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FIFTY YEARS OF THE ARCHIVES OF MECHANICS

Diffusion

Dedicated to Prof. Henryk Zorski
on the occasion of his 70-th birthday

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THE CLASSICAL FIELD of statistical mechanics – the theory of diffusion processes – is still offering considerable challenge when the physical problems to be described by it are more "realistic" than those easily envisioned as simple random walk. In this lecture I shall present our recent results on diffusion processes in two wide classes of physical problems: i) Diffusion in dense quasi-two-dimensional adsorbates on surfaces of the crystals, where the interparticle interactions and the interaction with the host solid cannot be neglected and play a mutually complementary role. These phenomena can be conveniently called the dynamics in $d = 2 + 1$ dimensions. ii) Diffusion in the crystals containing topological (line) defects, such as dislocations and disclinations. I shall present our results on use of the combined continuum theory of defects and the path integral approach to description of such diffusion processes. Possibility of generalization of these models for quantum particles will also be outlined.

1. Introduction

THE PHYSICAL PROCESS which keeps the fragrance producers and sellers in their lucrative business is the diffusion. Indeed, it is slow motion of the concentration profile, as compared to the thermal speed of a gas particle, which keeps the fragrance particle component close to our body. It also prevents the smell of burned bacon, or bouquet of just opened bottle of *Frankenwein*, from filling the interior of the house instantaneously. The slowness and the persistence of the diffusion is one of the reasons why this dynamical process is of such an importance in various branches of biology [1].

The theory of diffusion appears to be a mature field. Close scrutiny, however, reveals that it is still in the developing stage particularly when one attempts to describe phenomena, which albeit on the first glance are not that much different from the other "diffusion" processes, nevertheless, show dramatic differences from the textbook definition of diffusion as the long–time large–distances limit of the random walk. In this lecture I shall discuss two classes of such problems related to two fields of solid state physics: surface physics and theory of imperfect solids. Both of them can play an important role in analysis of the crystal growth phenomena, no attempts, however, will be made to discuss these potential applications in greater detail.

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The plan of my lecture is then as follows. In the following Sec. 2, I shall present a brief account of our recent extensive work on the use of a novel statistical mechanics technique – the local mean field theory – to the description of the diffusion on the surface of a solid. In particular I shall discuss recent attempt to formulate a theory of diffusion in dense adsorbates, in which, due to adparticle interactions, one observes mutual competition between the flow and hopping characteristics of particle dynamics. In Sec. 3, I shall review our extensive work on the simple diffusion in the medium containing random arrangement of topological defects, i.e. dislocations and disclinations. I shall show that in this case, the long time and long distance limit of the mean square displacement of a particle is no longer proportional to time and that diffusion might show nonmarkovian character. In some special and highly idealized situations it may even exhibit Sinay-like behavior in more than one dimension. In Sec. 4, I shall very briefly discuss the problem of a single quantum particle moving on a lattice with topological defects. This section serves as an introduction to our recent and ongoing work in that field.

2. Surface diffusion

When a freshly cleaved surface of a crystal is exposed to an ambient gas, some of the gas particles get stuck to the surface in a process which we call adsorption. The adatoms do not get just to any point on the surface but to its specific points, called adsorption sites, which form a $d = 2$ lattice with structure not necessarily the same as the crystallographic structure of crystal surface. Formation of an adsorbate is a complex phenomenon, particularly since in most of the circumstances, electronic degrees of freedom of the adatoms are mixed with these of the host solid providing chemical-like binding between adatoms and the crystal. I shall restrict myself to seemingly simpler situation of a *physisorption*, that is when the chemical structure of adatom remains intact throughout the formation, equilibration and future dynamical history of the adsorbate. As we shall see, this is a sufficiently rich model to analyze fundamental problems of the diffusion theory [2–4]. It is a very important model, for it permits us to asses how the intricacies of interactions between the adsorbed particles and the host solid, mediated by solid phonons (both bulk and surface) can be handled in description of the dynamical properties of the adsorbates. Understanding of particle migration over the solid surface is also of considerable applied interest, for example the particle diffusion, along the surface of growing crystal, might change the morphological mode of the crystal growth [5]. In this lecture I shall be mostly concerned with fundamental aspects of the surface diffusion, particularly for dense adsorbates, when mutual interactions among the adsorbate particles cannot be neglected. The wealth of phenomena in dense adsorbates becomes enormous, offering possibility of studying transitions from localized (registered and nonregistered) phases

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to orientationally ordered (hexatic) fluids to two-dimensional fluid layers. Their extensive discussion can be found in the recent collection of articles [2]. In some sense these are $2+1$ dimensional systems, that is they permit us to see how the truly three-dimensional properties of the system are turned off and replaced by two-dimensional ones.

How do we describe diffusion in the adsorbates? Conventionally the starting point would be the kinetic lattice gas approach in which one postulates certain equation of motion for the multiparticle probability distribution function of finding $n_{\mathbf{R}}, n_{\mathbf{R}'}, \ldots$ particles at lattice sites $\mathbf{R}, \mathbf{R}', \ldots$ at a given instant of time – $P(\{n_{\mathbf{R}}\}, t)$. This equation, called the *Master* equation, is difficult to derive from the first principles for the lattice gas model does not have its own, endogeneous, dynamics. In contrast, the static properties of the lattice gas, and *eo ipso* these of modeled adsorbate, are fully determined by:

1) the lattice gas Hamiltonian, conveniently and conventionally written as:

$$\mathcal{H}(\{n_{\mathbf{R}}\}) = -\sum_{\mathbf{R},\mathbf{R}'} J_{\mathbf{R},\mathbf{R}'} n_{\mathbf{R}} n_{\mathbf{R}'} + \sum_{\mathbf{R}} V(\mathbf{R}) n_{\mathbf{R}} \,, \tag{1}$$

where the "exchange integral" $J_{\mathbf{R},\mathbf{R}'}$ describes the interparticle interactions and $V(\mathbf{R})$ is the on-site potential, describing, for example, binding of the particle to the host solid;

2) the choice of the ensemble used in the evaluation of the statistical sum; that is deep physical insight into what are the proper constraints imposed on the system.

To describe the lattice gas dynamics we must supply it with a model dynamics given by the master equation of the form:

$$\begin{aligned} \partial_t P(\{n_{\mathbf{R}}\}, t) \\ = \sum_{\{n'_{\mathbf{R}}\}} W(\{n_{\mathbf{R}}\}, \{n'_{\mathbf{R}}\}) P(\{n'_{\mathbf{R}}\}, t) - \sum_{\{n'_{\mathbf{R}}\}} W(\{n'_{\mathbf{R}}\}, \{n_{\mathbf{R}}\}) P(\{n_{\mathbf{R}}\}, t) \,, \end{aligned} \tag{2}$$

with the properly chosen transition amplitudes W, which are functionally dependent on the occupations $\{n_{\mathbf{R}}\}$. The only guiding principles we have in constructing these transition amplitudes are: our knowledge of underlying physics (which might be far from complete) and the detailed balance condition. The later assures that all the solutions of Eq. (2) tend asymptotically to the equilibrium solution $P^{\mathrm{eq}}(\{n_{\mathbf{R}}\}) \propto \exp(-\beta \mathcal{H}(\{n_{\mathbf{R}}\}))$.

As it stands, Eq. (2) presents formidable, and with exception of simple cases, unsolvable, mathematical problem. Variety of approximate schemes have been advocated in the literature. In a series of publications [6–8] we have proposed a new method to analyze such an equation which uses so-called local mean field approximation. We found our method to be quite useful for moderately dense adsorbates with attractive interactions, for which a good agreement can be obtained

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between predictions of our model [7] and Monte Carlo simulation results [9]. For systems with repulsive interactions [8] we have obtained sensible agreement between our prediction for the behavior of the diffusion coefficient in the 2×2 ordered region of the phase diagram, shown in Fig. 1, and the reported experimental data. In Fig. 2 we have shown the behavior of the diffusion coefficient as a function of the lattice gas density plotted for various values of the temperature, corresponding to ordered and disordered region of the phase diagram in Fig. 1.

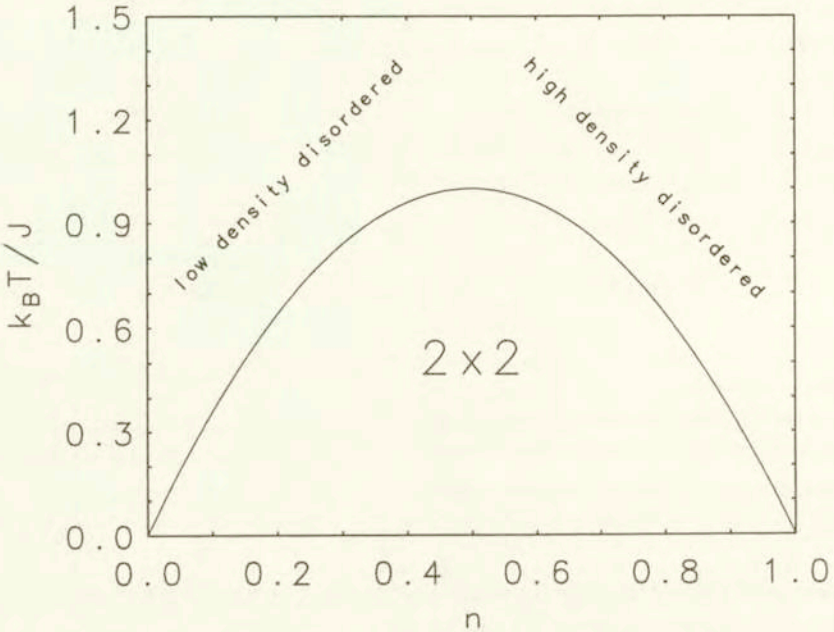

FIG. 1. The mean field phase diagram for lattice gas with repulsive interactions.

In spite of this progress one easily recognizes that the lattice gas models suffer from a serious drawback, namely they cannot account for any *flow* properties of the dense adsorbate. When the density of adsorbate increases, particularly above that of a monolayer, fluid-like properties of the adsorbate gain importance, diffusion ceases to be hopping-like, and the kinetic lattice gas approach becomes deficient. To analyze such situations we have proposed in Ref. [10] a fluid-like mesoscopic model which takes into account details of dynamic (phonon mediated) interactions between the adsorbate and the host solid. This model results in a hydrodynamic-like equations for the adsorbate fluid. These equations describe the fluid flow for which the momentum is not conserved on account of a single particle friction term violating the Gallilean invariance of the model containing new "transport" coefficient ζ. This breakdown of conservation law for momentum emerges from the fully Gallilean invariant original model after phonons are projected out and transient in time terms are averaged out. This procedure effectively assumes that the host solid is "infinitely" heavy, and that

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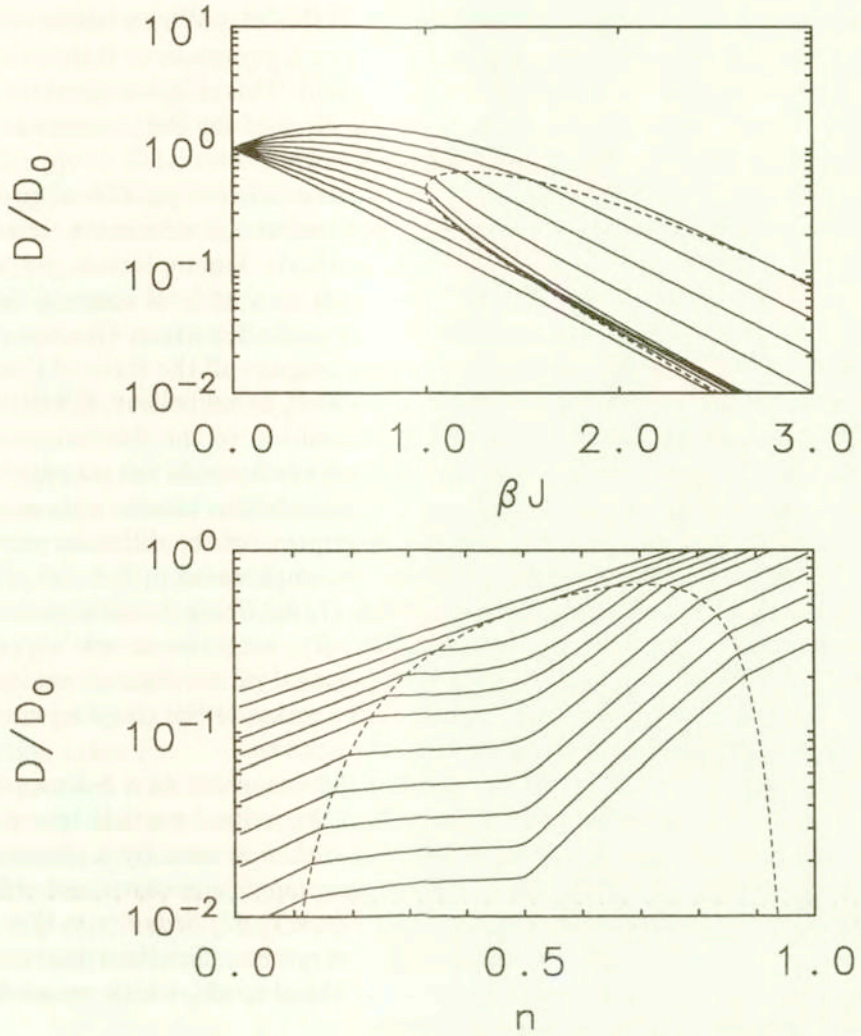

FIG. 2. a. Diffusion coefficient of the interacting lattice gas D/D_0 versus βJ. Adsorbate concentrations n decrease by 0.1, from $n = 0.9$ for the topmost line down to $n = 0.1$ for the lowest one. b. Adsorbate concentration dependence of D/D_0. Parameter βJ increases by 0.1 from $\beta J = 0.9$ for the topmost line up to $\beta J = 1.4$ and then by 0.2 up to 3.0 for the lowest one. $V = 1.5J$ and $D_0 = \nu_0 z/2d$ in both panels.

its center of mass can "absorb" arbitrary amount of momentum restoring the overall Gallilean invariance.

This new hydrodynamic picture of the dense adsorbate dynamics is difficult to use. In order to see how it can be utilized in practice we have created its toy version [11] based on the cellular automata paradigm [12–14]. The cellular automata models explore the complementary to lattice gas feature of the lattice models concentrating entirely on the velocity degrees of freedom of the migra-

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ting particles. The important role in the model [11] is played by a lattice collision operator constructed such as to mimic the physical processes of interaction between the adatom and the phonons of the host solid. This collision operator turns out to be closely related to cellular automata version of the Boltzmann – Lorentz model, well known from the classical kinetic theory.

As we have discussed it above, we do have three different possible approaches to the analysis of the seemingly simplest problem of the adsorbate dynamics, namely the diffusion processes. Each of the methods, kinetic lattice gas, mesoscopic density functional, and cellular automaton, can address some of the features of the adsorbed dynamics and fails to account for the other. Can one devise a model which will, within some limitations, encompass all the three of them? In a recent paper [15] we have proposed a model which, as we believe, does actually this. The basic ingredient of our model is generalized to the $2d$-dimensional μ space master equation which in well defined limits reduces to the standard form of master equation [7] or to the Boltzmann – Lorentz-like kinetic equation [11]. We have shown that our model provides a description of the diffusion processes in which fluid – like characters of the processes, emphasized in Ref. [10, 11] are combined with the hopping mechanism of Ref. [7, 8]. Using suitable generalization of the local mean field analysis from Ref. [7], we derive a new expression for the diffusion coefficient which permits us to analyze its dependence on several parameters, like temperature, density and a value of the coupling constant measuring the strength of mutual particle interactions.

Within the model of Ref. [15] we envisage the adsorbate as a d-dimensional, classical, many-particle system dense enough so the mutual particle interactions cannot be neglected. We describe the state of such a system by a μ-space distribution function $F(\mathbf{r}, \mathbf{v}, t)$ where $\mathbf{r}$ and $\mathbf{v}$ denote particle position and velocity, respectively. The customary normalization of $F(\mathbf{r}, \mathbf{v}, t)$ is $\int d\mathbf{r}d\mathbf{v}F(\mathbf{r}, \mathbf{v}, t) = N_{\text{tot}}$, where N_{tot} is the total number of particles in the system. This distribution function obeys the generalized master equation in the μ-space, which we postulate in accord with two fundamental requirements.

The first one is that this equation reduces to the well known master equation for a lattice gas (in the continuum limit) when the velocity degrees of freedom of particles are "averaged out". This means that in some limit, discussed below, the diffusion process described by our new model has to reduce to that discussed in Ref. [7]. The second requirement is that in the opposite limit, when fluid properties of the system are of greater importance than the hopping ones embodied in master equation of Ref. [7], we recover the description provided either by mesoscopic model of Ref. [10] or by the cellular automaton model [11]. This in turn implies that the master equation in the μ-space must bear a similarity to the Boltzmann–Lorentz kinetic equation, an essential ingredient of the model in Ref. [11]. The third condition imposed on our model is that it must take into account mutual interactions between particles in such a way as to make the applications of the local mean field model discussed in Ref. [7] possible.

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The master equation, which fulfills the above conditions reads:

$$\partial_t F(\mathbf{r},\mathbf{v},t) = -\mathbf{v}\cdot\nabla F(\mathbf{r},\mathbf{v},t) + \widehat{W}\{F\}\,. \tag{3}$$

To construct the operator $\widehat{W}$ we follow the lattice gas parlance and consider the full μ space distribution as a cell variable. The μ-space cells are constructed by splitting the configuration space into (quasi) lattice with a spacing a, and letting a particle in each configuration space cell to explore the entire momentum (or velocity) space.

The operator $\widehat{W}$ acting on the phase space function $F(\mathbf{r},\mathbf{v},t)$ can be written down explicitly in the following form:

$$\widehat{W}F(\mathbf{r},\mathbf{v},t) = \phi_B(\mathbf{v})\int d\mathbf{v}' \sum_{\mathbf{a}} \Gamma(\mathbf{r}+\mathbf{a},t)F(\mathbf{r}+\mathbf{a},\mathbf{v}',t) - z\Gamma(\mathbf{r})F(\mathbf{r},v,t)\,, \tag{4}$$

where $\phi_B(\mathbf{v})$ is the Maxwell–Boltzmann distribution function. The sum in Eq. (4) runs over all z nearest neighbors of the particle located at a site $\mathbf{r}$. The coefficients Γ are the transition rates for particle short range "jumps" between the sites $\mathbf{r}$ and $\mathbf{r}+\mathbf{a}$. Equation (4) resembles closely the generalization of the Boltzmann–Lorentz collision operator [15]. Indeed, replacing Γ's by averaged values and replacing $\phi_B(\mathbf{v})\int d\mathbf{v}'$ by the integral operator averaging velocities over the surface of a unit sphere in the velocity space, we obtain the Boltzmann–Lorentz operator. In a general case, the operator $\widehat{W}$ is nonlinear due to the F dependence of the transition rates Γ.

To proceed with analysis of Eq. (4) we follow our version of the local mean field theory discussed in length in Refs. [6, 7]. In this procedure one is replacing the many-body master equation by an effective single particle one in which the transition rates are functionally dependent on a single-site effective field which is randomly distributed. The effective master equation has to obey the H-theorem, thus for each realization of the local field distribution the density differs from its global mean value ρ_0 by a factor $\propto \Gamma^{-1}$:

$$\rho(h) = \Gamma^{-1}(h)\frac{\rho_0}{\int dh f(h)\Gamma^{-1}(h)}\,, \tag{5}$$

where $\Gamma(h)$ is the effective transition rate which depends on the value of the local field h, and $f(h)$ is the field distribution. The main point is now how one gets the field distribution $f(h)$. The explicit mean field procedure for the construction of $f(h)$ was provided in our earlier work Ref. [6, 7], we quote here only the final result. Denoting by $\subset A \supset = \int dh f(h)A(h)$ the average over the random local field, we obtain the following expression for the diffusion coefficient [15]:

$$D = \frac{a^2}{\subset \Gamma^{-1} \supset} + \frac{c^2 \subset \Gamma^{-2} \supset}{\subset \Gamma^{-1} \supset} = D_{\text{hopping}}\left(1 + \frac{c^2}{a^2} \subset \Gamma^{-2} \supset\right), \tag{6}$$

where D_{hopping} is the value of the diffusion coefficient following the kinetic lattice gas model discussed in Ref. [7] and at the beginning of this section.

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The above equation combines two contributions to the diffusion process: the one which is due to fluid – like properties of the system and that which is due to its lattice gas properties. It is the inverse averaged transition rate dependence of this coefficient which makes a comparison with the Monte Carlo data in our recent work [7] so effective.

Following the analysis from [7], one can obtain from Eq. (6) the following „engineering"-like expression for the diffusion coefficient

$$D = D_0 \left[\exp[-\rho_0 z(e^{\beta J} - 1)] + AT \exp[\rho_0 z e^{\beta J}(e^{\beta J} - 1)] \exp[2\beta V]\right], \tag{7}$$

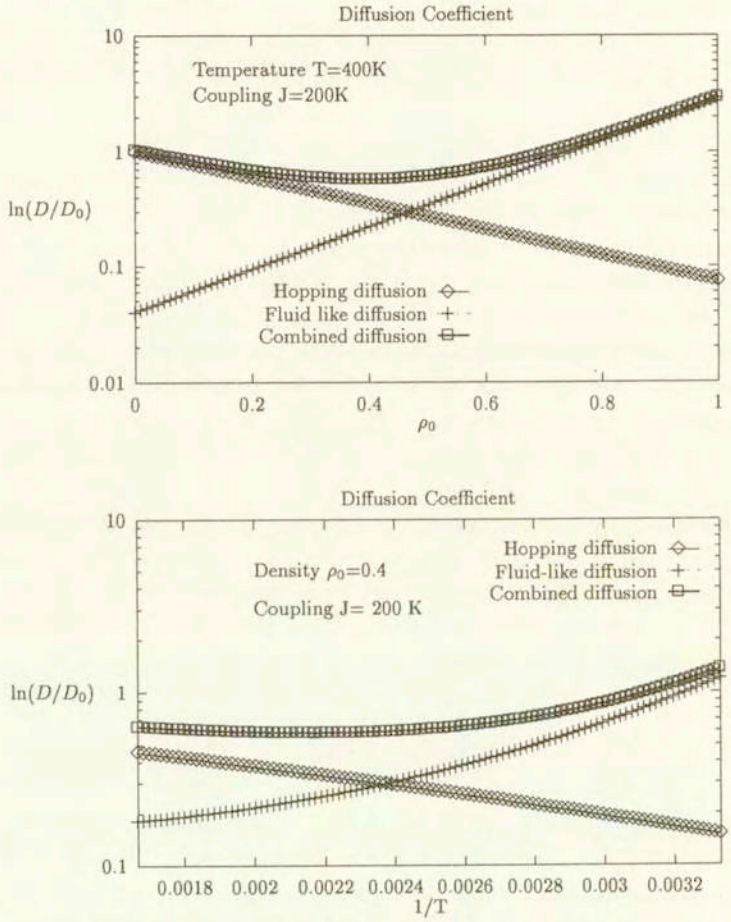

FIG. 3. a. Diffusion coefficient for $T = 400$ K plotted as a function of density ρ_0. The dotted line is for pure lattice gas model, the dashed one is the "fluid" contribution to the diffusion coefficient, and the solid one is the total diffusion coefficient. b. Diffusion coefficient for density $\rho_0 = 0.4$ plotted as a function of inverse temperature $1/T$. The dotted line is for pure lattice gas model, the dashed one is the "fluid" contribution to the diffusion coefficient, and the solid one is the total diffusion coefficient. $A = 10^{-4}\,\mathrm{K}^{-1}$ and $J = 200$ K in both panels.

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where $A = k_B/(mz\nu_0 a^2)$ and ν_0 is the overall rate factor setting a universal inverse time unit of our model. $D_0 = \nu_0 a^2 \exp(-\beta V)$ is the diffusion coefficient for the noninteracting lattice gas. For heavy adsorbates on metal surfaces the prefactor ν_0 is typically of the order of 10^{12}sec^{-1}. Assuming the mass of an adatom to be that of an oxygen atom and using the square lattice model with $a = 10^{-8}$ cm we obtain $A = 0.00143\,\text{K}^{-1}$. Varying the mass and using different values of the prefactor we find that A may change between $10^{-1} < A < 10^{-5}\text{K}^{-1}$. Values of the on-site potential and of the exchange coupling are chosen as in the Monte Carlo simulations of GOMER *et al.* [9] and in Ref. [7]. At low densities the hopping term dominates, while for larger ones the contribution due to the fluid – like behavior starts to grow and eventually it dominates. For reasons discussed in Ref. [15] our model should be treated with caution for large densities. In Fig. 3 we have shown the density and temperature dependence of the diffusion coefficient, respectively. The general behavior of it agrees with the physical picture one has concerning in what regime which contribution, hopping one or fluid one should dominate.

3. Diffusion in the presence of topological defects

So far we have discussed diffusion in systems where interparticle interactions modify the usual picture of diffusion viewed as a limit of the random walk. The resulting description still gives Einstein-like relation between the root mean square displacement of a "typical" particle and time $\langle r^2 \rangle \propto t$. The difficulty was how to calculate the proportionality coefficient i.e the diffusion coefficient. In this section I would like to discuss a different problem. I shall consider as simple random walk problem as possible – a single particle making unbiased jumps on a *locally* perfect lattice. The point here is in the word "locally". The lattice of adsorption sites in Sec. 2 was perfect. What happens when this lattice, and as a matter of fact any lattice, is imperfect?

The analysis of influence of various types of defects on simple diffusion is clearly beyond the scope of the lecture. I shall concentrate here on a particular type of extended line defects in solids, namely the *topological defects*. To be specific I shall consider edge and screw dislocations and disclinations of a sort (Kleinert disclinations). The latter are of a rather academic interest but they lead to a dramatic change in the diffusion behavior, they lead to so-called Sinay diffusion in more than $d = 1$ case. The material in this section is based on recent series of publications [16–19] and covers only salient features of our theory. No dislocation theory primer is included in this paper. The reader is referred to the wealth of available literature for necessary details of continuum dislocation theory [20–22].

Imagine a two-dimensional plane on which a Brownian particle has left its chalk–trace. Take now a black marble and roll it down that plane over the particle trajectory,without the slip. The chalk leaves the image on the marble surface.

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The question might arise, and actually it did to BOCHNER [23], what are the statistical properties of this image trace. The mathematical problem is that at each instance of the marble motion the plane is tangent to it, and in that tangent plane we have quite ordinary random walk; that is an "easy" part of the story. The difficult one is that we have to paste together pieces of locally normal random walks all over the *curved* surface. This kind of "academic" problem is precisely the one one encounters when studying diffusion in crystal which contains continuous distribution of dislocations and/or disclinations [21, 22]. Following main assumptions of this theory, a diffusing particle sees a locally perfect crystal. It recognizes that it moves in topologically distorted medium only after completing its path. Since the diffusion process involves all paths between two remote points, thus the presence of topological defects might affect the diffusion. Moreover, in a real crystal one controls neither the position nor the topological charges (Burgers vectors and Frank angles) of the defects. Both of these characteristics of the defects and their distribution are therefore random quantities. The statistics of them is independent of the thermal ensemble used to discuss the diffusion. Defects are a random *quenched* distortion of the lattice and therefore we have to incorporate them carefully into description of the diffusion.

In a series of papers [16–19] we just have proposed such an approach in which the diffusion process in the crystal with a given density of dislocations is visualized as a random walk in which the particle makes a jump from one allowed lattice site to another, with the jump probabilities the same as in the simple random walk, but only in the local frame. In local coordinates (ξ^α) the Langevin equation for such a process is then very simple and reads:

$$\frac{d}{dt}\xi^\alpha = l^\alpha , \tag{8}$$

where l^α is the usual Langevin force representing white noise with zero average and variance

$$\langle l^\alpha(t) l^\beta(t')\rangle = 2D\delta^{\alpha\beta}\delta(t-t') . \tag{9}$$

In the above formula $\langle f\rangle$ denotes the ensemble average and D is the bare diffusion coefficient in the medium free of dislocations.

Transforming the Langevin equation Eq. (8) back to the laboratory frame (x^i) we have:

$$\dot{x}^i(t) = B^i_\alpha(x(t)) l^\alpha(t) , \tag{10}$$

where $B^i_\alpha(x)$ is the "distortion"tensor (which differs from Kröner's by a unit tensor) specific to, and *known*, for all interesting types of defects. In Ref. [17] we have shown that the correct interpretation of the stochastic equation (10) is the Stratonovich one, which leads to the covariant diffusion equation of the form

$$\partial_t P(x,t) = D\Delta^T P(x,t), \tag{11}$$

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where

$$\Delta^T = g^{ij}\nabla_i^T\nabla_j^T\,, \qquad \nabla_i^T = \nabla_i + 2T_{ik}^k\,, \tag{12}$$

and g^{ij}, the inverse metric tensor, and the torsion vector $2T_{ik}^k$, are all given in terms of the distortion field B_α^i. In Eq. (11) $P(x,t)$ is a scalar probability distribution for a particle occupying site x at the time t.

Note, that equation (11) is the most general Fokker–Planck equation describing random walk on a manifold with non-zero torsion. Note also that the coefficients of this equation depend on the distortion field generated by dislocations. In case of random distribution of defects these coefficients become quenched random variables. I note in passing, that Eq. (11) is the fundamental equation in a not really explored field of random statistical geometry, which has many applications in general relativity, pattern recognition etc.

To discuss the diffusion process one has to average over a quenched random distribution of topological defects. This is conveniently done in a Martin–Siggia–Rose-type path-integral representation [24]. In refs. [16, 17] we have discussed in greater detail the predictions of the above outlined theory for quenched distribution of random disclinations and screw dislocations. Disclinations are the most prominent "topological" defects and their presence leads to the dramatic changes in the character of diffusion processes. Equation (11) for disclination case assumes the form of the Fokker–Planck equation with random drift velocity $V^i = -D\delta^{ij}\partial_j\Omega\Phi$, where Ω is the Frank angle and Φ is the two-dimensional Coulomb potential. For distribution of dislocation, statistical properties of the defects density $\rho(x)$ becomes important. We have studied defects distribution which is Gaussian with zero mean and has translational invariant second moments which include possibility of screening of topological charges [16, 17]. Denoting the screening length as κ we have shown that the particle exhibits nonuniversal subdiffusion with:

$$\overline{\langle x^2\rangle}(t) \sim t^{1-\gamma/8\pi\kappa}\,, \tag{13}$$

where γ is the strength of the defects distribution correlation.

The unscreened case is even more dramatic. For $\kappa = 0$ we have shown, following arguments of BOUCHARD, COMTET, GEORGE and LE DOUSSAL [25] that the particle diffusion becomes Sinay-like:

$$\overline{\langle x^2\rangle}(t) \sim (\ln t)^2. \tag{14}$$

As far as I know, it is the first example for Sinay diffusion in more than one dimension.

The quenched distribution of screw dislocations is more interesting due to the role played by these defects in crystal growth phenomena [26]. In this case our statistical model turns out to be, in a sense, exactly solvable (viz. Ref. [16, 17]). For the mean-square displacement of the particle we find an anisotropic normal diffusion behavior, enhanced in the z-direction. The latter is plausible since the

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locally isotropic random steps globally lead to climbing up or down of the particle on the spiral staircases of the screw dislocations. This effect is not strong enough to generate a superdiffusive (at least logarithmic) correction in the z-direction. However, anomalies do show up in higher cumulants of the particle position. E.g., for the fourth-order cumulants we find $\langle x^4 \rangle_c = 0$, and

$$\langle x^2 z^2 \rangle_c \sim \langle z^4 \rangle_c \sim t \ln t \tag{15}$$

for $t \to \infty$. Thus, topological defects give rise to a non-Gaussian random walk process. A measure of the deviation from Gaussian behavior are the relative cumulants which exhibit long-time tails, e.g. $\langle z^4 \rangle_c / \langle z^2 \rangle^2 \sim \ln t / t$. It is an open question whether one can observe this anomaly either in computer simulations or in laboratory experiments.

4. Quantum dynamics

In previous section I have analyzed the classical diffusion of a Brownian particle on a Riemann–Cartan manifold representing a crystal with frozen-in (quenched) topological defects [16, 17] (see also [27]). In an identical setting we now want to establish a general framework for the discussion of the long-wavelength quantum states of a single particle. For special cases of single straight dislocation lines this problem has repeatedly been discussed in the literature. The main physical effects connected with screw dislocations are the Bohm–Aharonov-type interference effects [28] and the (questionable) possibility of bound states of the particle to the dislocation lines [29]. For edge dislocations the existence of bound states has been demonstrated [30] on the basis of the deformation-potential approximation, see e.g. [31]. We will specify our general form of the Schrödinger equation on a manifold to these cases and comment on the most significant physical implications. This section contains most of the results contained in a recent work by RICHARD BAUSCH, RUDI SCHMITZ and myself [19].

In order to construct a foundation for our quantum mechanical analysis, in Ref. [19], we propose a model guided by the picture of a classical random walk of a particle in a topologically distorted crystal, which is the quantum tight-binding model on a d-dimensional lattice being coherently deformed due to the presence of frozen-in topological defects. With the notations $\mathbf{n}$ for the position vectors of the lattice sites and $\mathbf{a}(\mathbf{n})$ for the vectors pointing from $\mathbf{n}$ to the nearest-neighbor sites of $\mathbf{n}$, our model Hamiltonian reads

$$H = -\frac{1}{2} \sum_{\mathbf{n}} v(\mathbf{n}) \sum_{\mathbf{a}(\mathbf{n})} t(\mathbf{a}(\mathbf{n})) \left[\varphi^\dagger(\mathbf{n} + \mathbf{a}(\mathbf{n})) \varphi(\mathbf{n}) + \varphi^\dagger(\mathbf{n}) \varphi(\mathbf{n} + \mathbf{a}(\mathbf{n})) \right]. \tag{16}$$

Here $v(\mathbf{n})$ is the volume of the lattice unit cell at $\mathbf{n}$, $t(\mathbf{a}(\mathbf{n}))$ is the transfer energy along the bond $\mathbf{a}(\mathbf{n})$, and $\varphi^\dagger$, φ are the particle creation and annihilation operators obeying the commutation (or anti-commutation) relations.

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In order to reveal the long-wavelength quantum states of the particle, one has to expand the φ-operators depending on $\mathbf{a}(\mathbf{n})$ in (16) to second order in the lattice constant a of the undistorted lattice. The details of this analysis require careful but rather straightforward application of the rules of differential geometry. The resulting continuum limit of the Hamiltonian (16) for a model with a distortion-independent transfer energy $t = \hbar^2/(2ma^2)$ where m is an effective mass of the particle is:

$$H = -\frac{\hbar^2}{2m} \int d^d x \sqrt{g}\, \varphi^\dagger \left[g^{ij} \nabla_i^T \nabla_j + (g^{ij} \nabla_i^T T_{jk}{}^k) \right] \varphi , \tag{17}$$

where the operators $\varphi, \varphi^\dagger$ obey the commutation relations $\left[\varphi(x), \varphi^\dagger(y)\right] = \delta(x-y)/\sqrt{g(x)}$.

The Hamiltonian (17) is manifestly covariant as a consequence of the special form (16) chosen for the lattice model. The expression $g^{ij}\nabla_i^T \nabla_j$ in the kinetic part of (17) is identical to the Laplace–Beltrami operator $(1/\sqrt{g})\partial_i \sqrt{g} g^{ij} \partial_j$ and in general differs from the operator $g^{ij}\nabla_i^T \nabla_j^T$ entering the diffusion equation on a manifold [16]. The potential energy in (17) is proportional to the divergence of the torsion vector $T^i \equiv g^{ij} T_{jk}{}^k$ which is the only nontrivial scalar of the manifold in addition to the scalar curvature R. Whereas one finds $\nabla_i T^i = 0$ for screw dislocations and $\nabla_i T^i \neq 0$ for edge dislocations, the condition $R = 0$ is valid for both types of dislocations [32]. As an example of a defect with $R \neq 0$, we mention a kind of disclination defined by a distortion field $B_i^\alpha(x)$ which describes local rotations of the lattice [33] and implies $\nabla_i T^i = R/4$.

In Ref. [19] we have discussed application of Eq. (17) to the problems known in the literature and concerning the existence and/or nonexistence of the bound states formed for quantum particles by the topological lattice defects. We have clarified this issue by showing that the model in Eq. (17) does not allow for existence of the bound states for edge and screw dislocations. To describe the possibility of these bounds state one has to generalize the model allowing the transfer energy t to become space-dependent. Details of that discussion are outside of the scope of this lecture.

The other quantum mechanical model of the particle motion in the presence of the topological disorder was discussed by Andrzej ŁUSAKOWSKI and myself [34]. This model analyzes the tight binding Hamiltonian Eq. (16) in the presence of the random arrangement of the Bohm–Aharonov magnetic field fluxes penetrating the lattice cells. The position and value of the flux are quenched random variables. The analysis provides the analytic expression for the density of states of the particle shown in Fig. 4. The divergence of the density of states typical for a two-dimensional system is gone but the density is shrinked, the zone boundary is moved inwards. The shrinking of the zone depends on the jump anisotropy coefficient r but it is already clearly visible for isotropic case $r = 1$. This unexpected and puzzling result is well confirmed by the numerical simulations [35]. The the-

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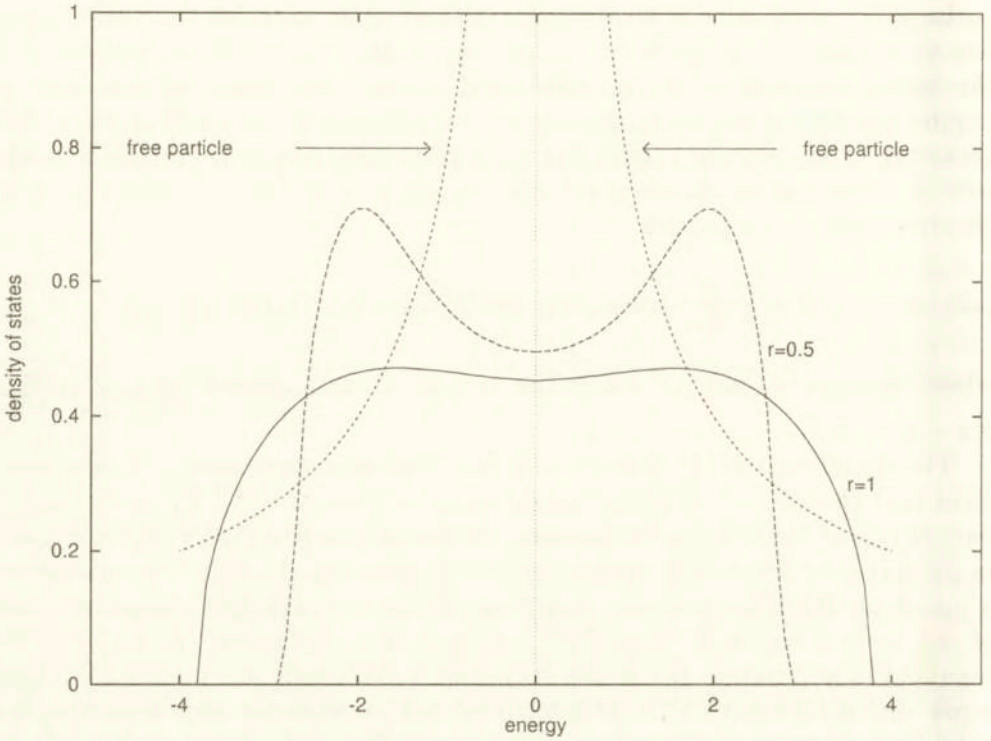

FIG. 4. Density of states plotted for various values of the ratio $r = K_x/K_y$. Upper line $r = 0.5$. Bottom line $r = 1$. Two-dimensional density of states for free particle is shown for comparison.

ory presented in Ref. [34] is a "first step" to the analysis of one of the most challenging problems in contemporary quantum statistical mechanics, namely the theory of quantum particle motion in a random magnetic field. Preliminary results obtained by us recently indicate, among others, that there is no simple diffusion there and that the system exhibits long time tails in the current–current correlation functions leading to the not yet fully explored memory effects in the dynamics of particles in random magnetic field. Work along this line has just been published [36].

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