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Abstract - The effect of heat-bath coupling on the conditions of access to saddle-point configurations of vacancy jumps in solid-state diffusion is investigated by analysing, in the framework of quantum statistics, the interplay between i) the rate of phonon-phonon collisions caused by anharmonicity, representing the bath rate, ii) the resonant mode of the defect and its lifetime determined by the additional anharmonicity caused by the defect, and iii) the rate of barrier relaxation of the multivariate deformable barrier. At low temperature where damping is small, the resulting jump rate closely approaches the rate law of Vineyard (1957) characterized by the fully relaxed saddle point.

With increasing temperature, damping of the resonant mode increases, allowing but for a partial relaxation; jumps occur at reduced rate over non-equilibrium configurations of the saddle point with increased migration enthalpy and, caused by large spatial gradients of the energy, with enlarged values of migration entropy and activation volume. The typical non-Arrhenius form of the rate resulting from temperature-dependent damping allows to interpret self-diffusion in many metals by jumps of monovacancies only.

Anharmonic damping of the resonant mode involves essentially low-frequency phonons not contained in the spectrum of crystallites with up to 1000 atoms. Computer modelling of jump rates thus underestimates the relevant damping and yields always the low-temperature approximation, that is the Vineyard rate.

I - INTRODUCTION

The temperature dependence of experimental data of the tracer self-diffusion coefficient D^T of metals usually exhibits curved Arrhenius plots lg D^T vs 1/T, /1/; the curvature is strong for bcc metals like Nb, Ta, Mo, W and Na while it is small but experimentally well established for the fcc metals Cu, Ag, Au, Ni, Pt, /1-3/. This curvature may be caused either by the contributions D_i^T of at least two migrating types of intrinsic atomic defects i with suitably differing activation parameters, or by curvature of $D_i^T = f_1\, a^2\, c_1\, \Gamma_1$ of one defect only, due most likely to its jump rate Γ_1. The jump rate of atomic defects has so far been estimated by transition state theory (TST) /4,5,6/ and its extensions /7,8/ based on the assumption of the equilibrium distribution of states and implying the relaxed Vineyard saddle point SP_{Vin}. The activation enthalpy of this saddle point depends but little on temperature /9/; hence TST supports two-defect models of self diffusion /10,11,12/.

Any rate theory which is more complete than TST has to evaluate the deviations from the equilibrium distribution. This affords consideration of the coupling to the heat bath, which on the one hand establishes a temperature $\beta^{-1} = k_B T$ and thermal fluctuations providing for hopping of atomic defects, and on the other hand imposes damping or dissipation on the dynamical motions. These two effects of a heat bath are inseparably interconnected like either side of one coin, as it is expressed in

the fluctuation-dissipation theorem, cf. /13/. TST neglects dissipation and establishes thereby an upper bound for any rate. Besides the early work of Kramers /14/ on this topic, several hundred papers have appeared in the past eight years, cf. /15/ for a review, dealing often with reactions in molecules immersed in a solvent. The present note discusses the elements to treat the jump rate of atomic defects in crystals for the example of the monovacancy in metals.

II - THE ONE-DIMENSIONAL PROBLEM

We consider a particle with mass M in a potential U(x), Fig. 1, describing a metastable well at x = 0 and a barrier with height U^b at x^b. The curvatures in the bottom and at the barrier are measured by ω° and $\omega^b > 0$, respectively. Coupling to a heat bath provides the inverse temperature β and imposes a friction $\zeta(x)$ or a damping rate $\gamma(x) = \zeta(x)/M$. TST yields the rate of escape

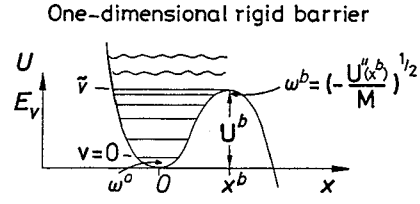

Fig. 1. The metastable well with basic parameters U^b, ω°, ω^b.

$$\Gamma_{TST} = \nu^\circ \exp(-\beta U^b); \qquad (1)$$

we use $\omega = 2\pi\nu$ throughout. Neither ω^b nor γ are contained in this rate law. Kramers /14/ found that in the limit of low friction (I) the thermal activation in the well is the rate-limiting process and the rate is proportional to $\gamma^\circ \approx \gamma(0)$: with the transmission coefficient $r \equiv \Gamma/\Gamma_{TST}$, he obtained

$$r_I = \gamma^\circ \beta U^b/\nu^\circ \text{ for } \gamma^\circ \to 0. \qquad (2)$$

For intermediate and high friction (II), activation of the particle to the barrier is so fast that escape over the barrier is the rate-determining process. There, damping at the barrier $\gamma^b \approx \gamma(x^b)$ is essential in reducing the equilibrium rate Γ_{TST}. With the normalized barrier damping $\alpha \equiv \gamma^b/2\omega^b$ the result is

$$r_{II} = \omega_R^b/\omega^b = \alpha\{(1+1/\alpha^2)^{1/2} - 1\}, \qquad \alpha \gtrsim 1/6, \qquad (3)$$

yielding $r_{II} \to 1/2\alpha = \omega^b/\gamma^b$ for $\alpha > 1$ and $r_{II} \approx 0.8$ for $\alpha = 1/6$. ω_R^b and ω^b are the friction-induced and the bare transmission frequencies of the barrier, respectively. This expression, formerly often judged as an approximate interpolation formula, is now well established: it appears as the classical limit of the quantum-statistical rate for linear coupling to the bath and for Ohmic or viscous damping /16,17/, and it is obtained for non-Markovian dynamics /18,13/ where a memory-renormalized $\hat{\alpha}$ replaces α.

The complete solution combining the regimes I and II for arbitrary but uniform damping $\gamma = \text{const}(x)$ is worked out in /13/, approximate solutions are given in /19,20/. In regime I, U^b in the exponent is replaced by $U_1(\gamma)$ with $U_1 \to U^b$ for $\gamma \to 0$ and $U_1 \to 0$ if r_I approaches unity /13/. This decrease of the activation energy in the transition region is a new result not obtained in the Kramers limits.

III - THE MULTI-DIMENSIONAL CASE

The rate constituting the diffusion coefficient of a monovacancy is the jump rate of one nearest neighbour of the vacancy over the barrier formed mainly by one gate of four gate atoms in the fcc lattice and by two consecutive gates of three atoms each in the bcc lattice. Various saddle-point configurations SP_c are distinguished by c; the equilibrium saddle point is SP_{Vin}. The infinitesimal potential at extreme points is described by mass weighted normal co-ordinates q_λ, q_μ and normal mode frequencies ω_λ, ω_μ where λ and μ count modes in the ground state at the bottom of the well and at the top of the energy barrier, respectively:

$$2U(q_\lambda) = \Sigma_1^N \omega_\lambda^2 q_\lambda^2; \qquad 2U(q_\mu) = 2U_c - (\omega_c^b)^2 q_1^2 + \Sigma_2^N (\omega_\mu^c)^2 q_\mu^2. \qquad (4)$$

Here ω_c^b is the bare transmission frequency and N the total number of degrees of freedom. These harmonic modes are mutually coupled by the anharmonic terms of the lattice potential leading to the damping parameters γ_λ, γ_μ /21/

$$\gamma_\lambda = a \sum_{\lambda_1\lambda_2} |V^{(3)}_{\lambda\,\lambda_1\lambda_2}|^2 T + b \sum_{\lambda_1\lambda_2\lambda_3} |V^{(4)}_{\lambda\,\lambda_1\lambda_2\lambda_3}|^2 T^2 + \ldots \qquad (5)$$

and a corresponding expression for γ_μ. The $V^{(n)}_{\lambda\ldots}$ and $V^{(n)}_{\mu\ldots}$ depend on the n-th derivative of the potential about the well bottom and the barrier top, respectively. For the stable modes the contributions to the γ are interpreted as n-phonon collisions which for $T > T_E$ (≈ Einsteintemperature) are $\sim T^{(n-2)}$. The γ_λ are the phonon widths or the inverse of the lifetimes τ_λ. The entirety of modes λ or μ represent the heat bath coupled by the anharmonicities of the potential to the modes involved immediately in the dynamics of the jump process. In the perfect lattice, theory /22/ and experiment /23/ indicate $\gamma_\lambda \lesssim 0.5\ \omega_\lambda$ at $T = T_m$ and $\gamma_\lambda \approx 0.05\ \omega_\lambda$ for $T \to 0$. The vacancy introduces strong additional anharmonicities, especially at the barrier, where on symmetry grounds the even coefficients are essential for the transmission damping: $\gamma_c^b \approx B_c T^2 + D_c T^4$. The normalized barrier damping $\alpha_c = \gamma_c^b/2\omega_c^b$ depends thus on the configuration c and on T.

The TST result for the vacancy has been given by Vineyard /5/

$$\Gamma_{TST} = \nu_{Vin} \exp(-\beta U_{Vin}), \qquad \nu_{Vin} = \prod_{\lambda=1}^{N} \nu_\lambda / \prod_{\mu=2}^{N} \nu_\mu . \qquad (6)$$

Again neither ω_c^b nor any damping parameter do appear in this expression.

The regime I of low damping $\gamma_\lambda \ll \omega_\lambda$ where vibrational energy transfer in the well is rate limiting is possibly realized for $T \to 0$. Assuming that N_c modes λ have to be excited to reach SP_c, the reduced rate in N_c dimensions is /24,25/

$$r_I \lesssim \gamma (\beta U_c)^{N_c} \exp(-\beta(U_c - U_{Vin}))/(N_c!\ \nu_{Vin}), \qquad \gamma = \sum_{\lambda}^{N_c} \gamma_\lambda \qquad (7)$$

going to the Kramers limit for $N_c = 1$. Since $\beta U_c \gg 1$ at low T, the rate is dramatically increased with respect to the one-dimensional case and the turnover between I and II /25/ should hardly be observable in solid-state diffusion; the TST rate is expected to hold at low T until α_c starts to increase.

Regime II where barrier damping reduces successful barrier crossings is governed by α_c. Expanding (3) we obtain

$$r_{II} \approx \omega_c^b \exp(-\beta(U_c - U_{Vin}))/\gamma_c^b(T), \qquad (8)$$

which for fixed c is an exponential whose pre-factor decreases as T^{-2} or T^{-4} with increasing temperature. The magnitude of the pre-factor depends on the ratio of the harmonic to the anharmonic parts of the barrier and varies with c. Consider the bcc lattice with its double-gate structure of the barrier of the vacancy jump. In the relaxed state c = Vin it tends to be close to a rectangular barrier with very small ω^b and large γ^b. This case exhibits a strong reduction of r_{II} by damping due to numerous recrossings of the diffusing particle before it moves away from the barrier. For the unrelaxed or partially relaxed barrier with $U_c > U_{Vin}$ ω_c^b is increased and γ_c^b decreased, and it depends on β what configuration is the most favourable: at intermediate $T < T_m/2$ the influence of the exponential is strong and $U_c \approx U_{Vin}$ with a decreasing pre-factor is preferable while at high temperature $T \approx T_m$ the decrease of the pre-factor would be severer and the largest contribution to the rate comes from jumps over non-equilibrium configurations of the partially relaxed barrier with increased migration enthalpy and, caused by the finite spatial gradients of U_c, with enlarged values of migration entropy and activation volume. These are the very features found in the analysis of self-diffusion in bcc metals; two-defect models /10-12/ to explain these properties are clearly not supported or postulated by the present rate theory which goes beyond TST by estimating all implications of the heat bath coupling. For fcc metals the effects are similar but less pronounced due to the simpler barrier structure. It appears that the recrossings due to damping are at least as important as the correction caused by dynamical return jumps /7,8/ associa-

ted with anharmonicity and curvature of the saddle surface.

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