The Structure of Self-Interstitial Atom Defects

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Introduction

The first question that one encounters in the field of radiation damage and radiation stability of materials is the question about the structure of the most fundamental objects generated by irradiation, the point defects. There are two basic types of point defects, a vacancy and a self-interstitial atom. Other defects form when vacancies or self-interstitial atoms agglomerate, or when they react with other elements of microstructure (for example with grain boundaries). It is surprising that although the science of radiation damage has a 60 years long history, it is only in the last few years that consistent information about the structure of point defects became available. Contrary to the established pattern of development of understanding of radiation damage where simulations mostly ”predicted the past”, the new information came directly from calculations.

These notes describe recent progress in understanding the structure of defects in the non-magnetic body-centred cubic metals and in iron.

SUMMARY

- Structure of defects in bcc metals and iron
- The solvable models of defects
- Brownian motion of defects

Crystal structure of metals and the Periodic Table

There are seven metals in the Periodic table that have body-centred cubic structure. They are vanadium, niobium and tantalum (V, Nb and Ta) forming group 5B of the periodic table, chromium, molybdenum and tungsten (Cr, Mo and W) forming group 6B of the periodic table, and iron (Fe), the position of which in group 8B of the periodic table is anomalous. The word ”anomalous” is used here in the sense that while elements of groups 5B and 6B *all* have the same bcc crystal structure, the two other elements of group 8B, ruthenium and osmium have the hexagonal closed packed crystal structure. We now know that it is magnetism that is responsible for the fact that the crystal structure of iron is anomalous.

The Periodic Table

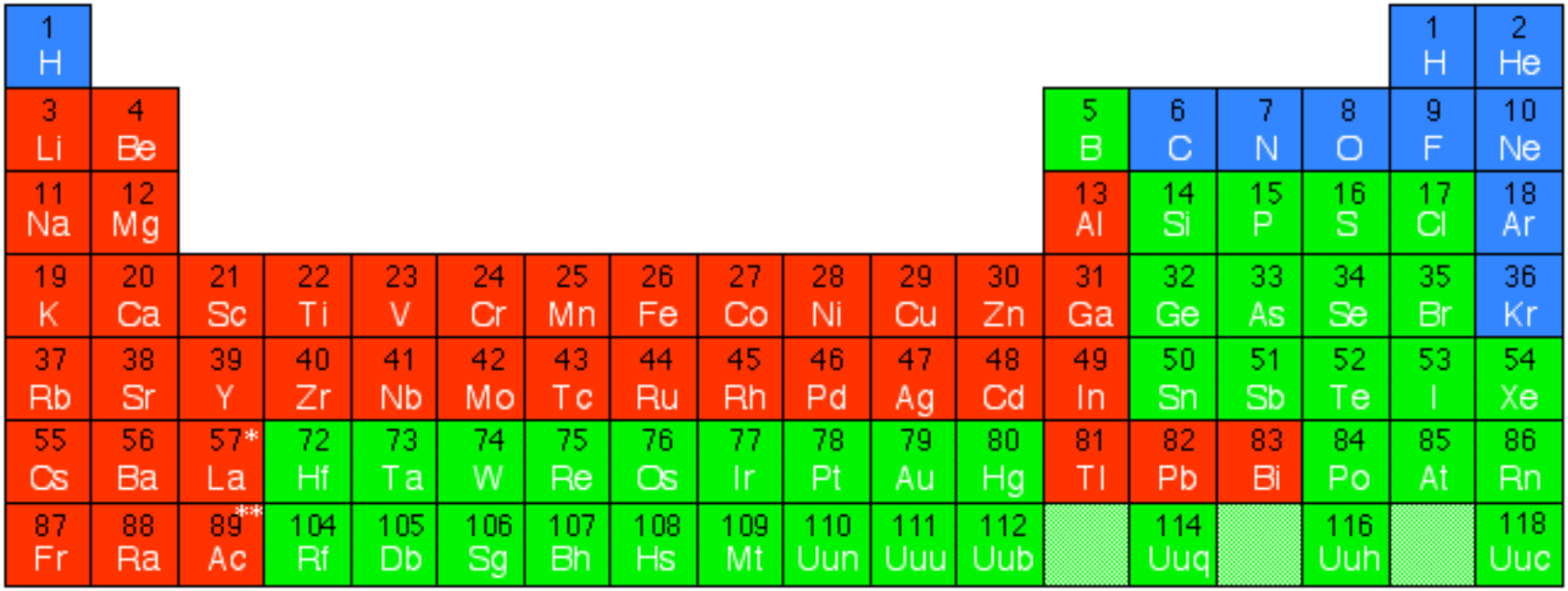

Figure 1: Vanadium, niobium and tantalum form group 5B. Chromium, molybdenum and tungsten form group 6B. Iron is at the top of group 8B.

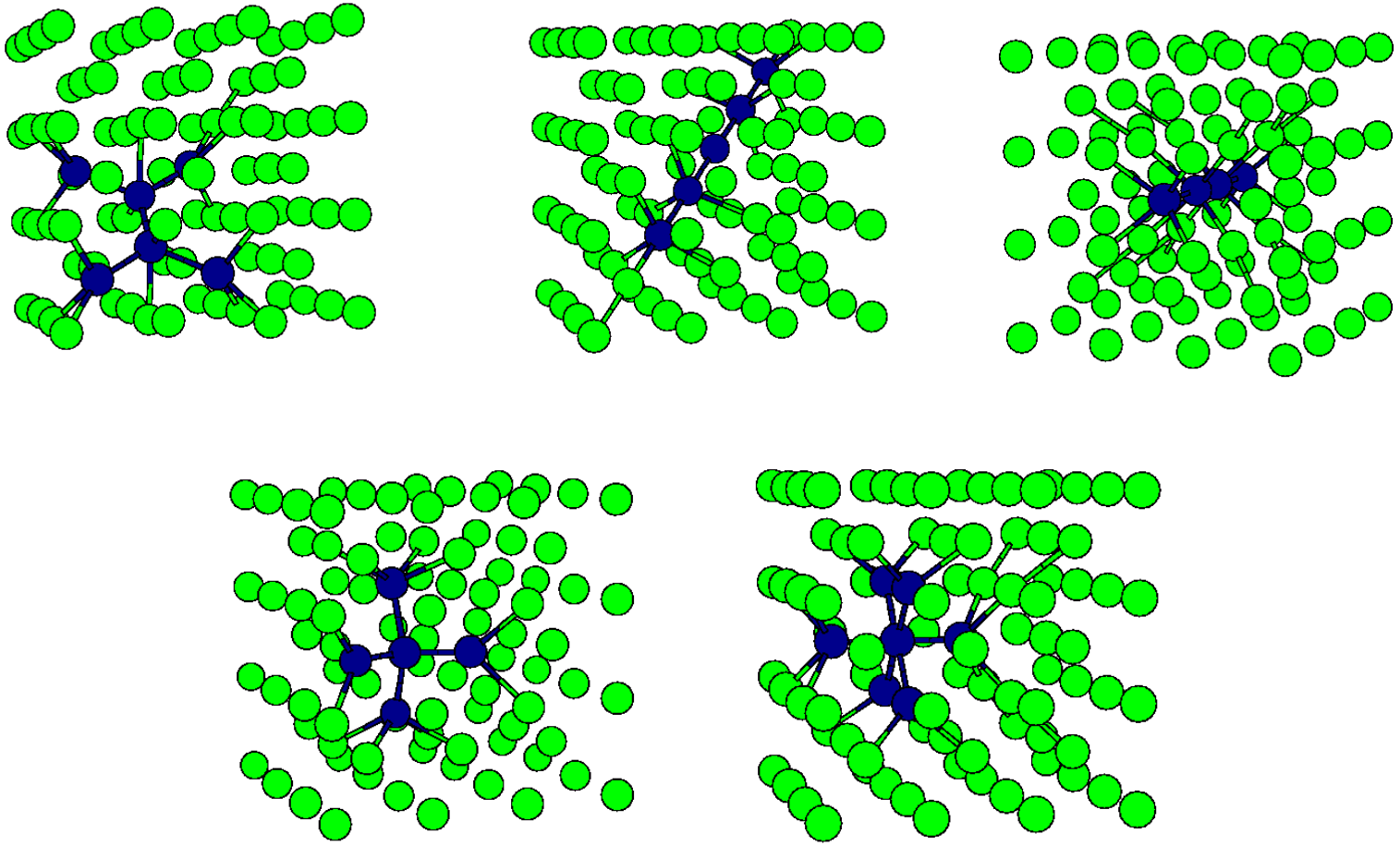

Figure 2: The five fundamental structures formed by inserting an extra atom in bcc crystal lattice. From left to right this figure shows, top row: (a) the 110 dumbbell (b) the 111 crowdion, (c) the 100 crowdion; bottom row (d) the tetrahedral configuration and (e) the octahedral configuration.

Table 1: Basic parameters of bcc transition metals evaluated using density functional theory, and the formation energies (in eV) of point defects in groups 5B and 6B and bcc iron, Refs. [4] and [5].

	V	Nb	Ta	Cr	Mo	W	Fe
a (Å)	3.04 *3.03*	3.32 *3.30*	3.31 *3.30*	2.85 *2.88*	3.17 *3.15*	3.18 *3.16*	2.88 *2.87*
B (Mbar)	1.71 *1.62*	1.73 *1.70*	1.99 *2.00*	1.92 *1.90*	2.68 *2.72*	3.05 *3.23*	1.80 *1.68*
H^v (eV)	2.51 *2.1–2.2*	2.99 *2.6–3.1*	3.14 *2.8–3.1*	2.64 *2.0–2.4*	2.96 *2.6–3.2*	3.56 *3.5–4.1*	2.07 *1.8 – 2.2*
H^v_m (eV)	0.62 *0.5-1.2*	0.91 *0.6-1.0*	1.48 *0.7-1.9*	0.91 *0.95*	1.28 *1.3-1.6*	1.78 *1.7–2.0*	0.67 *0.55*
$\langle 111 \rangle$ dumbbell	3.367 *3.14*	5.253 4.795	5.832 7.157	5.685	7.417 *7.34*	9.548 8.919	4.45
$\langle 111 \rangle$ crowdion	3.371 *3.15*	5.254 4.857	5.836 7.158	5.660	7.419 *7.34*	9.551 8.893	4.45
$\langle 110 \rangle$	3.652 *3.48*	5.597 4.482	6.382 6.847	5.674	7.581 *7.51*	9.844 9.641	3.75
tetrahedral	3.835 *3.69*	5.758	6.771	6.189	8.401 *8.20*	11.05	4.26
$\langle 100 \rangle$	3.918 *3.57*	5.949 4.821	7.003 8.068	6.643	9.004 *8.77*	11.49 9.815	4.75
octahedral	3.964 *3.62*	6.060	7.095	6.723	9.067 *8.86*	11.68	4.94

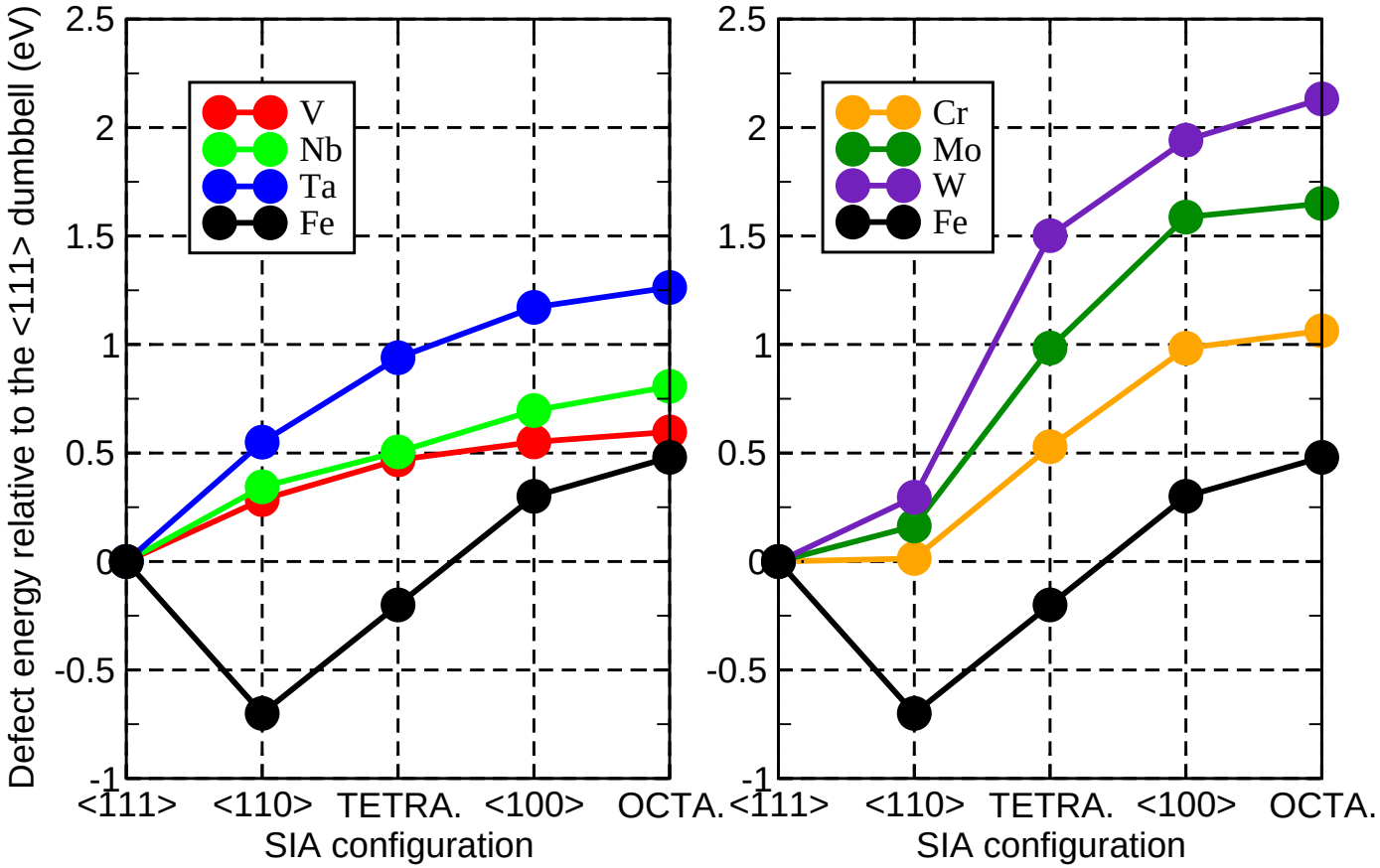

Figure 3: Formation energies of the five fundamental configurations of self-interstitial atom defects plotted for metals of group 5B and iron (left) and for metals of group 6B and iron (right) [from Ref. 5]. The curves show that in all the non-magnetic bcc metals the 111 crowdion configuration has the lowest formation energy. The ”anomalous” trend exhibited by iron is due to magnetism.

Table 2: A more extensive compilation of calculated and experimentally observed parameters, Ref. [6]

	V	Nb	Ta	Cr	Mo	W	Fe
a (Å)	3.04	3.32	3.31	2.85	3.17	3.18	2.84
	3.03	3.30	3.30	2.88	3.15	3.16	2.87
B (Mbar)	1.71	1.73	1.99	1.92	2.68	3.05	1.82
	1.62	1.70	2.00	1.90	2.72	3.23	1.68
H_f^v	2.51	2.99	3.14	2.64	2.96	3.56	2.15
	2.1–2.2	2.6–3.1	2.8–3.1	2.0–2.4	2.6–3.2	3.5–4.1	1.6–2.2
H_m^v	0.62	0.91	1.48	0.91	1.28	1.78	0.64, 0.67
	0.5–1.2	0.6–1.0	0.7–1.9	0.95	1.3–1.6	1.7–2.0	0.55
$H_f^{2v}(1NN)$	4.94	5.62	6.01	5.01	5.60	6.71	4.08
	3.90–3.99	5.11	5.47	3.34	5.75	7.32	3.31, 3.85
$H_f^{2v}(2NN)$	4.80	5.57	5.89	5.16	5.78	6.93	4.01
	3.90–4.21	5.11	5.50	3.35	5.77	7.36	3.34, 3.83
$H_b^{2v}(1NN)$	0.08	0.36	0.27	0.27	0.32	0.41	0.22
	0.30–0.45	0.39	0.43	0.26	0.45, 0.39	0.58, 0.45	0.27, 0.22, 0.19
$H_b^{2v}(2NN)$	0.22	0.41	0.39	0.12	0.14	0.19	0.29
	0.30–0.23	0.39	0.41	0.25	0.43, 0.25	0.54, 0.29	0.24, 0.15, 0.30, 0.21
$\langle 111 \rangle$ dumbbell	3.367	5.253	5.832	5.685	7.417	9.548	4.61
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octahedral	3.964	6.060	7.095	6.723	9.067	11.68	5.21
	3.62		7.020		8.86		5.34, 4.94

References

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Introduction to Part II

We now know that single self-interstitial atom defects in *all* the non-magnetic bcc metals adopt linear 111 crowdion configurations. It appears to be possible to formulate a simple yet still fairly accurate analytically solvable model describing not only the individual 111 crowdion defects, but also clusters of crowdion defects. A similar model can be used to follow the link between mathematical solutions describing a single interstitial defect (in other words, an extra atom embedded in a crystal lattice) and an edge dislocation (i.e. a half-plane of atoms embedded in a crystal lattice). In these notes we first investigate the conventional Frenkel-Kontorova model, then introduce the *multistring* Frenkel-Kontorova model, and prove that in the continuous limit the latter is equivalent to the Peierls-Nabarro model of an edge dislocation.

SUMMARY

- The Frenkel-Kontorova model
- Crowdion as a solution of the sine-Gordon equation
- Comparison with atomistic simulations
- The multistring Frenkel-Kontorova model
- Exact solution for an edge dislocation and comparison with the Peierls model

We start from defining the notion of a string of atoms in a crystal lattice. This concept is central to the formulation of what is known as *the Frenkel-Kontorova model*.

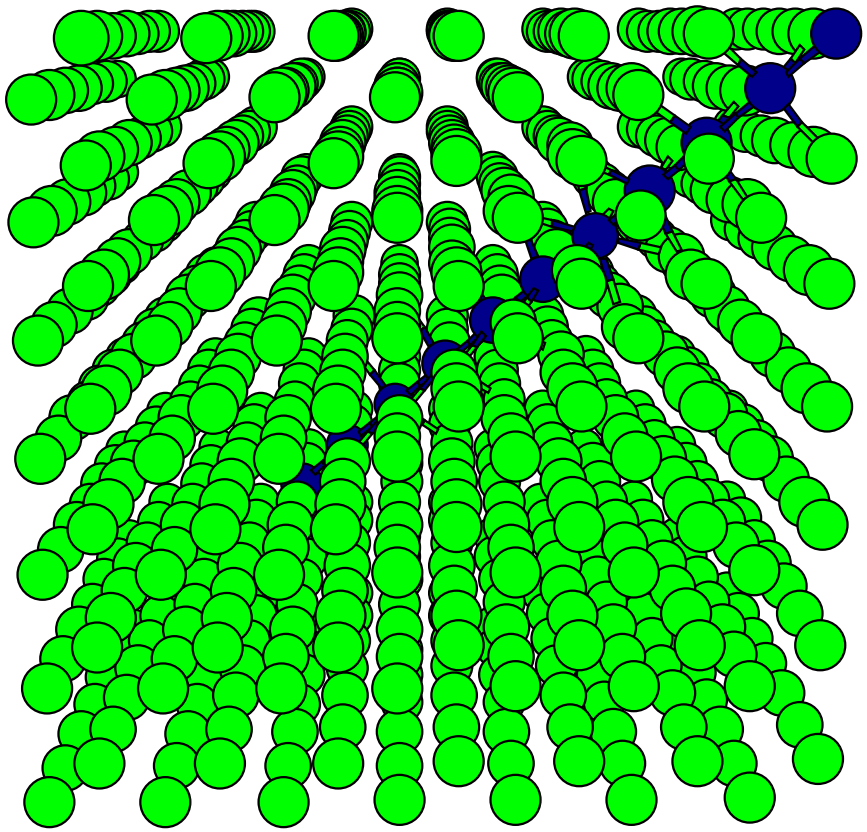

Figure 4: Atoms shown in blue colour form a string running in the 111 direction. This string contains one extra atom in comparison with similar strings that surround it.

Examination of Fig. 4 shows that any closed-packed string of atoms in a crystal lattice satisfies two conditions. 1. If we freeze the surrounding lattice and translate the string in the direction of its axis then the potential felt by atoms forming the string is *periodic*. 2. Atoms in the string interact by means of elastic compression or extension of bonds linking neighbouring atoms. These two, fairly natural, assumptions represent the content of the "classical" Frenkel-Kontorova model.

This model is described by the Lagrangian

$$\mathcal{L} = \sum_{n=-\infty}^{\infty} \frac{m\dot{z}_n^2}{2} - \frac{\alpha}{2} \sum_{n=-\infty}^{\infty} (z_{n+1} - z_n - a)^2 - \frac{m\omega_0^2 a^2}{2\pi^2} \sum_{n=-\infty}^{\infty} \sin^2\left[\frac{\pi z_n}{a}\right]. \qquad (1)$$

A Lagrangian is the difference between the kinetic and potential energies of the system $\mathcal{L} = \mathcal{T} - \mathcal{U}$, expressed in terms of velocities and positions of atoms. In equation (1) the first term is the total kinetic energy of all the atoms *of the mobile string* (but not of the surrounding lattice!). The two other terms are the elastic energy of interaction between atoms in the string

$$\frac{\alpha}{2} \sum_{n=-\infty}^{\infty} (z_{n+1} - z_n - a)^2,$$

and the potential energy of interaction between atoms of the string with the surrounding crystal lattice (which is assumed to be frozen in its ideal equilibrium configuration)

$$\frac{m\omega_0^2 a^2}{2\pi^2} \sum_{n=-\infty}^{\infty} \sin^2\left[\frac{\pi z_n}{a}\right].$$

The Frenkel-Kontorova model

It is not overly significant that the potential energy of interaction between atoms of a string and the surrounding lattice is taken in the form of a sum of $\sin^2\left[\pi z_n/a\right]$ functions. Any "reasonable" periodic function is just as suitable for the investigation of solutions of the model as the sine function chosen above. Parameter ω_0^2 defines the scale of potential energy of interaction between the string and the surrounding lattice. The potential energy of interaction between atoms in the string is taken in the simplest possible form consistent with elasticity, i.e. that the energy of interaction between any two atoms in the string is minimum if they are a distance units apart, and it is assumed that the energy increases quadratically if interatomic bonds are stretched or compressed.

We now investigate equations of motion of atoms in the string. They are the conventional Lagrangian equations of classical mechanics

$$\frac{d}{dt}\left(\frac{\partial \mathcal{L}}{\partial \dot{z}_n}\right) = \frac{\partial \mathcal{L}}{\partial z_n}.$$

By differentiating Lagrangian (1), we find equations of motion of all the atoms in the mobile string

$$m\frac{d^2 z_n}{dt^2} = \alpha(z_{n+1} + z_{n-1} - 2z_n) - \frac{m\omega_0^2 a}{2\pi}\sin\left(\frac{2\pi z_n}{a}\right). \qquad (2)$$

A close look at the last equation shows that it satisfies the fundamental requirement of the theory of elasticity (see for example Ref. [4]), namely that the positions of atoms themselves are themselves not the relevant variables, and only the *differences* between positions of atoms represent physically relevant quantities. For example, equations (2) can be expressed in terms of displacements u_n of atoms from the equilibrium lattice positions $u_n = z_n - an$ as

$$m\frac{d^2u_n}{dt^2} = \alpha[(u_{n+1}-u_n)-(u_n-u_{n-1})] - \frac{m\omega_0^2 a}{2\pi}\sin\left(\frac{2\pi u_n}{a}\right). \tag{3}$$

In the limit of small displacements $|u_n| \ll a$ we expand the last term in the right-hand side in the Taylor series and write

$$m\frac{d^2u_n}{dt^2} = \alpha[(u_{n+1}-u_n)-(u_n-u_{n-1})] - m\omega_0^2 u_n. \tag{4}$$

Looking for a solution of this equation in the form $u_n \sim \exp(ikan - i\Omega t)$ we find the dispersion relation for the waves propagating through the string

$$\Omega^2(k) = \frac{2\alpha}{m}[1-\cos(ka)] + \omega_0^2. \tag{5}$$

Since $\lim_{k\to 0}\Omega(k) = \omega_0 > 0$, this equation shows that there are no acoustic phonons in the spectrum of vibrational excitations of the Frenkel-Kontorova model.

The crowdion solution of the Frenkel-Kontorova model

We now consider the case where the string of mobile atoms contains an extra atom. In this case it is no longer possible to place *all* the atoms of the string at the minima of the external periodic potential

$$\frac{m\omega_0^2 a^2}{2\pi^2}\sin^2\left[\frac{\pi z_n}{a}\right].$$

Hence it is no longer possible to find an equilibrium solution of equations (3) where atoms in the string occupy ideal lattice sites. To find a solution of the model we assume that the field of atomic displacements u_n is a smooth function of the index of an atom in the string n. We replace the set of discrete variables $\{u_n\}$ by a continuous function $u(n)$ and write

$$m\frac{\partial^2 u(n,t)}{\partial t^2} = \alpha\frac{\partial^2 u(n,t)}{\partial n^2} - \frac{m\omega_0^2 a}{2\pi}\sin\left(\frac{2\pi u(n,t)}{a}\right). \tag{6}$$

Since the coordinate of an atom z in this approximation is related to n *via* $z = na$, equation (6) is replaced by

$$\frac{\partial^2 u(z,t)}{\partial t^2} = c^2\frac{\partial^2 u(z,t)}{\partial z^2} - \frac{\omega_0^2 a}{2\pi}\sin\left(\frac{2\pi u(z,t)}{a}\right), \tag{7}$$

where $c^2 = \alpha a^2/m$. This equation is known as the sine-Gordon equation. In the limit $\omega_0 = 0$ this equation describes ordinary sound waves, where the speed of sound c is given by $c = \sqrt{\alpha a^2/m}$.

We now investigate if equation (7) has solutions describing propagating quasiparticles. In practical terms this means that we investigate solutions describing objects moving at a constant velocity V through the crystal. To do this we consider the Galilean transformation to the moving frame $z - Vt$.

$$\begin{aligned}
\frac{\partial u(z-Vt)}{\partial z} &= u'(z-Vt) \\
\frac{\partial^2 u(z-Vt)}{\partial z^2} &= u''(z-Vt) \\
\frac{\partial u(z-Vt)}{\partial t} &= -Vu'(z-Vt) \\
\frac{\partial^2 u(z-Vt)}{\partial t^2} &= V^2 u''(z-Vt)
\end{aligned} \tag{8}$$

This transforms equation (7) into

$$V^2 u''(z-Vt) = c^2 u''(z-Vt) - \frac{\omega_0^2 a}{2\pi} \sin\left(\frac{2\pi u(z-Vt)}{a}\right), \tag{9}$$

or, in other words, into an ordinary second-order non-linear differential equation of the form

$$u'' = \frac{\omega_0^2 a}{2\pi\left(c^2 - V^2\right)} \sin\left(\frac{2\pi u}{a}\right). \tag{10}$$

To integrate equation (10) we multiply it by u' and write

$$u'u'' = \frac{1}{2}\left[(u')^2\right]'. \tag{11}$$

We also transform the term containing the $\sin(...)$ function as

$$u'\frac{\omega_0^2 a}{2\pi\,(c^2-V^2)}\sin\left(\frac{2\pi u}{a}\right) = -\frac{\omega_0^2 a^2}{(2\pi)^2(c^2-V^2)}\left[\cos\left(\frac{2\pi u}{a}\right)\right]'. \tag{12}$$

Combining (11) and (12) we find the first integral of equation (10), namely

$$(u')^2 = Const - \frac{2\omega_0^2 a^2}{(2\pi)^2(c^2-V^2)}\cos\left(\frac{2\pi u}{a}\right). \tag{13}$$

The boundary condition $u'(-\infty) = 0$ requires that we choose the value of $Const$ as $Const = 2\omega_0^2 a^2/(2\pi)^2(c^2-V^2)$. In this case equation (13) acquires the form

$$(u')^2 = \frac{2\omega_0^2 a^2}{(2\pi)^2(c^2-V^2)}\left[1-\cos\left(\frac{2\pi u}{a}\right)\right] = \frac{4\omega_0^2 a^2}{(2\pi)^2(c^2-V^2)}\sin^2\left(\frac{\pi u}{a}\right). \tag{14}$$

This is equivalent to a first-order differential equation

$$u' = -\frac{2\omega_0 a}{2\pi\sqrt{c^2-V^2}}\sin\left(\frac{\pi u}{a}\right). \tag{15}$$

the choice of the minus sign here is significant.

We chose the minus sign in the right-hand side of equation (15) in order to comply with the boundary conditions. These conditions are $u(-\infty) = a$ and $u(\infty) = 0$. These conditions ensure that the string contains an extra atom *somewhere* in the interval $[-\infty, \infty]$. Using the formula

$$\frac{dx}{\sin(x)} = d\left[\frac{1}{2}\ln\left\{\tan\left(\frac{x}{2}\right)\right\}\right]$$

we find the solution of (15)

$$u(z,t) = \frac{2a}{\pi}\arctan\left\{\exp\left[-\frac{\omega_0}{c\sqrt{1-V^2/c^2}}(z - z_0 - Vt)\right]\right\}. \qquad (16)$$

This solution describes a solitary wave (a soliton) moving uniformly with velocity V in the positive direction of z-axis. At $t = 0$ the centre of the soliton is at $z = z_0$. This solution is called the *crowdion*.

The distribution of strain $\partial u(z)/\partial z$ in the stationary case ($V = 0$) has the form

$$\frac{\partial u(z)}{\partial z} = -\left(\frac{a\omega_0}{\pi c}\right)\frac{1}{\cosh\left[\dfrac{\omega_0(z - z_0)}{c}\right]}. \qquad (17)$$

The negative sign of strain shows that atoms in the centre of the crowdion are strongly compressed. In real metals the degree of compression reaches exceedingly high values of the order of -20% (see the figure shown in the following page).

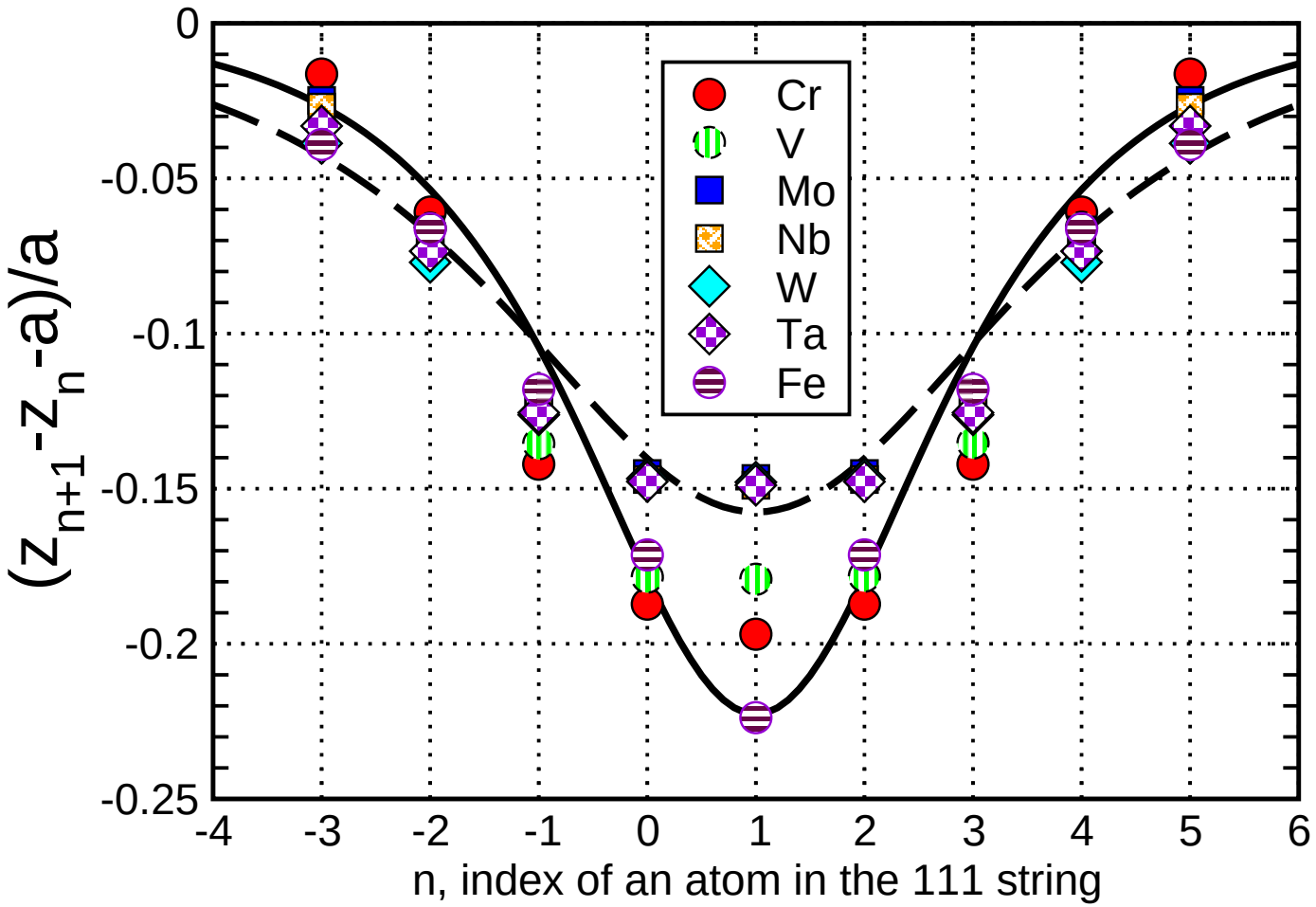

Figure 5: Atomic displacement fields in the central string of the $\langle 111 \rangle$ crowdion self-interstitial atom configuration evaluated using density functional theory for all the bcc transition metals. The solid and the dashed lines show the analytical soliton solutions of the sine-Gordon model plotted for $\mathcal{N} = 1.4$ and $\mathcal{N} = 1.9$. Note the surprising *universality* of the distribution of strain in the crowdion defect in all the six metals, see Ref. [1].

What is the energy of the crowdion solution? Naturally it is given by the *sum* of the kinetic and potential energies of all the atoms in the mobile string (compare this with the Lagrangian (1), which is given by the *difference* of these energies)

$$E = \sum_{n=-\infty}^{\infty} \frac{m\dot{u}_n^2}{2} + \frac{\alpha}{2} \sum_{n=-\infty}^{\infty} (u_{n+1} - u_n)^2 + \frac{m\omega_0^2 a^2}{2\pi^2} \sum_{n=-\infty}^{\infty} \sin^2\left[\frac{\pi u_n}{a}\right]. \tag{18}$$

Assuming that $u_n \equiv u(n)$ is a smooth function of variable n and replacing summation over n by integration

$$\sum_{n=-\infty}^{\infty} f(n) \approx \int_{-\infty}^{\infty} dn f(n) = \frac{1}{a} \int_{-\infty}^{\infty} dz f(z/a)$$

we find

$$E = \frac{1}{a} \int_{-\infty}^{\infty} dz \left[\frac{m}{2} \left(\frac{\partial u}{\partial t}\right)^2 + \frac{\alpha a^2}{2} \left(\frac{\partial u}{\partial z}\right)^2 + \frac{m\omega_0^2 a^2}{2\pi^2} \sin^2\left(\frac{\pi u}{a}\right) \right]. \tag{19}$$

Substituting the field of displacements given by equation (16) into this formula (19), we arrive at a compact and physically transparent result

$$E = \frac{m^* c^2}{\sqrt{1 - V^2/c^2}} \approx m^* c^2 + \frac{m^* V^2}{2}, \quad \text{for } V \ll c, \tag{20}$$

where $m^* = m(2a\omega_0/\pi^2 c)$.

The Crowdion

Equation (20) tells a very interesting story. It shows that the solution (16) that we found by solving a problem of an infinite number of strongly interacting atoms in a string, behaves as if it is a free particle capable of propagating at a constant velocity through the crystal lattice. This "quasi-particle" has an effective mass m^* that is proportional to the mass of an atom, but which also contains an extra factor $2a\omega_0/\pi^2 c$ related to the strength of interaction between atoms.

What is the meaning of this factor? By examining formula (17) we see that quantity $\mathcal{N} \sim c/a\omega_0$ is the effective number of atoms forming the crowdion (this quantity, multiplied by $\pi^2/2$, characterizes the width of the curve shown in Figure 5). Figure 5 shows that this width is relatively large (typically a crowdion is spread over five or six interatomic distances), and hence the effective mass m^* of the crowdion is considerably smaller than the mass m of the atoms that form it. Hence a crowdion is a *light* quasi-particle capable of gliding at a constant velocity through the lattice without friction.

Note that just as any massive particle in a theory of relativity the velocity of propagation of a crowdion through the lattice cannot exceed the speed of sound c in the material. As V approaches c from below the crowdion solution (16) becomes progressively narrow and effects of discreteness of the lattice become significant well before the velocity of the crowdion reaches c. Moreover, the discreteness of the lattice is significant and it affects the motion of crowdions also in the limit of low velocities $V \ll c$.

The *multistring* Frenkel-Kontorova model

So far we considered the case where atoms in one only string were allowed to move. Atoms forming the rest of the lattice remained frozen at ideal lattice sites. We can relax this constraint by introducing a general model where atoms in *any* string can move along the direction parallel to the direction of strings themselves.

Since the energy of interaction between strings depends only on the *relative* positions of atoms, we write

$$\mathcal{L}=\sum_{\mathbf{j}}\sum_{n=-\infty}^{\infty}\left[\frac{m\dot{z}_{n,\mathbf{j}}^2}{2}-\frac{\alpha}{2}(z_{n+1,\mathbf{j}}-z_{n,\mathbf{j}}-a)^2\right]-\frac{m\omega^2a^2}{2\pi^2}\sum_{\mathbf{j},\mathbf{h}}\sum_{n=-\infty}^{\infty}\sin^2\left[\frac{\pi(z_{n,\mathbf{j}}-z_{n,\mathbf{j}+\mathbf{h}})}{a}\right], \tag{21}$$

Summation over $\mathbf{j}$ and $\mathbf{h}$ is performed over pairs of neighbouring interacting strings of atoms in the crystal. The last term in equation (21) shows that it is not the position of an atom $z_{n,\mathbf{j}}$ itself, but rather the position of it in relation to its peers in the neighbouring strings that determines how strongly the strings interact.

From (21) it is easy to recover the conventional Frenkel-Kontorova model (1). To do this we freeze the atoms in all the strings but one ($\mathbf{j}=0$) at equilibrium lattice positions $z_{n,\mathbf{j}+\mathbf{h}}=an$.

Since

$$\sin\left[\frac{\pi\left(z_{n,\mathbf{j}}-z_{n,\mathbf{j}+\mathbf{h}}\right)}{a}\right] = \sin\left[\frac{\pi z_{n,\mathbf{j}}}{a}\right]\cos\left[\frac{\pi z_{n,\mathbf{j}+\mathbf{h}}}{a}\right]-\cos\left[\frac{\pi z_{n,\mathbf{j}}}{a}\right]\sin\left[\frac{\pi z_{n,\mathbf{j}+\mathbf{h}}}{a}\right]$$
$$= \sin\left[\frac{\pi z_{n,\mathbf{j}}}{a}\right]\cos\left[\pi n\right]-\cos\left[\frac{\pi z_{n,\mathbf{j}}}{a}\right]\sin\left[\pi n\right]=(-1)^n\sin\left[\frac{\pi z_{n,\mathbf{j}}}{a}\right]$$

we find that

$$\sin^2\left[\frac{\pi\left(z_{n,\mathbf{j}}-an\right)}{a}\right]=\sin^2\left[\frac{\pi z_{n,\mathbf{j}}}{a}\right]$$

We see that in the single-string limit the Lagrangian of the multistring Frenkel-Kontorova model is equivalent to the original Lagrangian (1) where parameter ω_0^2 is replaced by $\omega^2\zeta$, where ζ is the number of neighbouring strings surrounding a given string. For example, in the case of 111 strings in bcc lattice $\zeta=6$.

Now we consider a cluster of mobile strings and assume that atoms in the rest of the lattice remain frozen at their equilibrium positions. In this case the Lagrangian has the form

$$\mathcal{L} = \sum_{\mathbf{j}}\sum_{n=-\infty}^{\infty}\left[\frac{m\dot{z}_{n,\mathbf{j}}^2}{2}-\frac{\alpha}{2}\left(\frac{\partial z_{n,\mathbf{j}}}{\partial n}\right)^2\right]-\frac{m\omega^2}{2}\sum_{\mathbf{j},\mathbf{h}}\sum_{n=-\infty}^{\infty}\left(\mathbf{h}\cdot\frac{\partial z_{n,\mathbf{j}}}{\partial\mathbf{j}}\right)^2$$
$$-\mathcal{Z}\frac{m\omega^2a^2}{2\pi^2}\sum_{\mathbf{j}'}\sum_{n=-\infty}^{\infty}\sin^2\left[\frac{\pi z_{n,\mathbf{j}'}}{a}\right], \qquad (22)$$

where summation over $\mathbf{j}'$ in the last term is performed over strings forming the perimeter of the cluster.

Inside the cluster the relative displacements of atoms in the neighbouring strings are small and we expanded the term

$$\sin\left[\frac{\pi\left(z_{n,\mathbf{j}}-z_{n,\mathbf{j}+\mathbf{h}}\right)}{a}\right]$$

in the Taylor series as

$$\sin\left[\frac{\pi\left(z_{n,\mathbf{j}}-z_{n,\mathbf{j}+\mathbf{h}}\right)}{a}\right]\approx\frac{\pi}{a}\mathbf{h}\cdot\left(\frac{\partial z_{n,\mathbf{j}}}{\partial\mathbf{j}}\right)$$

Since atoms in the surrounding frozen lattice occupy equilibrium positions and hence the difference $z_{n,\mathbf{j}}-z_{n,\mathbf{j}+\mathbf{h}}$ is not small, we cannot use the Taylor expansion to simplify terms describing interaction between strings at the perimeter of the cluster. In equation (22) $\mathcal{Z}$ is the “average” number of perfect lattice strings interacting with a string situated at the edge of the cluster.

The fact the Taylor expansion *can* be used everywhere inside the cluster of strings but not at its perimeter naturally gives rise to the fact that the field of atomic displacements inside the cluster is described by the Laplace-like partial differential equation

$$\frac{\partial^2 u}{\partial z^2}+\frac{\omega^2\bar{l}^2}{(c^2-V^2)}\frac{\partial^2 u}{\partial\mathbf{R}^2}=0. \qquad (23)$$

Here $\bar{l}$ is the distance between neighbouring strings in the (x, y) plane. Interaction between the surrounding frozen lattice is described by the boundary condition at the perimeter of the cluster

$$\frac{2\pi}{p}\frac{\omega\bar{l}}{\sqrt{c^2-V^2}}\left(\mathbf{n}\cdot\frac{\partial u}{\partial \mathbf{R}}\right)+\sin\left[\frac{2\pi u}{a}\right]=0. \tag{24}$$

Here p is a dimensionless parameter, given by a somewhat cumbersome equation, $p=\omega Z/\nu\bar{l}^2G^{1/2}(c^2-V^2)^{1/2}$, where ν is the number density of atoms in the crystal, $G=2$ for square and $G=3$ for a hexagonal lattice, and $\mathbf{n}$ is the vector of external surface normal to the perimeter of the cluster.

The last two equations can be simplified by introducing a dimensionless variable $\boldsymbol{\rho}=\mathbf{R}\sqrt{c^2-V^2}/\omega\bar{l}$. Equation (23) and the boundary condition (24) for the displacement field of atoms in a cluster now have the form

$$\frac{\partial^2 u}{\partial z^2}+\frac{\partial^2 u}{\partial \boldsymbol{\rho}^2}=0, \tag{25}$$

and

$$\frac{2\pi}{p}\left(\mathbf{n}\cdot\frac{\partial u}{\partial \boldsymbol{\rho}}\right)+\sin\left[\frac{2\pi u}{a}\right]=0. \tag{26}$$

It is remarkable that there is at least one case where this partial differential equation with a non-linear boundary condition can be solved *exactly*. This solvable case describes an edge dislocation and the solution that we are going to discuss now describes what is called the Peierls model.

The Peierls model

In this model we consider the edge of a very large cluster. Only two variables (x in the plane of the cluster and z normal to the plane of the cluster) are required to formulate the problem.

Equations (25) and (26) now have the form

$$\begin{aligned} \frac{\partial^2 u}{\partial z^2} + \frac{\partial^2 u}{\partial x^2} &= 0, \\ \frac{2\pi}{p}\frac{\partial u}{\partial x} &= \sin\left[\frac{2\pi u}{a}\right]. \end{aligned} \tag{27}$$

The cluster of strings now occupies the region $x > 0$ and $-\infty < z < \infty$. We would like to find a solution of equations (27) in this region.

We will do this by means of Green's functions of the Laplace equation. We all know from classical electrostatics that the Green function of the three-dimensional Laplace equation has the form

$$G(\mathbf{r},\mathbf{r}') = -\frac{1}{4\pi|\mathbf{r}-\mathbf{r}'|}.$$

In two dimensions the Green's function of the Laplace equation is

$$G(x,x',z,z') = \frac{1}{4\pi}\ln\left[(x-x')^2+(z-z')^2\right].$$

The two-dimensional Green's function that vanishes at $x = 0$ is

$$G_P(x,x',z,z') = \frac{1}{4\pi}\left\{\ln\left[(x-x')^2+(z-z')^2\right] - \ln\left[(x+x')^2+(z-z')^2\right]\right\}.$$

Using this Green's function (see for example Ref [5]) we find

$$\begin{aligned} u(x,z) &= -\int_{-\infty}^{\infty} dz' u(0,z') \frac{\partial}{\partial x'} G_P(x,x',z,z')\Big|_{x'=0} \\ &= \int_{-\infty}^{\infty} dz' u(0,z') \frac{1}{\pi} \frac{x}{x^2+(z-z')^2} \end{aligned} \tag{28}$$

The boundary condition (27) relates the function $u(x,z)$ and its derivative at $x = 0$. We "invert" this condition and write

$$u(0,z) = \frac{a}{2\pi} \arcsin\left[\frac{2\pi}{p}\frac{\partial}{\partial x} u(x,z)\Big|_{x=0}\right]. \tag{29}$$

Now we substitute this into equation (28) and find

$$u(x,z) = \frac{a}{2\pi^2}\int_{-\infty}^{\infty} dz' \frac{x}{(z-z')^2+x^2} \arcsin\left[\frac{2\pi}{p}\frac{\partial}{\partial x} u(x,z')\Big|_{x=0}\right]. \tag{30}$$

To solve this equation we introduce the notation

$$\Gamma(z') = \arcsin\left[\frac{2\pi}{p}\frac{\partial}{\partial x}u(x,z')\Big|_{x=0}\right].$$

Similarly to the boundary condition that we used when investigating the crowdion solution of the conventional Frenkel-Kontorova model, we write $\Gamma(-\infty) = 2\pi$ and $\Gamma(\infty) = 0$.

Integrating (29) by parts, we arrive at

$$u(x,z) = -\frac{a}{2\pi^2}\int\limits_{-\infty}^{\infty} dz' \arctan\left[\frac{z'-z}{x}\right]\frac{d\Gamma}{dz'}. \tag{31}$$

Differentiating this equation by x and taking the limit $x \to 0$, we find

$$\frac{\partial u}{\partial x}\Big|_{x\to 0} = \frac{a}{2\pi^2}\left[\wp\int\limits_{-\infty}^{\infty}\frac{dz'}{z'-z}\frac{d\Gamma}{dz'}\right]. \tag{32}$$

Using the definition of function $\Gamma(z)$ and replacing the derivative of u in the left-hand side by a function of $\Gamma(z)$ we find a closed equation on $\Gamma(z)$

$$\sin[\Gamma(z)] = \frac{a}{\pi p}\left[\wp\int\limits_{-\infty}^{\infty}\frac{dz'}{z'-z}\frac{d\Gamma}{dz'}\right]. \tag{33}$$

Rudolf Peierls (see Ref. [6]) *guessed* the solution of this equation in 1940. This solution is (it is easy to

verify that it is correct by substituting back into the original equation)

$$\Gamma(z) = \pi - 2\arctan\left(\frac{pz}{a}\right). \tag{34}$$

There is extensive literature on this solution. This solution is the central result of what is known as the Peierls model of a dislocation. We will not discuss the contents of the model here. It is probably worth mentioning that this solution shows that an edge dislocation (described by the distribution of strain at the edge of a large cluster of interstitial atoms) has characteristic width given by

$$\mathrm{width} \sim a/p.$$

In the context of these notes, the significance of the solution given above is in that it shows an explicit traceable link between the concepts of a crowdion and that of an edge dislocation.

This is why it is not surprising that in various phenomena that we encounter in the field of radiation damage we see a fundamental link and similarity between the dynamics of interstitial defects and the dynamics of dislocations.

The Peierls potential for a crowdion defect

The solution of the crowdion problem given by equation (16) states that the *static* field of atomic displacements in the defect is given by

$$u(z,t) = \frac{2a}{\pi} \arctan \left\{ \exp \left[-\frac{\omega_0 (z - z_0)}{c} \right] \right\}. \tag{35}$$

But does this formula actually solve the original set of equations for the atoms forming the string? (here we are talking again about the *single-string* Frenkel-Kontorova model). The way to answer the question is to substitute (35) into the original Lagrangian describing a *discrete* set of atoms, and see what comes out. The direct calculation gives a somewhat unexpected result [2,7,8] , stating that the energy in fact depends on z_0:

$$E(z_0) = m^* c^2 + 8mc^2 \exp\left(-\frac{\pi^2 c}{\omega_0 a} \right) \cos\left(\frac{2\pi z_0}{a} \right). \tag{36}$$

The second term in this equation is very significant. It shows that crowdion moving through the crystal lattice is not quite the free quasiparticle as the sine-Gordon limit of the Frenkel-Kontorova model suggests. There is in fact additional, relatively weak, ”effective potential” felt by the crowdion propagating through the lattice

$$U_{eff}(z_0) = 8mc^2 \exp\left(-\frac{\pi^2 c}{\omega_0 a} \right) \cos\left(\frac{2\pi z_0}{a} \right)$$

which comes from the fact that crystal lattice is discrete. This effective potential is called the Peierls potential.

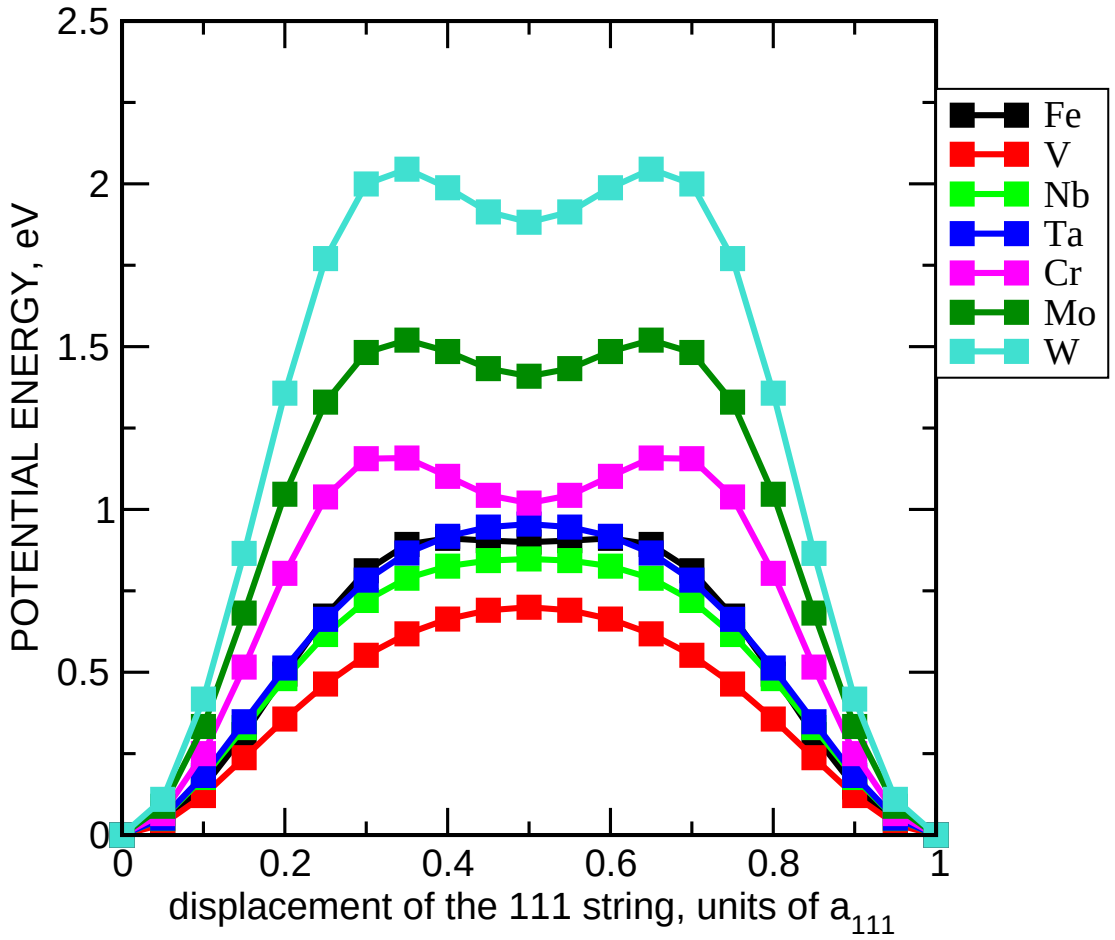

Figure 6: The potential energy (the third term in the Lagrangian of the Frenkel-Kontorova model) determined from *ab-initio* calculations. Note that for metals of group VIB (chromium, molybdenum, tungsten) the shape of the potentials energy curve is significantly different from the $\sin^2\left[\pi z_n/a\right]$ form assumed in equation (1). It is possible to find an analytical solution of the FK model for this case, too [8].

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Introduction to Part III

Analysis given above fully described the structure of defects, and also showed that in some important cases it is possible to develop exactly solvable models for defects and dislocations. However we have not yet answered the question about why in electron microscope observations, and in simulations, we see that defects move. What makes them move, and in view of the connection between defects and dislocations, why is it that defects move on their own, while we need to apply stress to move a dislocation line? To answer these questions we need to extend the Frenkel-Kontorova model and include the treatment of thermal vibrations of atoms, see Refs. [1], [2], [3].

SUMMARY

- What is non-Arrhenius diffusion?
- The fluctuation-dissipation theorem, and statistical treatment of diffusion
- Comparison with atomistic simulations

The Arrhenius law for thermally activated migration

Thermally activated migration of vacancy and self-interstitial atom defects is the main mechanism driving microstructural evolution of materials under irradiation. The 'standard model' for migration of radiation defects is the Arrhenius law, where the frequency $\nu_{i\to f}$ of hops between the initial (i) and the final (f) equilibrium configurations of a defect in the crystal lattice is given by the Arrhenius equation

$$\nu_{i\to f} = \nu_0 \exp\left(-\frac{E_a}{k_B T}\right), \tag{37}$$

where ν_0 is the attempt frequency, E_a is the activation energy for migration, and T is the absolute temperature. In this equation the attempt frequency ν_0 is a constant quantity, and the magnitude of E_a depends only on the type of the defect and on the local environment of the defect in the initial (i) and final (f) configurations. The calculated activation energies for migration of single vacancies in body-centred cubic (bcc) transition metals vary between approximately 0.62 eV in vanadium, 0.65 eV in iron, and 1.78 eV in tungsten. These values are many times $k_B T$ even for the highest temperatures of operation of materials in a fusion or a fission power plant. Hence migration of vacancies in materials is well described by the Arrhenius equation (37) above, in which the argument of the exponential function is large and negative, and the exponential factor itself is very small $\exp(-E_a/k_B T) \ll 1$.

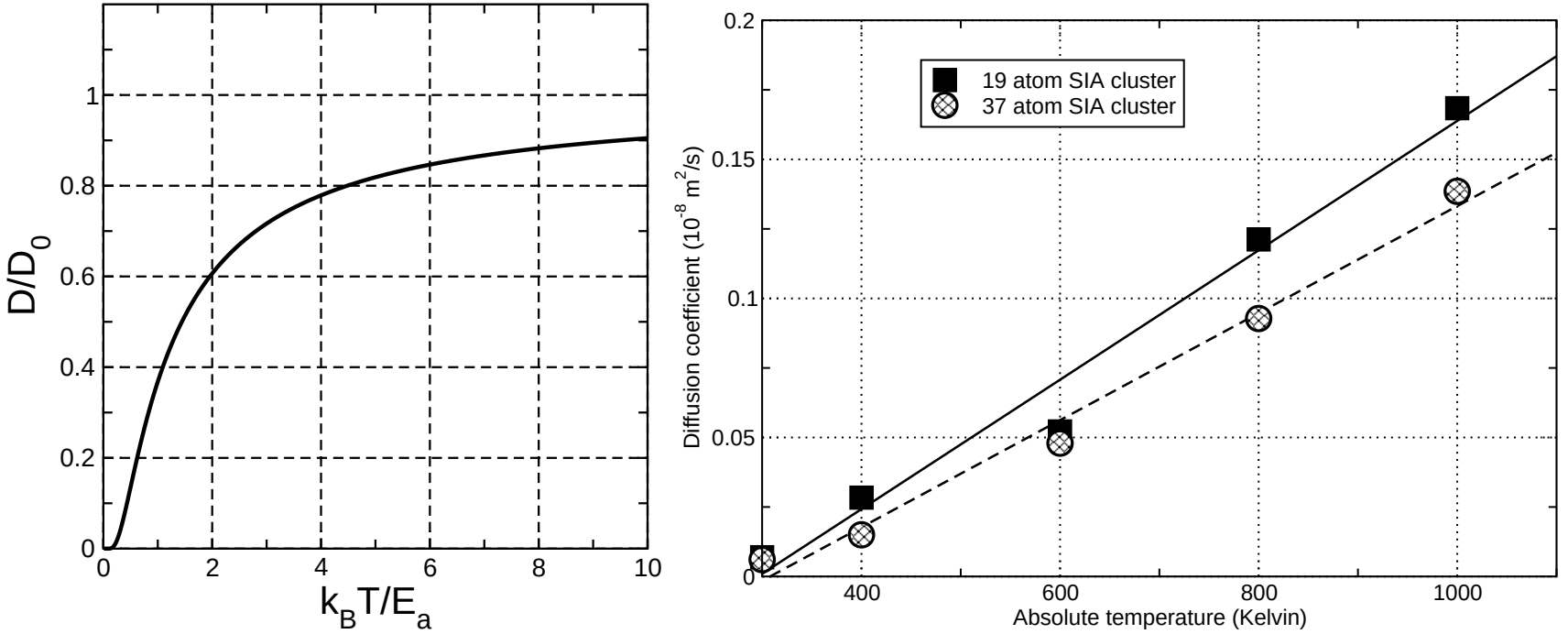

Figure 7: (Left) Plot illustrating the temperature dependence of the diffusion coefficient of defects given by the Arrhenius equation. (Right) Coefficients of thermal diffusion of a 19 self-interstitial atom cluster and a 37 self-interstitial atom cluster in tungsten found by analyzing the trajectories of migration of mesoscopic defects in the crystal lattice. Straight lines are linear fits to the values found using molecular dynamics simulations. It is *obvious* that the temperature variation of the diffusion coefficient for self-interstitial clusters is non-Arrhenius.

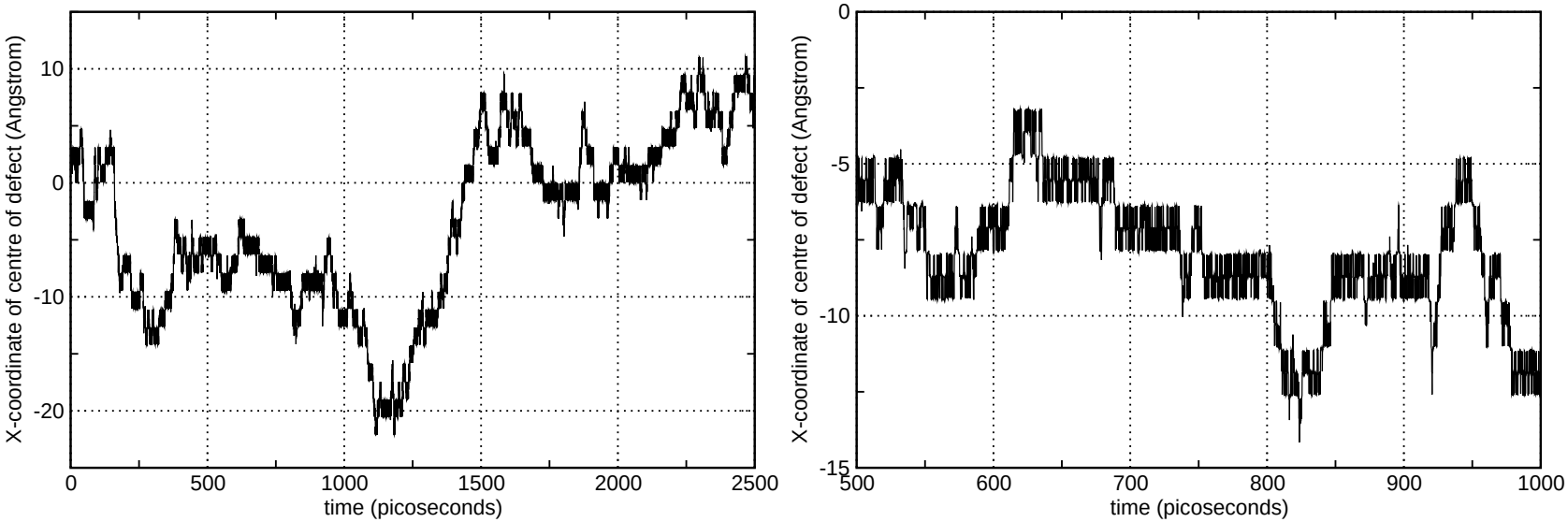

Figure 8: Extracting the diffusion coefficient from a simulated trajectory of a migrating defect is not a very straightforward matter. This figure show the x-coordinate of the centre of the $\langle 111 \rangle$ crowdion defect performing one-dimensional (in the direction of the axis of the defect) random Brownian walk in tungsten at $T = 150$ K. The right panel shows the full simulated trajectory of the defect while the left panel shows a part of the same trajectory corresponding to the interval of time $500 < t < 1000$ picoseconds.

The breakdown of the Arrhenius law for crowdion defects

On the other hand, migration of self-interstitial atom defects in non-magnetic bcc metals is characterized by the comparatively low activation energies. In ferromagnetic iron the activation energy for migration of a single interstitial atom defect is approximately 0.34 eV, which is half the migration energy for a vacancy. In all the *non-magnetic* bcc metals a self-interstitial atom defect adopts the linear $\langle 111 \rangle$ crowdion configuration, and the activation energy for migration of this configuration is exceedingly low, ranging between 0.02 and 0.05 eV for all the metals forming groups V and VI of the Periodic Table [4]. Furthermore, molecular dynamics simulations show that similar small activation energies characterize thermal migration of mesoscopic self-interstitial atom clusters in *all* the bcc metals, including iron. In this case at and above the room temperature we have $E_a \leq k_B T$, and the exponential factor in equation (37) is of the order of unity. The pattern of migration of a self-interstitial defect now no longer looks like an Arrhenius-like sequence of infrequent hops between equilibrium positions, separated by the relatively long intervals of time during which a defect resides at a certain point in the crystal lattice.

Brownian motion of a defect in a crystal lattice

Once a representative trajectory of a defect is simulated, the diffusion coefficient for a migrating defect can be found using the Einstein formula

$$D = \lim_{t\to\infty} \frac{\overline{[\mathbf{R}(t) - \mathbf{R}(0)]^2}}{6t}, \tag{38}$$

which is subject to the condition that $\mathbf{R}(t) - \mathbf{R}(0)$ is a random process with zero mean, i.e. that $\overline{[\mathbf{R}(t) - \mathbf{R}(0)]} = 0$. The bar above a function denotes averaging over statistical realisations of the trajectory of a migrating defect. Condition $\overline{[\mathbf{R}(t) - \mathbf{R}(0)]} = 0$ means that *on average* a migrating defect remains at its initial position $\mathbf{R}(0)$. Since the diffusion coefficient (38) represents a measure of fluctuations of the position of the defect, the presence of any 'drift' terms giving rise to the non-zero values of $\overline{[\mathbf{R}(t) - \mathbf{R}(0)]}$ has to be excluded from the statistical analysis involving equation (38).

We now try to find a connection between equation (38) and the treatment of Brownian motion based on the classical Langevin equation

$$m^* \frac{d\mathbf{v}}{dt} = -\gamma \mathbf{v}(t) + \mathbf{f}(t). \tag{39}$$

Here m^* is the effective mass of the defect, γ is the coefficient of dissipative friction and $\mathbf{v}(t)$ is the velocity of migrating defect. The term $\mathbf{f}(t)$ in the right hand side of the above equation represents a random thermal force acting on the defect. Equation (39) does not include the effect of any periodic crystal lattice potential on Brownian motion of a defect. This aspect of the problem has recently received attention and considerable progress was made in solving it. Here we are interested in the treatment of diffusion of defects in the high-temperature limit $k_B T/E_a \geq 1$ where the influence of the periodic component of the potential can be neglected.

Assuming that $\overline{\mathbf{f}(t)} = 0$ or, equivalently, that migration of the defect is ergodic, in which case

$$\lim_{t_0\to\infty} \frac{1}{t_0} \int_{t'}^{t'+t_0} \mathbf{f}(t)dt = 0$$

for any arbitrarily chosen t', we find that $\overline{\mathbf{v}(t)} = 0$ and that the average kinetic energy of a migrating defect is given by

$$\frac{m^*\overline{\mathbf{v}^2(t)}}{2} = \frac{1}{2m^*} \int_{-\infty}^{t} d\tau \int_{-\infty}^{t} d\tau' \exp\left[-\frac{\gamma}{m^*}(t-\tau)\right] \exp\left[-\frac{\gamma}{m^*}(t-\tau')\right] \overline{\mathbf{f}(\tau)\cdot\mathbf{f}(\tau')}. \quad (40)$$

The stochastic thermal force is delta-correlated

$$\overline{\mathbf{f}(\tau)\mathbf{f}(\tau')} = \overline{\mathbf{f}^2}\delta(\tau-\tau'). \quad (41)$$

Applying the classical equipartition principle $m^*\overline{\mathbf{v}^2(t)}/2 = (3/2)k_BT$, from equations (40) and (41) we find

$$\frac{m^*\overline{\mathbf{v}^2(t)}}{2} = \frac{3}{2}k_BT = \frac{\overline{\mathbf{f}^2}}{2m^*} \int_{-\infty}^{t} d\tau \exp\left[-\frac{2\gamma}{m^*}(t-\tau)\right] = \frac{\overline{\mathbf{f}^2}}{4\gamma}. \quad (42)$$

This condition relates the amplitude of stochastic fluctuations of the thermal force and the coefficient of dissipative friction γ, namely

$$\overline{\mathbf{f}^2} = 6\gamma k_B T. \tag{43}$$

This equation is an example of the so-called Fluctuation-Dissipation Theorem that relates the rate of dissipation of energy by a moving defect (given by parameter γ) and the variance of random thermal force acting on the defect. Note that we proved this relation by using the equipartition principle.

Now it is a simple matter to show that the correlation function of velocities of a defect is

$$\begin{aligned}\overline{\mathbf{v}(t)\cdot\mathbf{v}(t')} &= \left(\frac{1}{m^*}\right)^2 \int_{-\infty}^{t} d\tau \int_{-\infty}^{t'} d\tau' \exp\left[-\frac{\gamma}{m^*}(t-\tau)\right] \exp\left[-\frac{\gamma}{m^*}(t'-\tau')\right] \overline{\mathbf{f}(\tau)\cdot\mathbf{f}(\tau')} \\ &= \frac{\overline{\mathbf{f}^2}}{2\gamma m^*} \exp\left[-\frac{\gamma}{m^*}|t-t'|\right] = \frac{3k_BT}{m^*} \exp\left[-\frac{\gamma}{m^*}|t-t'|\right]. \end{aligned} \tag{44}$$

Integrating this correlation function over time we arrive at

$$\int_0^\infty \overline{\mathbf{v}(t)\cdot\mathbf{v}(0)}dt = \frac{3k_BT}{\gamma}. \tag{45}$$

Defining the coordinate of the defect as an integral of its velocity

$$\mathbf{R}(t) = \int_0^t \mathbf{v}(\tau) d\tau,$$

where $\mathbf{R}(0) = 0$, and evaluating the average square of this quantity using equation (44), we find an equation that was first derived by Chandrasekhar

$$\begin{aligned} \overline{\mathbf{R}^2(t)} &= \int_0^t d\tau \int_0^t d\tau' \overline{\mathbf{v}(\tau)\cdot\mathbf{v}(\tau')} = \frac{3k_B m^* T}{\gamma^2} \int_0^{\frac{\gamma t}{m^*}} d\theta \int_0^{\frac{\gamma t}{m^*}} d\theta' \exp\left[-|\theta-\theta'|\right] \\ &= \frac{6k_B m^* T}{\gamma^2}\left\{\frac{\gamma t}{m^*} - \left[1-\exp\left(-\frac{\gamma t}{m^*}\right)\right]\right\}. \end{aligned} \tag{46}$$

Combining (46) with the Einstein equation (38), we find a condition that relates the diffusion and the friction coefficients

$$D = \lim_{t\to\infty} \frac{\overline{\mathbf{R}^2(t)}}{6t} = \frac{k_B T}{\gamma} = \frac{6(k_B T)^2}{\overline{\mathbf{f}^2}} = \frac{1}{3}\int_0^\infty \overline{\mathbf{v}(t)\cdot\mathbf{v}(0)} dt. \tag{47}$$

Comparing equations (46) and (47) we see that taking the limit $t \rightarrow \infty$ is equivalent to evaluating the right-hand side of equation (46) for $\gamma t/m^* \gg 1$. Estimates show that $m^*/\gamma \sim 1$ ps and hence the minimum length of an interval of time required for evaluating the diffusion constant cannot be shorter than approximately 10 ps. In other words, *the motion of the defect is ballistic over intervals of time shorter that approximately 1 ps, and is diffusive on the intervals of time much longer than 10 ps*.

Equation (47) shows that if we assume that the variance of the stochastic thermal force $\overline{\mathbf{f}^2}$ varies linearly as a function of absolute temperature then the diffusion coefficient would also vary linearly as a function of T. The friction coefficient γ in this case is a constant quantity independent of absolute temperature T.

By generalising the Frenkel-Kontorova model to the case where atoms occupy not the ideal regular lattice sites, but are randomly displaced from these sites due to temperature fluctuations, it is possible to show [1], [3] that the correlation function of the random force acting on the defect is indeed a linear function of the absolute temperature T, namely

$$\overline{\mathbf{f}(t)\cdot\mathbf{f}(t')} = \frac{64}{\pi^2}\Omega\frac{k_B T}{Mc^3}(m^*\omega^2)^2\mathtt{N}\delta(t-t'), \tag{48}$$

where M is the mass of an atom, c is the average speed of sound in the material, and Ω is the volume per atom. This equation shows that the phonon force acting on a defect is linear in absolute temperature and it is delta-correlated as a function of time. Combining this with the analysis given in the preceding section we see that the diffusion coefficient of crowdions migrating in a pure bcc metal is expected to vary linearly as a function of absolute temperature (as opposed to it approaching saturation in the high temperature limit as predicted by the Arrhenius equation)

$$D \sim T. \tag{49}$$

The statistical analysis of trajectories of migrating crowdions given in Figure 7 confirms this prediction. In real materials defects migrate much slower: there impurities (for example carbon or nitrogen atoms) trap migrating defects, and the trajectory of motion observed experimentally often looks like a sequence of long periods of time when a defect resides at one point in the lattice, followed by an almost instantaneous transition to another point in the lattice where again defect remains almost motionless for another long period of time.

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