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Molecular-dynamics study of self-diffusion in Na: Validity of transition-state theory

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A molecular-dynamics study of self-diffusion in Na is performed based on volume-dependent pair potentials constructed from second-order pseudopotential perturbation theory. It is shown that the migration energy of monovacancies as deduced from mean-square displacements agrees well with the migration energy predicted by the transition-state theory. The contributions of thermally excited Frenkel pairs to self-diffusion and specific heat at high temperatures is estimated. [S0163-1829(97)09237-0]

One of the most popular theories for atomic jump frequencies is the transition-state theory, which was applied to solid-state problems first by Wert and Zener[1] and, subsequently, by Vineyard.[2] The key assumption of this theory is that for calculating the classical jump frequency ν of atoms in a crystal, it is not necessary to follow explicitly their trajectories but that ν can be obtained by means of a statistical-mechanics description in the configurational space of the $3(N-1)$ coordinates and the $3(N-1)$ momenta of all the atoms in the system. It is not *a priori* obvious that this assumption is admissible for at least three reasons: (i) The probability distributions describe the statistics of the configurations only on a coarse-grained scale in the configuration space. (ii) For this coarse-grained scale the distributions are constructed in such a way that they yield the correct thermal averages of thermodynamic variables. This does not guarantee that they yield correct statistical results also for dynamical variables. (iii) During the derivation of the probability distributions a Markovian approximation is performed. In spite of the resulting ample criticism of the transition-state theory the various extensions of the theory and the development of alternative theories[3,4] the conventional version of the theory is still successfully applied to describe diffusional properties in many systems. For definiteness, we consider here the jumps of neighboring atoms into an adjacent lattice site. This leads to ‘‘vacancy migration,’’ which in many crystals is the dominant process of self-diffusion. The present note is concerned with testing, by means of molecular dynamics simulations, two aspects of the transition-state theory in its original form: (i) Within the framework of the transition-state theory the Arrhenius law

$$\nu=\nu_0 \exp\left(-\frac{E^{\mathrm{M}}}{k_{\mathrm{B}}T}\right), \tag{1}$$

where both ν_0 and E^{M} are independent of the temperature T, and k_{B} denotes Boltzmann’s constant, is derived under the assumption $E^{\mathrm{M}} \gg k_{\mathrm{B}}T$. It is generally assumed[5] that Eq. (1) should hold to a good approximation if E^{M} is at least three times larger than $k_{\mathrm{B}}T$. Does Eq. (1) hold also if E^{M} is not much larger than $k_{\mathrm{B}}T$? (ii) Provided that the above discussed inequality holds, the migration energy E^{M} in transition-state theory is given by the difference in potential energy for two totally relaxed static configurations, the first one with the considered atom in the saddle point configuration between the initial and the final state of the jump and the other with the atom at the initial potential minimum. Is this correct also for small values of $E^{\mathrm{M}}/k_{\mathrm{B}}T$? For the test, two types of calculations are performed: First, the energies of the fully relaxed static configurations with the considered atom in the saddle point configuration and the initial configuration are determined, yielding the ‘‘static’’ migration energy $E^{\mathrm{M}}_{\mathrm{TST}}$. Second, we go back to the original definition (1) of the migration energy which does not involve any model or approximation and determine the ‘‘dynamical’’ migration energy according to $E^{\mathrm{M}}=-k_{\mathrm{B}}\partial \ln\nu/\partial(1/T)$. In principle we could perform this test for any model system with interatomic potentials which yield a low migration energy. Instead, we consider a model potential which represents as accurately as possible the case of bcc Na. In Na, self-diffusion is dominated at least at intermediate temperatures by a monovacancy mechanism with a formation energy $E^{\mathrm{F}}_{1\mathrm{V}}$ which is much larger than the migration energy $E^{\mathrm{M}}_{1\mathrm{V}}$ (as in the case of Li[6]): The most recent *ab initio* pseudopotential calculations[7,8] yield $E^{\mathrm{F}}_{1\mathrm{V}}=(0.34\pm0.02)$ eV and $\Delta E^{\mathrm{M}}_{1\mathrm{V,TST}}=(0.05\pm0.01)$ eV and hence an activation energy for self-diffusion via monovacancies of 0.39 eV in very good agreement with the lower activation energy (0.37 eV) found by Mundy[9] by a fit of two exponentials to the self-diffusion data from tracer experiments. Since the melting temperature is 371 K it becomes obvious that in the high-temperature diffusion experiments the ratio $\Delta E^{\mathrm{M}}_{1\mathrm{V,TST}}/k_{\mathrm{B}}T$ is smaller than 2 so that the above assumption is not fulfilled. Insofar Na represents an interesting test for the validity of the conventional transition-state theory in a system with low migration energy. Furthermore, the molecular dynamics simulation can answer the question whether there are in addition to the monovacancy mechanism other contributions to self-diffusion and specific heat at high temperatures in Na.

A volume-dependent pair potential constructed from second-order pseudopotential perturbation theory according to Rasolt and Taylor[10] is used with an exponential damping[11] of the long-range oscillatory behavior and a cutoff radius of 13.5 Å, which is about half the extension of the supercell. In the simulations a cubic supercell containing 686 lattice sites is used, and periodic boundary conditions are applied. It should be noted that this form of the pair potential is not able to describe really accurately the defect energetics of real Na. For instance, the vacancy formation energy was only about

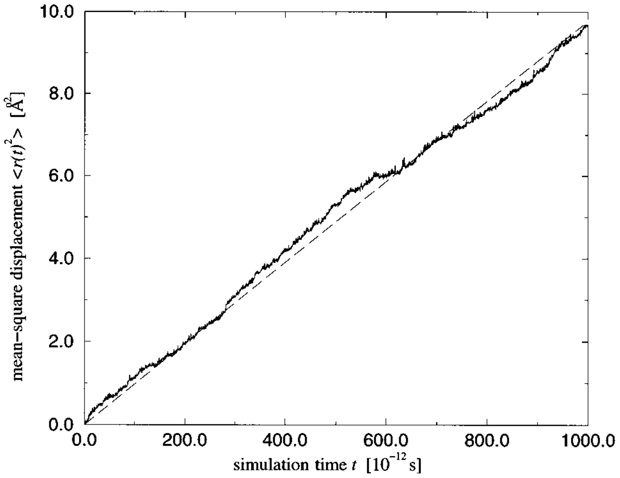

FIG. 1. Mean-square displacement of all atoms in a supercell containing 686 sites and one vacancy for $T=270$ K and $p=0$ Pa. The line represents a least-mean-square fit.

half the value found by the *ab initio* calculations, and the vacancy migration energy appeared to be about 30 % larger than the *ab initio* value (see below). Furthermore, the calculated pre-exponential factor for the diffusion coefficient (see below) appears to be by a factor of about 2 larger than the value obtained by Mundy[9] (see above) from his tracer experiments. Insofar, our pair potential is not able to yield highly reliable quantitative results for Na. It thereby should be noted that the potential does not contain any fit parameter which could be adjusted to experimental data in order to avoid the deviations between theory and experiment. However, for the test of the transition-state theory this does not matter: It is not the purpose of the present paper to test the transition-state theory just for Na, but we want to investigate the validity of this theory in general for systems for which the migration energy is not much larger than k_BT, and the model system defined by our pair potential belongs to this class of systems.

The molecular-dynamics simulations are based on the Nosé-algorithm,[12] which allows us to prescribe temperature T and pressure p. For an investigation of vacancy migration a single vacancy is introduced in the supercell and then the mean-square displacement of all the atoms,

$$\langle r^2(t)\rangle=\frac{1}{N}\sum_{i=1}^{3N}[q_i(t)-q_i(0)]^2, \tag{2}$$

is calculated (an example is given in Fig. 1), thereby taking into account only the diffusional jumps and neglecting the thermal vibrations around the lattice positions. The diffusion coefficient $D^{\mathrm{MD}}\propto \nu a^2$ (a denotes the lattice constant) then is obtained from

$$D^{\mathrm{MD}}=\frac{\langle r^2(t)\rangle}{6t}. \tag{3}$$

The system becomes unstable at about 340–350 K. We determined the quantity D^{MD} only up to $T=300.6$ K because for higher temperatures, a spontaneous formation of Frenkel pairs occurs (see below) and their contribution to D^{MD} cannot be strictly separated from the vacancy contribution.

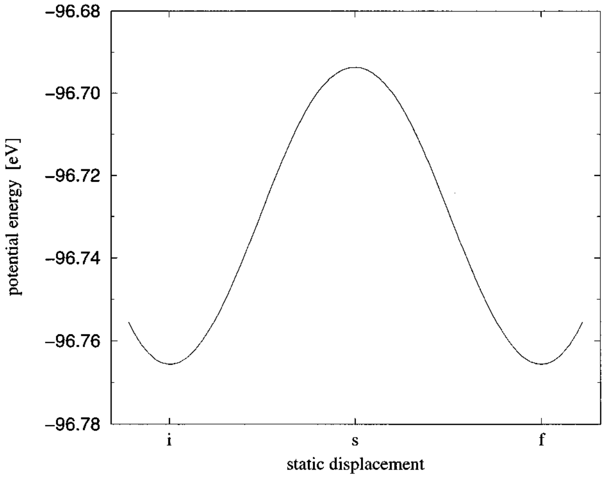

FIG. 2. The potential energy of the supercell as function of the static displacement of an atom into a nearest-neighbour vacancy along ⟨111⟩ from the initial site i over the saddle point s to the final site f.

Figure 2 represents the potential energy Φ as function of the static displacement of an atom from the initial state i into the final position f at a nearest-neighbor vacancy along ⟨111⟩ through the saddle point s half way, the system being fully relaxed for each position of the atom. The static migration energy as given by the difference in the potential energies between the saddle point s and the initial state of the jump is $E^{\mathrm{M}}_{1\mathrm{V,TST}}=(72.0\pm0.2)$ meV. The temperature dependence of the diffusivity is shown in Fig. 3. The full line corresponds to a least-mean-square fit, yielding via Eq. (3) the dynamical migration energy of $E^{\mathrm{M}}_{1\mathrm{V}}=(76.8\pm5.8)$ meV, in good agreement with the static value. Obviously, the transition-state theory yields a reliable prediction for the migration energy although the ratio $\Delta E^{\mathrm{M}}_{1\mathrm{V}}/k_BT$ decreases below the value of 3 when increasing the temperature up to 300 K. It should be noted that Willaime and Massobrio[13] performed a similar comparison of the static and the dynamic migration energy for the case of bcc-Zr (for which $\Delta E^{\mathrm{M}}_{1\mathrm{V,TST}}/k_BT$ is also about 2–3) and also found good agreement.

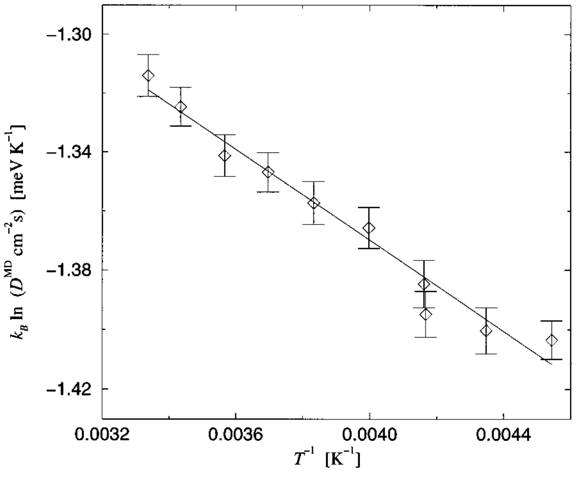

FIG. 3. Temperature dependence of D^{MD} with 2σ error bars estimated via $\sigma/D^{\mathrm{MD}}=1/\sqrt{z}$, where z is the total number of diffusional jumps during the simulation time.

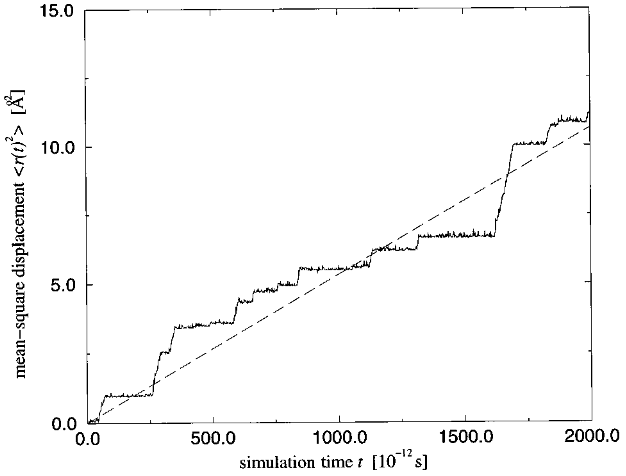

FIG. 4. Mean-square displacement of all atoms in a supercell ($T=310$ K, $p=0$ Pa) due to the spontaneous formation of Frenkel pairs. The line represents a least-mean-square fit.

For temperatures larger than 300 K we observe the spontaneous formation of Frenkel pairs, i.e., an atom is displaced from its original lattice site, leaving back a vacancy and a second-nearest neighbor atom (i.e., along $\langle 100 \rangle$) on an interstitial site. The vacancy and the interstitial atom separate from each other and migrate for some time more or less independently until they meet again and recombine. Such processes were found already by Doan and Adda[14] in their molecular dynamics simulation of Na. It should be noted that this process, which is a succession of individual jump events of the two constituents of the Frenkel pair, is different from the ring mechanism introduced by Zener[15] (see also Ref. 5), which represents a cooperative motion of two or more atoms in a ring. (It has been demonstrated by *ab initio* calculations[16] that in Na the activation energy for a direct exchange of two atoms is by a factor of about 4 larger than the vacancy formation energy). To investigate the formation and diffusion of the Frenkel pairs we perform molecular dynamics simulations for $T>300$ K for a supercell without vacancy. The ''fingerprint'' of the formation and diffusion of the Frenkel pair is the sudden increase of the mean-square displacement, followed by a longer period for which nothing happens after the recombination of vacancy and interstitial atom (Fig. 4). Our objective is to compare the contributions of vacancies and of Frenkel pairs to the total diffusion coefficient. The contribution of the Frenkel pairs, $D_{\mathrm{FP}}^{\mathrm{MD}}$, is directly given via Eq. (3) by the mean-square displacement obtained from the molecular dynamics simulation for the supercell without vacancy. In contrast, the contribution of the vacancies, $D_{\mathrm{1V}}^{\mathrm{MD}}$, must be calculated as

$$D_{\mathrm{1V}}^{\mathrm{MD}}=D_{\mathrm{1V}}^{\mathrm{MD}}(C=1/686)\cdot\frac{C_{\mathrm{1V}}^{\mathrm{eq}}}{1/686}, \tag{4}$$

where $D_{\mathrm{1V}}^{\mathrm{MD}}(C=1/686)$ is obtained via Eq. (3) from the simulation for a supercell containing 686 sites and one vacancy, and $C_{\mathrm{1V}}^{\mathrm{eq}}$ is the concentration of monovacancies in thermal equilibrium,

$$C_{\mathrm{1V}}^{\mathrm{eq}}=\exp(S_{\mathrm{1V}}^{\mathrm{F}}/k_{\mathrm{B}})\exp(-E_{\mathrm{1V}}^{\mathrm{F}}/k_{\mathrm{B}}T). \tag{5}$$

TABLE I. The ratios and the scaled ratios (see text) of the contributions of Frenkel pairs and monovacancies to the diffusion coefficient.

T [K]	$D_{\mathrm{FP}}^{\mathrm{MD}}/D_{\mathrm{1V}}^{\mathrm{MD}}$	$D_{\mathrm{FP}}^{\mathrm{MD}}/D_{\mathrm{1V}}^{\mathrm{MD}}$ scaled
300	$(1.8\pm1.3)\times10^{-2}$	5.2×10^{-10}
310	$(8.3\pm2.0)\times10^{-2}$	1.7×10^{-9}
320	$(14.9\pm2.5)\times10^{-2}$	5.1×10^{-9}
325	$(15.8\pm2.3)\times10^{-2}$	8.6×10^{-9}
330	$(22.5\pm3.1)\times10^{-2}$	1.4×10^{-8}

Here $S_{\mathrm{1V}}^{\mathrm{F}}$ and $E_{\mathrm{1V}}^{\mathrm{F}}$ denote the vacancy formation entropy and energy, which we calculate for the model system defined by our volume-dependent pair-potential on the lines described in Ref. 6. The numerical results for the diffusion coefficients may be represented by $D_{\mathrm{1V/FP}}^{\mathrm{MD}}=D_{\mathrm{1V/FP}}^{0}\exp(-E_{\mathrm{1V/FP}}/k_{\mathrm{B}}T)$ with $D^0=1.15\times10^{-6}$ m^2 s^{-1} (4.02 m^2 s^{-1}) and activation energy $E=0.25$ eV (0.72 eV) for monovacancies (Frenkel pairs). The large pre-exponential factor D^0 for the Frenkel pairs is in the present calculation responsible for an appreciable contribution of the Frenkel pairs to the total diffusion (Table I), in spite of the fact that the activation energy E_{FP} is by about a factor of 2.9 larger than that for vacancies, E_{1V}. However, we must recall that the pair potential used (which is the same as the one of Doan and Adda[14]) yields a vacancy formation energy which is by about a factor of 2 smaller than the value obtained by *ab initio* calculations. If we scaled the pair-potential by a factor of p to obtain the correct vacancy formation energy, the activation energies would also scale by a factor of p, whereas the formation and migration entropies should remain roughly constant. They would not change at all in a high-temperature quasiharmonic approximation. Thus, the ratio of the diffusion coefficients of Frenkel pairs and vacancies would be proportional to $\exp[-p(E_{\mathrm{FP}}-E_{\mathrm{1V}})/k_{\mathrm{B}}T]$, yielding the scaled ratios given in Table I, which are extremely small.

The excitation of atomic defects yields an anharmonic contribution to the specific heat. Ascribing this contribution to the thermal generation of monovacancies, Martin[17] obtained a formation energy for vacancies in Na of (0.35 ± 0.05) eV close to the above quoted result from the *ab initio* calculation.[7,8] From our molecular-dynamics simulations we have estimated the contribution of Frenkel pairs to the specific heat. For the unscaled pair-potential the effect of the Frenkel pairs is comparable to the monovacancy contribution for temperatures close to the melting point, whereas for the scaled pair-potential the contribution of the Frenkel pairs is negligibly small.

From the preceding discussion we conclude the following: The contributions due to the appearance of Frenkel pairs in thermal equilibrium at high temperatures to both self-diffusion and specific heat are characterized by distinctly higher pre-exponential factors and higher activation energies than those due to vacancies. They could therefore be easily recognized if they became significant well below the melting temperature. The strong increase of the specific heat observed in some refractory body-centred cubic metals (see, e.g., Ref. 18) at elevated temperatures might be caused by this mechanism. In Na the high-temperature formation of Frenkel pairs can give rise to observable effects only very close to the melting point, where they would be difficult to identify. Evidence for an additional contribution to the self-diffusivity of solid Na close to the melting point has been found by Mundy[9] by fitting a superposition of three Arrhenius laws to data from tracer self-diffusivity measurements. It remains to be seen whether this contribution is to be attributed to the Frenkel-pair mechanism.

Part of the calculations have been performed at the HLRZ of the Forschungszentrum Jülich (KFA).

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[1] C. Wert and C. Zener, Phys. Rev. **76**, 1169 (1949).

[2] G. H. Vineyard, J. Phys. Chem. Solids **3**, 121 (1957).

[3] C. P. Flynn, *Point Defects and Diffusion* (Clarendon Press, Oxford, 1972).

[4] P. Hänggi, P. Talkner, and M. Borkovec, Rev. Mod. Phys. **62**, 251 (1990).

[5] A. Seeger, Defect Diffus. Forum **95-98**, 147 (1993).

[6] W. Frank, U. Breier, C. Elsässer, and M. Fähnle, Phys. Rev. Lett. **77**, 518 (1996).

[7] U. Breier, W. Frank, C. Elsässer, M. Fähnle, and A. Seeger, Phys. Rev. B **50**, 5928 (1994).

[8] U. Breier, V. Schott, and M. Fähnle, Phys. Rev. B **55**, 5772 (1997).

[9] J. N. Mundy, Phys. Rev. B **3**, 2431 (1971).

[10] M. Rasolt and R. Taylor, Phys. Rev. B **11**, 2717 (1975).

[11] M. S. Duesbery, G. Jacucci, and R. Taylor, J. Phys. F **9**, 413 (1979).

[12] S. Nosé, J. Chem. Phys. **81**, 511 (1984).

[13] F. Willaime and C. Massobrio, Mater. Res. Soc. Symp. Proc. **209**, 293 (1991).

[14] N. V. Doan and Y. Adda, Philos. Mag. A **56**, 269 (1987).

[15] C. Zener, Acta Crystallogr. **3**, 346 (1950).

[16] U. Breier, PhD thesis, University of Stuttgart, 1996.

[17] D. L. Martin, Phys. Rev. **154**, 571 (1967).

[18] Y. Kraftmakher, Defect Diffus. Forum **143-147**, 37 (1997).