\cos(kx) = 0$, $y = 0$, $z = 0$ determines stationary points of the flow (17) which are stable if derivative of the right hand side of Eq. (17) is negative. Stationary points from a range $(-2\pi, 2\pi)$ as a function of the force constant F are shown in Fig. 1a for wave vector $k = 0.5$ and Fig. 1b for

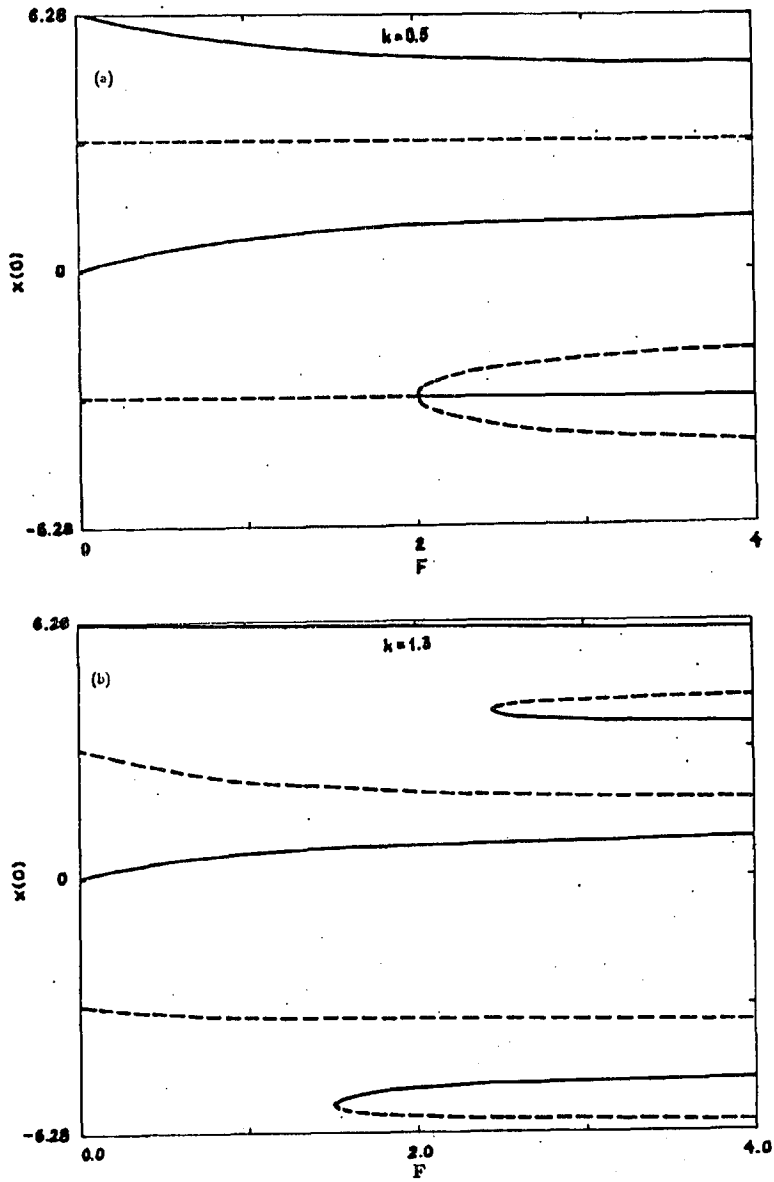

Fig. 1. Stationary points as a function of force amplitude F, (a) for $k = 0.5$ and (b) for $k = 1.3$.

$k = 1.3$. The branch of stable (unstable) stationary points is indicated by solid (broken) line. When k increases branching points move toward lower values of F. In general, branching points occur when wave vector $k = (4l + 3)/2n$, where n, l are integers and $n \neq 0$. Their coordinates on the (F, x)-plane are $F = 1/k$, $x = n$. There are also a number of turning points (saddle-node bifurcations), their density grows rapidly when k increases. Their coordinates (F, x), which, like branching points, depend on k as a parameter, satisfy the following set of equations:

$$\tan(x) - F\cos(kx) = 0 \quad \text{and} \quad k\sin(2x)\tan(kx) + 2 = 0.$$

Like before, when k increases turning points occur at lower force constant F and their density along x direction increases.

5. Periodic solutions

Periodic orbits of the nonlinear system are of great interest for many reasons and usually they are determined prior to discussion of more complex solutions. We have found (using standard path-following method, consult e.g. Ref. [5]) period-1 and period-2 orbits for a couple of parameter sets k, w and F at a constant initial velocity $v(0) = 0$ and an initial coordinate $-\pi \leq x(0) \leq \pi$. Among the period-1 orbits there are a number of symmetric orbits. According to e.g. Swift et al. [6] if the right hand side of the nonautonomous system of the first order ordinary differential equation (ODE), in our case it is

$$F(x,t) = \left\{ \begin{array}{c} y \\ -\sin x + F\cos(kx)\cos(wt) \end{array} \right\},$$

possesses property that $F(x,t) = -F(-x, t+T/2)$ the system is called symmetric. The periodic solution to the system is called symmetric if it satisfies

$$x(t) = -x(t + T/2) + 2n\pi,$$

$$y(t) = -y(t + T/2) \tag{18}$$

with n an integer. Therefore symmetric solution is invariant with respect to inversion about the point $x = n\pi$. To find a periodic solution we look for an initial coordinate $x(0)$ (always assuming $y(0) = 0$) such that the computed trajectory satisfies periodicity conditions with period T or $2T$. Afterwards we establish symmetry and stability of the orbit. The initial coordinate as a function of force amplitude F of period-1 solution for $k = 0$ and $w = 0.4$ is shown in Fig. 2. The same dependence of period-1 and period-2 solutions for $k = 0.25$, $w = 0.4$ and $w = 0.8$ are shown in Figs. 3 and 4, respectively. Numbers 1 or 2 denote period-1 or period-2 solutions, symmetric branches bear letter s. Stable solutions are indicated by solid lines and unstable one by broken lines. Stability of each orbit was determined according to eigenvalues of the monodromy matrix. Swift et al. [6] stated that the symmetric periodic orbit usually bifurcates to nonsymmetrical orbit before a period doubling occurs. We have found that not all symmetric solutions follow that rule. Exceptional are two symmetric orbits marked with H, one for $w = 0.4$ and one for $w = 0.8$, which experience Hopf bifurcation to period-2 orbit prior to bifurcation to nonsymmetric period-1 orbit.

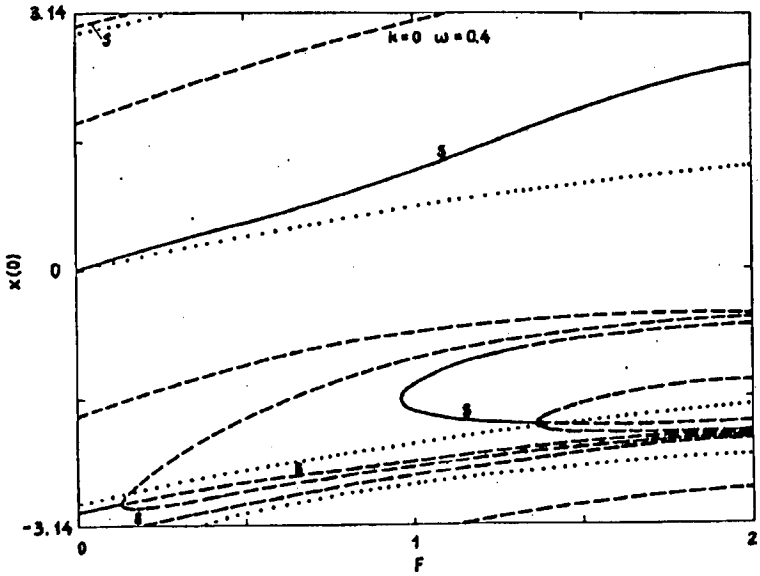

Fig. 2. Initial coordinate of period-1 solutions as a function of amplitude F for $k = 0$, $w = 0.4$. Dotted lines represent initial coordinate of approximate symmetric orbit (Eq. (20)).

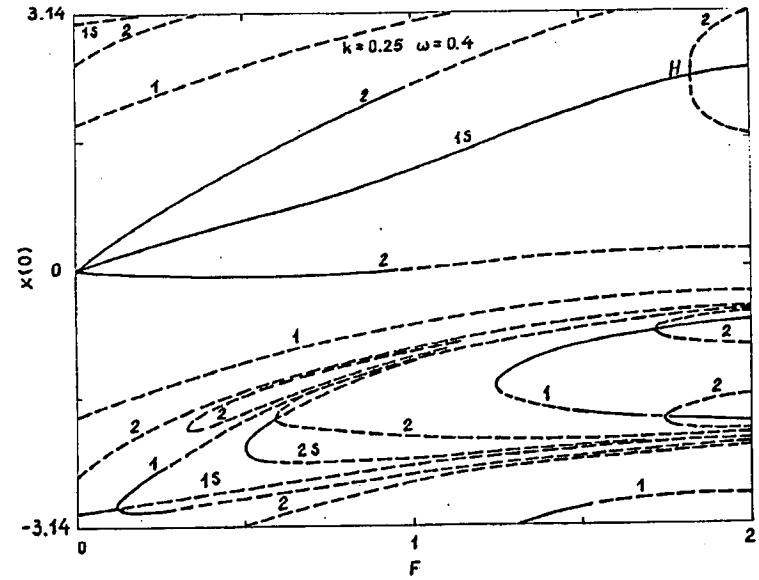

Fig. 3. Initial coordinate of period-1 and period-2 solutions as a function of amplitude F for $k = 0.25$ and $w = 0.4$.

In the end we tried to establish how far an approximate analytical method can be useful in predicting periodic solutions. We were using perturbation tech-

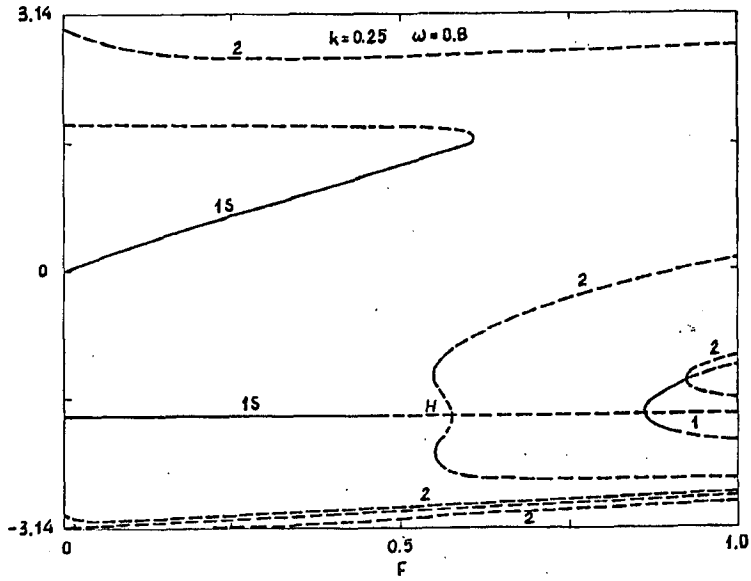

Fig. 4. Initial coordinate of period-1 and period-2 solutions as a function of amplitude F for $k = 0.25$ and $w = 0.8$.

nique, therefore we introduced a small parameter ε and looked for a solution of the form

$$X(t) \equiv x(t) - \xi = A\cos(wt) + X_1 + X_2,$$

where ξ is constant term, X_1 and X_2 are of order ε and ε^2, respectively. Equation (16) is rewritten in terms of $X(t)$ as follows:

$$\ddot{X} + w^2 X + \varepsilon f + \varepsilon^2 g = 0, \tag{19}$$

where

$$\varepsilon f = -w^2 X + \cos\xi \sin X - 0.5F \sum_{i=1}^{2} \cos(\alpha_i \xi)\cos(\alpha_i X)\cos(wt),$$

$$\varepsilon^2 g = \sin\xi \cos X + 0.5F \sum_{i=1}^{2} \sin(\alpha_i \xi)\sin(\alpha_i X)\cos(wt).$$

Here $\alpha_1 = 1 - k$, $\alpha_2 = 1 + k$. With the use of the asymptotic method developed first by Bogoliubov and Mitropolski [7] (see also recent application [8]) we have found that in general the approximate periodic solution is of the form

$$x(t) = \xi + (A + A_1)\cos(wt) + A_2\cos(2wt) + A_3\cos(3wt). \tag{20}$$

There is a set of two equations

$$-w^2 A + 2\cos\xi J_1(A) - 0.5F \sum_{i=1}^{2} \cos(\alpha_i \xi)[J_0(\alpha_i A) - J_2(\alpha_i A)] = 0,$$

$$\sin\xi J_0(A) + 0.5F\sum_{i=1}^{2}\sin(\alpha_i\xi)J_1(\alpha_i A) = 0,$$

which determine the constant term ξ and amplitude A, $J_n(x)$ denotes Bessel function of n-th order. The amplitudes A_1 to A_3 depend on ξ and A, we however do not quote corresponding equations because of their complexity. We have solved a relatively simple case of $k = 0$ and present results in Fig. 2, where dotted lines show the initial coordinate $x(0)$ of the approximate solution versus force amplitude F. We restrict ourselves to symmetric orbits ($A_2 = 0$) as nonsymmetric orbits following Eq. (20) rather badly approximate the exact ones.

6. Concluding remarks

In order to study the effect of phonons on diffusion of defects in crystals we propose the simple model of particle motion in the periodic lattice potential subject to additional force from modulated wave. We performed preliminary investigation of the model corresponding to the thermal equilibrium. The results can be summarized as follows: (i) The one-dimensional motion of the interstitial atom in the field of longitudinal lattice wave of wave vector k is considered. (ii) Stability points for some k and the wave amplitude F are found. (iii) Low order periodic orbits of the system are studied numerically and some of them are compared with approximate analytic solutions. (iv) The bifurcation diagrams showing an initial coordinate of periodic orbits versus F for some k are found.

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