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BACKGROUND MATERIAL FOR LECTURES ON "COMPUTER SIMULATION OF DEFECTS AND MECHANICAL PROPERTIES"

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Defect Calculations beyond the Harmonic Model

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Prefatory Remarks

Advances in the theory of atomic diffusion in crystals due to thermal generation and migration of point defects are currently sought in the two distinct direction of (i) an accurate determination of the interaction potential energy of the crystal as a function of atomic positions, and (ii) a precise calculation of the consequences of the N-body potential energy surface on thermodynamic and dynamic properties expressed as thermal averages.

Let us loosely characterize the present status of the theory. Regarding point (i), carefully determined potential functions have become available, often resulting from sophisticated ab initio calculations, if only for the simpler ionic, rare gas, and metallic crystals. Many body effects have also been introduced via polarization, screening, and the like.

The theoretical task is far from exhausted, however. An accurate and manageable description of the crystal energy is awaiting further progress for large and important classes of materials. This is the case most noticeably of transition metals and covalent-bonded solids. For these and other systems work is actively being done with pseudopotential theories (often pushing the expansion to higher order), self-consistent calculations, and other methods. Even for the simpler solids the available theoretical calculations are not final. Choice of theoretical parameters contained in the ab initio potentials, of the form for the dielectric function, of the description of the polarizability, and so on, are still a matter of debate. Because of the resulting variation of theoretical predictions, and because of further sources of indetermination in practical implementations, like inadequate treatments of the long-range part of the interaction, comparison with experiment is often aleatory and not conclusive.

Regarding point (ii), exact treatments of structural relaxation on the one hand, and of vibrational energy and entropy on the other, have made possible the numerical solution of the problem in the harmonic approximation and assuming memory randomization, using long-developed theoretical treatments based on equilibrium statistical mechanics and transition state theory. Within these limits, important factors in solid state diffusion, like defect concentration, jump frequency, and the isotope effect, can all be evaluated and compared with experiment. This achievement is made possible by the capability of modern electronic computers to handle large dynamical matrices in a reasonably short time.

However, the statistical mechanics problem should be approached in a manner amenable to solution without the assumptions and approximations mentioned above. The effect of anharmonicity on canonical averages as well as the role of crystal memory in such dynamical effects as multiple jumps and immediate return jumps remain largely open problems. As a consequence, such fundamental questions as the origin of curvatures of Arrhenius plots, high-temperature deviations from rate theory predictions, and anomalous isotope effects cannot be resolved. The conditions for a change of this situation have been brought about in the last decade by computer simulation techniques. These methods and their applications to point defects were discussed in a beautiful chapter by Bennett (1975). Bennett (1976a) also outlined a complete strategy based on them to calculate the features of point defect diffusion in simple model substances.

As a consequence, we should now be in a position to confront the task of precisely assessing the shortcomings of the harmonic model and of testing the adequacy of analytical treatments of anharmonicity in solid state diffusion.

I. Introduction

A. Plan of the Chapter

This chapter is devoted to a description of recent developments regarding the statistical mechanical treatment, using the computer, of point defect diffusion. In recent years Monte Carlo (MC) calculations, i.e., the numerical evaluation of the configurational integrals involved in thermal averages by using sampling techniques based on computer-generated random numbers [see, for example, Binder (1979) and references therein], and molecular dynamics (MD) calculations, i.e., the numerical solution of the classical equations of motion describing the time evolution of a system of interacting particles [see, for example, Kushick and Berne (1977) and references therein], have been carried out in this field for a few model crystals along with accurate lattice dynamics (LD) calculations, i.e. the numerical evaluation of the thermodynamic properties of a model crystal involving the knowledge of the crystal static energy in the equilibrium configuration along with its derivatives with respect to particle displacements [see, for example, Maradudin *et al.* (1971) and references therein]. Yet they have been far less extensive and have covered far less ground that one might have hoped ten years ago. This may be due to the fact that these calculations require both a great deal of computer time, and the use of rather sophisticated techniques to extract the interesting result, i.e., to isolate nonharmonic effects and dynamical memory effects. Account will be given here of what can be learned from such studies by comparing the results to LD calculations. Methods will be outlined along with examples of their application. The necessity for increased emphasis on the detailed analytical investigation of the N-body potential energy surface to include anharmonic features should become apparent from this presentation.

The precise nature of the assumed "force law" between the particles is not of paramount importance. Of course, care is taken to choose model potentials likely to embody the main qualitative features of the systems in hand, rare gas crystals, alkali metals, salts, or other. But the main thrust is always on the assessment of the precise consequences of an assumed force law on the statistical mechanical behavior of the model. This is because it is quite unknown at the outset what the findings will be, and because these are expected to be qualitatively similar for large classes of systems.

Because a presentation of this character is best developed from a single point of view, and even more because that work is better known to the present author, he shall mostly describe work in which he was directly involved. Part of it is yet to be published. Some of it is still under way. The resulting picture will be necessarily incomplete.

A major decision in preparing the chapter has been the inclusion of a rather extensive treatment of a specific investigation, i.e., lattice dynamics of an fcc Lennard-Jones model crystal containing a vacancy. This was done to create the occasion for pointing out the conceptual and methodological intricacies of defect thermodynamics. Vacancy formation at constant lattice parameter, constant atomic volume, and constant pressure will be compared showing the relation between LD predictions, both at zero and finite temperature, for the different circumstances. The possible size of errors involved in using approximate expressions to get one from the other, e.g., constant pressure results from constant volume data, or worse, in confusing one of these with the constant lattice parameter data, will be thus indicated. System size and long-range potential cutoff dependence of the results will be mentioned. Accurate treatment of these technical aspects of the calculation is important. Furthermore, classical and quantum mechanical LD results will be compared for the case of the Lennard-Jones model of argon.

The role of anharmonicity in the Lennard-Jones fcc crystal model has been studied by Monte Carlo (Holt *et al.*, 1970). Methods permitting the evaluation of free energy differences were successfully applied to the calculation of the free energy of formation of a lattice vacancy (Squire and Hoover, 1969; Jacucci and Ronchetti, 1980). A comparison of these thermodynamic results, including a recent calculation for the vacancy formation volume, with corresponding LD data (De Lorenzi *et al.*, 1984c), will indicate clearly the relevance of "explicit" anharmonic contributions, i.e., additional to those included in the quasiharmonic treatment via thermal expansion of the lattice.

Vacancy migration properties will also be discussed. Monte Carlo investigations of the free energy on the saddle plane are available (Bennett, 1975) and will be compared to recent accurate LD data (De Lorenzi *et al.*, 1984c).

Anharmonic effects on the jump event have been recently investigated by approximating the saddle surface S, using the Taylor expansion of the N-body potential energy surface truncated to third order (Jacucci *et al.*, 1984). Dynamical corrections to rate theory have thus been evaluated for the first time on realistic model systems. The temperature-dependent fraction of immediate return jumps and correction to the isotope effect factor are obtained to lowest order and compared to computer simulation studies.

These investigations provide a thorough testing of the conceptual foundations of rate theory and a demonstration of its wide applicability to diffusion in solids.

B. Scope of Machine Calculations on Point Defects

Consider a crystal consisting of N interacting atoms disposed either in a regular lattice or in a lattice containing a defect. Place it in contact with a heat bath at a given temperature and pressure. The exact evaluation of the energy, entropy, and volume of this system from knowledge of the interaction potential is a formidable computational task even for pair additive forces and $N \approx 100$.

Computer simulation techniques, or machine calculations, like MC and MD have been used extensively to this end for liquids and, more recently, high-temperature solids. These sampling techniques are needed to evaluate the $3N$-dimensional configurational integrals related to the desired thermodynamic quantities in classical statistical mechanics. No sufficiently accurate analytical treatment is available for such highly disordered systems.

A quite different case are crystals below the Debye temperature, whether consisting of regular, or defected, lattices. Here the disorder can be subjected to analytical treatment. Terms beyond quadratic in the Taylor expansion of the potential energy in powers at the atomic displacements about static equilibrium configurations can be neglected, the quadratic form diagonalized, and the integrals over normal coordinates analytically carried out to obtain precise expressions of the energy, entropy and pressure as a function of temperature and volume. The computational task is reduced to the determination of the crystal static energy ϕ and of the vibrational eigen-frequencies ω_α in the relaxed equilibrium configuration, as functions of the crystal volume. This task still requires the solution of an N-body problem. However, it can be carried out on modern machines for N up to ~ 100 using standard computer routines performing function minimization and matrix diagonalization. The results are of course affected by zero variance, these procedures being analytical, and not statistical, in character. These calculations are called lattice dynamics.

At temperatures at which atomic diffusion is important, terms beyond quadratic in the expansion of the crystal energy are not negligible. As a result, anharmonic contributions to the thermodynamics of lattice defects are to be expected. Of course, machine calculations such as MC and MD are exact in this respect. They properly include in the results the effect of all

features of a given interaction potential. The reason that existing calculations of this kind are so scarce is that point defects contribute only terms of the order of $1/N$ to the total crystal properties. As a consequence, the sought result is buried in the statistical noise in standard calculations. One must revert to sophisticated, if available, difference techniques. Apart from its use as a means of sampling configuration space to perform thermal averages, the MD method is the primary tool to investigate in full the dynamics of a classical many-particle system. Trajectories of the representative point of the system in $6N$-dimensional phase space can be generated and analyzed. Jump frequencies can be measured in a simple way, at least when the residence time of the defect is not much longer than a picosecond. The actual path taken in the jump process can be monitored. All questions connected with crystal memory and persistence in the direction of motion of the defect, multiple jumps, and anharmonic isotope effects are open to direct observation.

In short, there exist two essentially different ways to exploit the knowledge of the N-body potential energy surface ϕ. One was just mentioned, i.e., sampling configurations from a thermal ensemble using the potential energy as statistical weight in MC or MD calculations to evaluate thermal averages related to free energies, and jump frequencies. Alternatively, one can investigate the shape of the surface ϕ directly and make use of the information thus gained in the framework of an analytical theory. This is the strategy used in LD. From knowledge of ϕ and ω_α at special points, thermodynamic parameters of point defects are calculated with the quasiharmonic theory of lattice vibrations, and jump frequencies are derived with the help of transition state theory.

One can take the latter point of view and extend the Taylor expansion approach beyond harmonicity. While the harmonic treatment truncates the Taylor expansion of the energy surface to second order, the third-order terms can be calculated as a next step. Lowest-order anharmonic contributions to the free energy can be evaluated in this way, as well as lowest-order dynamical corrections to rate theory in the form of the occurrence of immediate return jumps or deviations from harmonic isotope effects.

Whether the evaluation of local properties of the N-body surface at special points (minima, saddle points, etc.) limited to third derivatives of the crystal potential energy ϕ with respect to atomic displacements is an exhausting undertaking, or even a relevant one, cannot be said at the start. Whether strongly anharmonic hills and canyons dominate the shape of the surface on a distance scale that is small compared with atomic displacements characteristic of diffusion paths, thus hindering the possibility of projecting the behavior of the surface looking out from special points and using only the first few terms in the Taylor expansion, is a matter to be settled by extensive testing. In view of the considerable success met by the harmonic approximation, it seems certainly highly desirable and probably a rewarding endeavor to investigate the role of the next order in the expansion and to consistently extend the theoretical description. Such an investigation represents a formidable computational problem, but it will probably bring about a most important advance in the fundamental theory of point defect diffusion.

C. POINT DEFECTS IN MACHINE CALCULATIONS

Well-localized point defects in otherwise perfect crystals are especially suited for investigation by using machine calculation methods on a crystal comprising a few hundred particles with periodic boundary conditions. Short-range interactions between point defect pairs can also be handled in this way. Information thus obtained is sufficient to describe the thermodynamics of point defects in crystals in the low concentration limit. At high concentration of lattice defects, e.g., in superionic conductors, deviations from isolated point defect properties should be expected. The time-honored Born–von Kármán cyclic conditions are still a good way to minimize the effect of surfaces or interfaces. The limit of large system size has, of course, to be considered.

In computer simulation studies certain types of defects can be spontaneously generated by thermal fluctuations. This is the case of Frenkel pairs in, e.g., CaF_2 (Jacucci and Rahman, 1978). However, because of the absence of sources and sinks for point defects (e.g., dislocations, grain boundaries, surfaces), in most such studies unpaired point defects like vacancies are not generated or annihilated. Furthermore, the free energy required to generate Frenkel pairs is too high in many systems, e.g., monoatomic solids. As a consequence, dynamical simulations of the migration of an isolated vacancy or interstitial in otherwise perfect crystals are easily carried out by artifically introducing a single defect into the lattice from the start. The situation is quite different in superionic conductors and on crystal surfaces. The generation of point defects on surfaces costs much less free energy than in the bulk. High concentrations of adatoms and surface vacancies are commonly attained above one half of the bulk melting temperature. As a consequence, point defect pairs spontaneously appear within a few picoseconds on the top of the few-hundred square angstrom surface being simulated (De Lorenzi *et al.*, 1982). The regular lattice structure of the surface is readily spoiled and the very description of the system in terms of point defects breaks down, as it happens, e.g., in bulk AgI or certain oxides.

A last remark is in order about machine calculations. The techniques employed in them have become rather involved and many practical details influence the final result. In a sense they have lost the character of directness and self evidence that theoretical work often has. They are really experiments, albeit numerical and on model systems, and should be regarded and treated as such. In reporting them it is essential to state precisely the nature and order of all the steps taken. All relevant technical details affecting procedures, routines and computer usage are essential parts of the experiment. Failure to record and convey to others all relevant aspects included in the calculation results in the impossibility to repeat the experiment recovering the same result. This general remark is expecially true for defect calculations, because defect properties are of order $1/N$. In order to assess whether a theoretical prediction of defect properties is really sound, it is essential that the model and techniques employed be consistently and extensively tested, so that all aspects of them be well understood by the authors as well as by others. This is seldom done. The one bad feature of this state of affairs is that often nobody knows how to assess the degree of confidence of numbers provided by calculations and being compared to experimental results!

II. Lattice Dynamics

A. BRUTE FORCE VERSUS ANALYTICAL APPROXIMATIONS

Until recently, coherent use of well-developed statistical mechanical concepts was hindered by computational limitations. Use of drastic approximations both in the models examined and in the technical procedures employed biased the resulting theoretical predictions in an essentially unknown manner. Starting about 25 years ago, a great deal of effort went into the development of valuable analytical schemes for calculating defect properties with an acceptable computational burden on available computers. Careful theoretical backing was provided for the various approximations involved. However, the precise determination of point defect properties has turned out to be an extremely difficult task that is very often out of the reach of simplified schemes.

It should be clearly stated that the older schemes are no substitute for current codes. The latter are specifically suited for handling disordered systems and investigating the N-body potential energy surface exactly. The earlier schemes are still of value insofar as a careful comparison of their predictions with the results of modern accurate calculations represents a test of the adequacy of well-identified theoretical approximations. But, unfortunately, their use for such careful comparisons is rare. In our opinion the use of old schemes has somewhat outlived their research value. The effort needed to precisely identify their limitations has outgrown any useful knowledge they provide.

To some, this transformation of the theoretical work in the direction of "brute force" methods may not be palatable. However, a comment similar to ours was made almost 15 years ago by Maradudin *et al.* (1971, p. 196), where a complete account can be found of the approximate methods that were introduced to study frequency distributions and related properties such as zero-point energies and Debye thetas in crystalline solids:

> In the final analysis, however, the advent of high speed computers may render obsolete approximate methods for the calculation of θ_D [and the frequency spectra, etc.] ... it is only necessary to solve for the eigenvalues of the dynamical matrix for a very large number of direction in q-space; [frequency spectra, etc.] can then be evaluated numerically to almost any desired degree of accuracy.

Here are some examples of highly idealized models and approximate procedures that were employed for defect studies in order to keep the computational task within the capability of available machines.

- (i) Regarding the interaction potential:
  - (a) limitation to first near neighbors only, or to the first few shells,
  - (b) approximation of the potential and forces at distorted lattice configurations using truncated Taylor expansion of the potential function from the regular lattice configuration.
- (ii) Regarding the determination of relaxed configurations:
  - (a) limitation of the relaxation to the shell of first neighbors of the point defect, or to the first few shells,
  - (b) approximation of the relaxed displacements as a truncated expansion in powers of the forces resulting from creation of the defect; a linear response scheme was used more often than not.
- (iii) Regarding the thermodynamic framework:
  - (a) formation of the defect at constant lattice spacing (without further discussion of the effect of imposing this condition, rather than constant pressure on the prediction of defect parameters),
  - (b) neglect of thermal expansion.
  - (c) neglect of finite temperature effects related to the crystal entropy and free energy when considering volume thermal expansions,
  - (d) neglect of the contribution of atomic vibrations to the pressure and to the compressibility.

It is only fair to repeat that not all restrictions are removed in up-to-date calculations. Apart from the fact already mentioned that fully anharmonic machine calculations are still very rare, and that the treatment of many-body forces is mostly limited to schemes including polarizability, it should be emphasized that the panorama of properLD calculations is far from complete even for the simpler model crystals, i.e., rare gases, alkali halides, and alkali metals. The situation is quite the opposite: The picture is so fragmented that it would be quite embarrassing to have to produce a detailed evaluation of it.

The author prefers to take up an example and to present it in some detail for the purpose of illustrating what can be learned from careful LD calculations. The scope of the calculation remains that of collecting in a consistent way information of a qualitative nature on defect properties, in view of the fact that the relevance of the models studied to the natural substances they are intended to model is still to be satisfactorily assessed. However, theoretical calculations of defect properties of these model substances now can, and should, be exact from the point of view of statistical mechanics, be it for the simplified quasi-harmonic hamiltonian of LD.

B. LD FORMULAS

Let us lay down the expressions of relevant thermodynamic quantities in LD. The free energy F of a vibrating crystal is expressed in terms of the potential energy ϕ_0 and the normal mode frequencies ω_α calculated at the relevant minimum $\mathbf{R}_0$ in $3N$-dimensional configurational space as

$$(F)_Q = \phi_0 + \frac{1}{2}\sum_{\alpha}^{3N-3} \hbar\omega_\alpha + k_B T \sum_{\alpha}^{3N-3} \ln\left[1 - \exp\left(\frac{-\hbar\omega_\alpha}{k_B T}\right)\right] \tag{1a}$$

which reduces at high temperatures (i.e., $\hbar\omega/k_B T \ll 1$) to the classical approximation

$$F = \phi_0 + k_B T \sum_{\alpha}^{3N-3} \ln \frac{\hbar\omega_\alpha}{k_B T} \tag{1b}$$

Having periodic boundary conditions in mind, one sees that the three translational degrees of freedom of the center of mass have been excluded from the sums. For pair potentials the potential energy is written as

$$\phi_0 = \sum_{i<j=1}^{N} v(r_{ij}) + \phi_c \tag{2}$$

with the term ϕ_c containing the correction due to long-range cutoff of pair contributions excluded from the sum for $r_{ij} > r_c$. The normal mode frequencies ω_α are simply related to the eigenvalues λ_α of the dynamical matrix $\|\phi_{lm}\|$:

$$\omega_\alpha = \sqrt{\lambda_\alpha/m} \tag{3}$$

m being the mass of the particles, here taken to be the same for all. Other relevant quantities are the internal energy U, the entropy $S = (U - F)/T$, and the pressure $P = -(\partial F/\partial V)_T$:

$$(U)_Q = \phi_0 + \frac{1}{2}\sum_{\alpha}^{3N-3} h\omega_\alpha + \sum_{\alpha}^{3N-3} \frac{h\omega_\alpha}{\exp(h\omega_\alpha/k_B T) - 1} \tag{4a}$$

$$U = \phi_0 + 3Nk_B T \tag{4b}$$

$$(S)_Q = -k_B\left\{\sum^{3N-3} \ln\left(1 - \exp - \frac{h\omega_\alpha}{k_B T}\right) + \sum^{3N-3} \frac{h\omega_\alpha/k_B T}{1 - \exp(h\omega_\alpha/k_B T)}\right\} \tag{5a}$$

$$S = -k_B\left[\sum^{3N-3} \ln\left(\frac{h\omega_\alpha}{k_B T}\right) - 1\right] \tag{5b}$$

$$P = P_\phi + P_\omega(T) \quad \text{with} \quad P_\phi = -\frac{\partial \phi_0}{\partial V} \quad \text{and} \quad P_\omega(T) = -\left(\frac{\partial(F - \phi_0)}{\partial V}\right)_T \tag{6}$$

When allowing for changes of the crystal volume V the parameters of the quasi-harmonic description, i.e., ϕ_0 and the ω_α, must change. Otherwise, the featureless, exactly harmonic description will be recovered, where there is no internal pressure. Given the interaction potential law, ϕ_0 and ω_α will be determined for the different equilibrium configurations corresponding to different values of the crystal volume V. And, quite naturally, they will depend on V. The internal pressure is then fixed by Eq. (6).

Thermal volume expansion is automatically included in this description. This is because P from Eq. (6) depends on the temperature at a given V. Fixing the value of the external pressure P_{ex} and letting T vary produces the LD equation of state for the crystal, i.e., the volume V for which P from Eq. (6) equals P_{ex} at a chosen T. The thermal expansion of the crystal volume being one of the effects of anharmonicity of lattice vibrations, LD is also called a quasi-harmonic treatment. It cannot be overemphasized that a thermodynamically consistent implementation of LD requires that when thermal volume expansion is considered and ϕ_0 recalculated at different values of V corresponding to values of T derived from some equation of state (not necessarily the LD one) the variations of ω_α should also be considered, together with the resulting variations of S and P (and eventually $(U)_Q$).

We see from Eq. (6) that P is the sum of two terms, one coming from variations of ϕ with V, the other from variations of ω_α with V. The first term is easily treatable analytically, giving the virial expression

$$P_\phi = -\left(\frac{N}{3V}\right)\sum_{i<j}^{3N-3} \frac{\partial v(r_{ij})}{\partial r_{ij}} r_{ij} + P_c \tag{7}$$

where P_c indicates the correction due to long-range cutoff. On the contrary,

P_ω is best evaluated numerically by using incremental ratios built from recalculations of the ω_α at two closely spaced values of V.

It is important to realize that the virial formula in Eq. (7) differs from the usual formula based on the thermal average of the virial sum precisely by the term $P_\omega(T)$:

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = -\left(\frac{N}{3V}\right)\left\langle \sum_{i<j}^{3N-3} \frac{\partial v(r_{ij})}{\partial r_{ij}} r_{ij} \right\rangle_T + P_c = P_\phi + P_\omega(T) \tag{8}$$

As a result the substitution of the thermal average of the virial sum with the value of the sum calculated in the most probable configuration, i.e., the equilibrium configuration $\mathbf{R}_0$, may lead to disastrous results, because it essentially consists in using P_ϕ alone disregarding the volume dependence of the ω_α. This is only correct at $T = 0$ and in the classical approximation.

Laboratory experiments are more commonly done at constant pressure. Machine calculations are more commonly done at constant volume, i.e., fixing the basic box of the cyclic boundary conditions, although constant pressure MC and MD schemes have also been used. Fixing the volume is a more or less imposed choice in LD. In the static lattice, with thermal vibrations frozen out, the pressure as read by the virial formula does not contain $P_\omega(T)$. This term, of course, can be evaluated separately and added on to get P from Eq. (6). However, a numerical iteration procedure is necessary to precisely determine V at given P_{ex} and T. This discussion should be generalized, if appropriate in view of the anisotropy of the solid, to constant stress or constant strain conditions. The formalism is easily extended, accordingly, by the introduction of the components of the strain tensor as variables on which ϕ_0 and ω_α depend.

C. FINDING EXTREMA

We have illustrated how LD calculations are based on the determination of the static equilibrium configuration $\mathbf{R}_0$ of the crystal. $\mathbf{R}_0$ is defined at fixed volume (or strain). The atomic positions correspond to a fully relaxed configuration, i.e., all forces are zero and $\nabla\phi(\mathbf{R}_0) = 0$. In regular crystals having a high degree of symmetry (e.g., sc, fcc, bcc), the configuration $\mathbf{R}_0$ is obvious. In defect formation calculations $\mathbf{R}_0$ denotes also the relaxed configuration of the crystal containing the defect. In defect migration studies, transition state theory requires use of the thermodynamic quantities given by Eqs. (1)–(7) evaluated at the saddle point $\mathbf{R}_s$ for the $3N - 1$ dimensional space normal to the eigenvector with negative eigenvalue, i.e., obtained by letting the reaction coordinate ξ equal zero, in order to estimate the jump frequency. In both cases, one needs to locate an extremum of ϕ, $\mathbf{R}_0$, or $\mathbf{R}_s$ ($\mathbf{R}_0$ being also a minimum). The location of one of these points is identified with the help of one of many function minimization routines applied to $|\nabla\phi|^2$, or even to ϕ itself for $\mathbf{R}_0$, starting the search from estimated configurations (Bennett, 1977). The chosen procedure has no relevance to the final result if one makes certain that the right extremum has been exactly determined within the numerical precision available. This is easily checked because, fortunately, the property of an extremum is a local property where $\nabla\phi(\mathbf{R}_0) = 0$. The neighborhood of $\mathbf{R}_0$ is first attained with routines that converge rather slowly but have a large radius of convergence. Then a few iterations of the extremely fast first-order Taylor expansion of the gradient bring the system exactly at $\mathbf{R}_0$ within the precision of the computer:

$$\Delta\phi(\mathbf{R})\cdot(\mathbf{R} - \mathbf{R}_0) = \nabla\phi(\mathbf{R}) \tag{9}$$

This, of course, requires matrix inversion, but the time involved is negligible with respect to that for the matrix diagonalization to follow.

Lattice dynamics, as with other techniques employed to study the N-body potential energy surface ϕ, is based on local differential properties of the surface. Therefore, it is essential that ϕ be continuous and differentiable, at least in a reasonably large domain including the special points $\mathbf{R}$ investigated. When ϕ is given as a sum of pair interactions that do not go smoothly to zero, but are cutoff at r_c, care must be used in the investigation of ϕ. Whenever two nearby configurations are compared, such as the evaluation of incremental ratios in computing P_ω, the list of interacting neighbors must be employed and kept unchanged. If the list of neighbors is kept constant during the search of $\mathbf{R}_0$, however, one last iteration of Eq. (9) must be tried as a check with the list recalculated in $\mathbf{R}_0$. Because the shape of the surface ϕ far from $\mathbf{R}_0$, as well as all thermodynamic consequences thereof, are solely predicted from shapes and curvatures of ϕ at $\mathbf{R}_0$, great care is required in dealing with such technical points in order to avoid gross miscalculations. Whether the curvatures of ϕ at $\mathbf{R}_0$ and $\mathbf{R}_s$, and eventually their spatial derivatives involving ϕ_{lmn}, are indeed sufficient information to accurately determine defect free energies at a given temperature is of course a different issue. But in order to properly test this very important point one has to be exceedingly careful in treating the N-body potential energy surface. In MC and MD calculations this problem does not exist because the representative point directly samples the various relevant regions in configuration space, and ϕ is properly recalculated at every point. Any residual roughness of ϕ due to cutoff effects is buried in the statistical noise.

Often model pair potentials are not very short range, and it is not possible to place the cutoff within the basic box to which periodic conditions apply. Use of larger boxes is hindered by computer limitations on N. The solution is to let each particle interact with all the images of the other particles within the appropriate cutoff distance r_c. Many shells of boxes surrounding the basic one may be included, for in LD calculations the time needed to sum up pair interaction is not the main limitation as in MC or MD. Again, all should be controlled by repeating the calculation for different values of N. In any way, use of short cutoff distances may result in much larger deviations from the sought result.

As a practical matter we remark that the classical approximation to the free energy equation [Eq. (1b)] can be obtained without performing the diagonalization of the dynamical matrix $\|\phi_{lm}\|$. Its determinant $D = \prod_\alpha \lambda_\alpha$ is invariant under coordinate transformations, and can be computed for the cartesian coordinate form of the matrix. For equal masses we have

$$\exp\left(\sum_{\alpha}^{3N-3} \ln\frac{\hbar\omega_\alpha}{k_B T}\right) = \prod_{\alpha}^{3N-3} \frac{\hbar\omega_\alpha}{k_B T} = \left(\frac{\hbar}{k_B T m^{1/2}}\right)^{3N-3} \sqrt{D}$$

In the evaluation of D care must be taken to deal with translational invariance and the three null eigenvalues thereof. The simplest way is to change these eigenvalues from zero to unity, leaving the rest unchanged, by adding to the hamiltonian harmonic potentials of appropriate force constants relative to displacements of the center of mass along the three cartesian coordinates. The sought value of D consisting in the product of the $3N - 3$ relevant eigenvalues is then obtained from the matrix $\|\phi_{lm}\|$, modified accordingly. If the masses are not all equal, the situation is, of course, more complicated [see, for example, Vineyard (1957), Jacobs *et al.* (1982)]. Otherwise, proper diagonalization is only needed for the exact quantum mechanical formulas [although the first quantum correction to Eq. (1b) is expressed in terms of the mean sqaure value of ω_α or the trace of $\|\phi_{lm}\|$, also invariant] and for the saddle point calculations, to determine the directions spanning the saddle plane, normal to the reaction coordinate, and the isotope effect factor. For many applications it is sufficient to determine the eigenvector corresponding to the lowest (negative) eigenvalue, i.e., to the reaction coordinate.

III. Vacancy Formation in fcc Lennard–Jones Crystals

A. LD FOR THE PERFECT LJ CRYSTAL

We shall discuss in some detail a recent LD study (De Lorenzi *et al.*, 1984c) of vacancy formation and migration in a simple model for rare gas crystals: the Lennard–Jones (6–12) pair potential

$$v(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6]$$

Within the framework of classical mechanics, thermodynamic quantities like F and P scale with σ and ε in this model. As a consequence, results in reduced units like $F^* = F/\varepsilon$ and $P^* = P\sigma^3/\varepsilon$, obtained in calculations performed at the state point ($V^* = V/\sigma^3$; $T^* = k_BT/\varepsilon$), can be referred to argon, e.g., by using appropriate values for σ and ε:

$$F = F^*\varepsilon_{Ar}, \qquad P = P^*\varepsilon_{Ar}/\sigma_{Ar}^3$$

Quantum mechanical expressions, however, do not scale. Fixing the value of Planck's constant h in reduced units $\sigma(m\varepsilon)^{1/2}$ is equivalent to picking a specific atomic element. This is consistent with the common fact that the magnitude of quantum effects is different for crystals of the various rare gas elements at corresponding state points. We must therefore specialize the quantum mechanical results to one element. Argon is chosen, and for simplicity all results will refer to it. The values employed for the parameters are $\sigma = 3.405$ Å and $\varepsilon/k_B = 119.8$ K.

Table I contains thermodynamic data for the perfect crystal in the fcc lattice structure at four different state points. Computations were done using a cutoff value of $r_c = 4.5\sigma$. Long-range corrections ϕ_c to U and P_c to P were added to the results. The basic box contains $N = 108$ atoms. All sums thus contain $3N - 3 = 321$ terms and the center of mass is considered fixed. A different treatment of the center of mass contribution to the thermodynamic properties would make a difference of order $1/N$ to the quantities per particle.

The most striking features of Table I refer to the pressure data. The four state points have been chosen on the equation of state of crystalline argon at vapor pressure, i.e., $P \ll 1$ in units of ε/σ^3. Therefore LD values of $|P| \ll 1$ would indicate that

(i) The LJ model provides a satisfactory description of the equation of state.

(ii) The values of σ and ε employed in converting V and T to reduced units have been chosen satisfactorily.

(iii) Quantum effects are either small (both $|P|$ and $|P_Q| \ll 1$) or satisfactorily taken into account (only $|P_Q| \ll 1$).

(iv) The residual anharmonicity of lattice vibrations, after the volume dependence of the ω_α has been taken into account, contributes only a small term to the free energy of the crystal; this contribution should be small at low T and vanish for $T = 0$ in classical mechanics.

TABLE I

LATTICE DYNAMICS RESULTS FOR AN FCC LENNARD-JONES CRYSTAL WITH $N = 108$ ATOMS AND CUTOFF DISTANCE $r_c = 4.5\sigma^a$

k_BT	0	0.3339 (~40 K)	0.4923 (~60 K)	0.6678 (~80 K)
V/N	0.9535	0.9734	0.9974	1.0323
P	−2.5510	−0.4024	0.1277	0.7778
P_Q	−0.1873	0.1285	0.4432	0.9662
P_ϕ	−2.5510	−3.5733	−4.5514	−5.5804
P_c	−0.2022	−0.1940	−0.1848	−0.1725
U/N	−8.5551	−7.4940	−6.9206	−6.2190
U_Q/N	−7.8250	−7.3405	−6.8377	−6.1802
ϕ/N	−8.5551	−8.4957	−8.4002	−8.2224
ϕ_c/N	−0.0964	−0.0944	−0.0922	−0.0891
S/Nk_B	—	2.1449	3.5314	4.7643
S_Q/Nk_B	—	2.3838	3.6289	4.8070
K_T	0.0184	0.0219	0.0278	0.0418
$(K_T)_Q$	0.0161	0.0204	0.0263	0.0398

[a] The value of h is $0.029569\sigma\sqrt{m\varepsilon}$. Energy is in units of ε and pressure in units of ε/σ^3; K_T is the isothermal compressibility.

In fact, Table I shows that

(a) P_Q is quite close to zero at small and intermediate temperatures,
(b) P is close to zero only at intermediate temperatures, and
(c) P_ϕ is large and negative everywhere, but much more so at high T.

Observations (a) and (b) indicate that points (i) and (ii) are satisfied, i.e., the model is not bad. Furthermore, quantum effects are rather large in argon. They are never really negligible in the pressure, the deviation from the classical value exceeding $0.5\varepsilon/\sigma^3$ below ~40 K.

Observation (c) indicates that the contribution of thermal vibrations to the pressure have a huge effect on the equation of state. We may expect in general that LD calculations neglecting P_ω can meet with disaster at high T.

When the volume dependence of ϕ_0 and the ω_α are correctly included in the calculation of the pressure by adding P_ϕ and P_ω, much of the anharmonicity of ϕ is accounted for in these quasi-harmonic calculations. This can be argued from the fact that the LD equation of state does not depart too much from that of the real crystal. In particular, P is less than one-fifth of P_ϕ for the state point of argon close to melting.

The residual anharmonicity quoted in (iv) is, of course, not taken into account by LD. This fact probably causes the positive deviations of P_Q and P from zero that grow towards high T. In fact, these deviations can be taken as a measure of the residual anharmonicity. A direct comparison of LD and MC data on the same model would definitely confirm this interpretation. The comparison indeed exists, and it had been carefully carried out by Holt *et al.* (1970). We note that LD results from Holt *et al.* (1970) and this work coincide to the reported precision when account is taken of the slightly different choice of state points.

From the results reported by Holt *et al.* (1970) we see that the effect of residual anharmonicity is to lower the value of P in MC with respect to P in

LD by about -0.17, -0.45, and -0.91 in units of ε/σ^3, at $T \sim 40$, 60, and 80 K, respectively. The deviations of $(U - \phi_0)/Nk_BT$ from the classical value of 3 in LD are also negative in MC. The measured values of this quantity at the same state point as previously specified are: 2.89, 2.85, and 2.79. The effect on the values of U/N listed in Table I is to lower them from -7.49, -6.92, and -6.22 to -7.53, -6.99, and -6.36 in units of ε, the effect of residual anharmonicity on U_Q probably being not too different. If we correct the value of P_Q in Table I with the deviation $P_{MC} - P_{LD}$ measured by Holt *et al.* (1970), we get the gratifyingly small values of -0.04, $+0.01$, and $+0.06$ at $T \sim 40$, 60, and 80 K, i.e., a good description of the argon crystal.

The LD values for the crystal entropy per particle are also a fair estimate of the properties of natural argon. The values in Table I can be transformed into excess entropies S_e/Nk_B with respect to the classical ideal gas at the same density and temperature. The values obtained for $T \sim 60$ *and* 80 K are -5.62 and -4.89, i.e., about 0.19 and 0.35 high with respect to experiment for Ar, and 0.29 and 0.43 high for Kr (Squire and Hoover, 1969). Note that these LD values do not include the correction term $-\ln(2\pi N)^{1/2} \sim -0.030$ from Stirling's formula. Furthermore, they are probably affected by small crystal corrections of order $\ln N/N$.

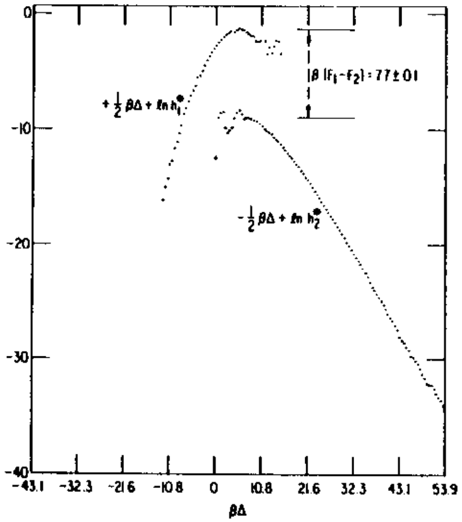

Fig. 1. Use of the graphical method for evaluation of free energy differences in the case of little or no overlap between the energy difference distributions $h_1^*(\Delta)$ and $h_2^*(\Delta)$. Data are taken from the comparison of an LJ crystal of fcc structure to the corresponding quasi-harmonic model. From the graph we get $\beta\,\Delta F$ per particle $= 0.143 \pm 0.002$ at $T = 0.5$ and $\rho = 1.0$. [From Rahman and Jacucci (1984).]

Whether the observed deviations from experiment are due to the neglect by LD of anharmonic terms can be checked using MC data. Rahman and Jacucci (1984) have measured the free energy difference between the fcc LJ crystal, at $T \sim 60$ K for Ar, and the corresponding harmonic solid (i.e., the LD approximation). Monte Carlo calculations based on the acceptance ratio method (Bennett, 1976b) and graphical display (see Fig. 1) gave $(F_{LJ} - F_{LD})/Nk_BT = 0.143 \pm 0.002$ for a 54 particle system. Previously quoted MC energy values gave $(U_{LJ} - U_{LD})/Nk_BT = -0.15$ at this temperature. As a result, we have $(S_{LJ} - S_{LD})/Nk_B = -0.29$, or $S_{LJ}/Nk_B = -5.62 - 0.29 = -5.91$, which compares favorably with the experimental values of -5.81 (Ar) and -5.91 (Kr). (Note that anharmonic contributions lower the energy, but lower the entropy twice as much, so that the effect on the free energy is a net increase.)

B. LD FOR THE LJ CRYSTAL CONTAINING A LATTICE VACANCY

Results for vacancy formation may be obtained by comparing properties relative to the regular lattice crystal C_0 containing N atoms with those relative to a crystal C_v containing $N - 1$ atoms, and one vacant site, both systems being subjected to periodic boundary conditions. Extensive properties of the regular lattice must be reduced by the factor $(N - 1)/N$ before taking differences, e.g.,

$$\Delta U = U(N - 1, v) - U(N, 0)(N - 1)/N$$

$$\Delta S = S(N - 1, v) - S(N, 0)(N - 1)/N$$

Because an extra bulk atom results upon forming the vacancy in a lattice. In fact, the Nth atom is missing from the system C_v containing the vacancy considered above, and it is not practical to introduce it anywhere in the lattice of the periodic box. Its properties can be taken to be identical to those of any one atom in the regular lattice C_0. Hence the factor $(N - 1)/N$ is to subtract its contribution from the extensive properties of C_0.

The vacancy formation process can be investigated in three different thermodynamic conditions: constant lattice (CL) parameter, constant atomic volume (CΩ), and constant external pressure (CP). In the CΩ calculation the lattice of C_v is squeezed so that its total volume V be reduced by the factor $(N - 1)/N$ to leave the atomic volume $\Omega = V/N$ unaltered. Of course, this procedure produces different values of the lattice parameter of C_v for different values of N. As a consequence, N-dependent correction terms may be expected to be substantial. In the CP calculation, the lattice parameter of C_v is varied until the reading of the pressure coincides with that of C_0. The resulting variation of the lattice parameter will be found to be smaller than in

$C\Omega$ calculations, for a given value of N. Relevant vacancy parameters are identified as limiting values obtained with these procedures for $N \to \infty$.

The values listed in Table II were obtained along these lines with $N = 108$ (De Lorenzi *et al.*, 1984c). The cutoff distance of the LJ potential was $r_c = 4.5\sigma$. Long-range corrections are not included in the values shown in the table, i.e., uncorrected values for the pressure $P - P_c$ have been employed in evaluating ΔH and ΔG, CP calculations refer to equal values of the uncorrected pressures, and so on. As a result, the data reported can be regarded as referring to a consistently treated interaction potential model, i.e., LJ + cutoff at the specified distance r_c. Thermodynamic checks can therefore be carried out precisely. In fact, long-range corrections due to cutoff are not as straightforward for C_τ as for C_0, and a consistent treatment for the full LJ potential is difficult. Cutoff dependence of the results will not be considered here.

We shall now briefly discuss these results, perform a thermodynamic check of their internal consistency, and verify quantitatively whether certain approximations often encountered in evaluations of defect properties are indeed acceptable. The discussion will be based on the material presented in Table II. Table III is included to display the role of quantum effects in argon, which are found to be rather small. For a further discussion of these effects, as well as extrapolations to large N and cutoff corrections, see De Lorenzi *et al.* (1984c).

As a first observation, we note that the formation volume at constant pressure is predicted to be always within about 10% of unity. As a consequence, CL values are much closer to CP value than to $C\Omega$ ones. The obtained $C\Omega$ values are indeed remarkable: $(\Delta S)_\Omega$ is large and negative, and $(\Delta U)_\Omega$ decreases roughly linearly with temperature, so that in $\Delta F = \Delta U - T\,\Delta S$ the temperature variation of the energy and entropy terms cancels to a large extent. Constant Lattice parameter and CP values for ΔU are much less dependent on T, and ΔS is much smaller and positive in those cases; as a consequence, ΔF is again only moderately dependent on T.

TABLE II

VARIATION OF LD THERMODYNAMIC QUANTITIES OF AN LJ CRYSTAL UPON THE FORMATION OF A LATTICE VACANCY[a]

k_BT	0	0.3339 (~40 K)	0.4932 (~60 K)	0.6678 (~80 K)
$(\Delta S)_L$	2.4493	2.3249	2.1451	1.7988
$(\Delta S)_\Omega$	−6.5043	−6.7791	−7.1558	−7.8234
$(\Delta S)_P$	3.0112	2.4658	2.1846	1.0130
$(\Delta U)_L$	8.4185	8.3810	8.2929	8.0894
$(\Delta U)_\Omega$	6.4502	5.3525	4.1880	2.7451
$(\Delta U)_P$	8.5583	8.4312	8.3111	7.6440
$(\Delta P)_L$	0.0309	0.0064	0.0014	−0.0182
$(\Delta P)_\Omega$	0.5460	0.4404	0.3464	0.2175
$(\Delta V)_P/\Omega$	1.0628	1.0155	1.0043	0.9184
$(\Delta F)_L$	8.4185	7.6047	7.2349	6.8882
$(\Delta F)_\Omega$	6.4502	7.6160	7.7172	7.9696
$(\Delta G)_P$	6.1781	7.4019	7.5468	7.8685
$(\Delta H)_P$	6.1781	8.2252	8.6242	8.5449

[a] All quantities are in reduced units; the values refer to the classical approximation.

TABLE III

VARIATIONS OF QUANTUM LD THERMODYNAMIC QUANTITIES OF AN LJ CRYSTAL UPON THE FORMATION OF A LATTICE VACANCY

k_BT	0	0.3339 (~40 K)	0.4932 (~60 K)	0.6678 (~80 K)
$(\Delta S)_L$	—	1.9835	1.9464	1.6533
$(\Delta S)_\Omega$	—	−5.6931	−6.7356	−7.6816
$(\Delta S)_P$	—	1.8743	1.7808	0.7126
$(\Delta V)_L$	7.9313	8.2018	8.1865	8.0202
$(\Delta U)_\Omega$	8.2061	6.1690	4.7028	3.0714
$(\Delta U)_P$	7.9315	8.1697	8.1168	7.5180
$(\Delta P)_L$	−0.0160	−0.0063	−0.0066	−0.0235
$(\Delta P)_\Omega$	0.5707	0.4582	0.3572	0.2237
$(\Delta V)_P/\Omega$	0.9716	0.9858	0.9810	0.8993
$(\Delta F)_L$	7.9313	7.5395	7.2265	6.9250
$(\Delta F)_\Omega$	8.2061	8.0699	8.0248	8.2012
$(\Delta G)_P$	7.9454	7.8533	7.8530	8.0992
$(\Delta H)_P$	7.9454	8.4792	8.7313	8.5751

Second, $(\Delta U)_L$ at $T = 0$ is not too different from $-U/N$ of Table I. As T increases, however, $-U/N$ decreases while $(\Delta U)_L$ remains remarkably constant. A similar comparison for $(\Delta F)_L$ and $-F/N$ shows that $-F/N$ increases with temperature while $(\Delta F)_L$ decreases. In conclusion, the formation energy of the vacancy is not accurately described by the opposite of the energy per particle, relative deviations of about one third being observed close to the melting temperature.

Third, $(\Delta F)_\Omega$ and $(\Delta G)_P$ are always only a few percent apart. This is a gratifying result and it constitutes the first indication that the thermodynamics of the vacancy formation process are correctly described. It is in fact a general result (Flynn, 1972) that in thermodynamic transformations involving volume changes one has

$$(\Delta F)_\Omega = (\Delta G)_P \tag{10}$$

to order $\Delta V/V$, or $1/N$ in this case. This result conveys the information that energy and entropy changes in the transformations with and without lattice dilatation balance out. Therefore, only a thermodynamically consistent description can reproduce it.

C. Test of Common Approximations

The basic approximation to be encountered in this type of calculation is the static model, i.e., the neglect of entropy and related contribution, resulting from lack of knowledge of the ω_α. Therefore, the only quantity entering the description is ϕ_0. Quantum mechanics is, of course, out of the reach of this approach. However, since the contributions related to entropy are invariably multiplied by the factor T, this description becomes exact at $T = 0$ in classical mechanics, the expected errors growing with T. One simple check of the magnitude of these errors can be performed on the mentioned equality $(\Delta G)_P = (\Delta F)_\Omega$ (to order $1/N$), that can also be written as

$$(\Delta H)_P = (\Delta U)_\Omega + T[(\Delta S)_P - (\Delta S)_\Omega] \qquad (11)$$

This relation is particularly useful whenever CΩ calculations are to be preferred, e.g., for metals described with the pseudopotential model (Jacucci and Taylor, 1979). The outcome of these calculations is $(\Delta U)_\Omega$, and $(\Delta H)_P$ is the sought result, being the slope of experimental Arrhenius plots. We see from Table I that the neglect of the entropy term in argon at high temperature brings disaster: $(\Delta U)_\Omega$ is only about one-third of $(\Delta H)_P$. It has become customary in these cases to evaluate separately the entropy term using a value for the thermal expansion coefficient α_P independently available (often from experiment) and the approximate relation (Flynn, 1972; Jacucci and Taylor, 1979)

$$T(\Delta S_P - \Delta S_\Omega) \cong T\,\Delta\Omega_P\,\alpha_P/K_T \qquad (12)$$

based on the evaluation of the entropy change upon expansion of the regular lattice C_0. It is indeed found that the estimate of Eq. (12) provides the desired value of the entropy difference term within the LD model to order $1/N$. However, in the model argon being investigated MC values of $(T\Delta\Omega_P\,\alpha_P)/K_T \equiv P_\omega$ are some 15% lower than LD values at $T \sim 80$ K (see pressure comparisons for the perfect lattice reported above; the discrepancy would be even larger were it not for a partial cancellation of differences in α_P and K_T). As a result, the value of $T(\Delta S_P - \Delta S_\Omega)$ at high temperature predicted in this way is accordingly lower than what it would be using LD consistently.

Another feature of the static approximation is to neglect the entropy related term P_ω in the pressure. We already noted that the size of this term is by no means negligible for the external pressure of the regular crystal. Let us see what the value of $(\Delta P_\phi)_L$ is and compare it with the sum $(\Delta P_\phi)_L + (\Delta P_\omega)_L = (\Delta P)_L$. It is found (De Lorenzi *et al.*, 1984c) that $(\Delta P_\phi)_L$ is 0.0567, 0.0828, and 0.1136 at $T \sim 40$, 60, and 80 K, instead of the values for $(\Delta P)_L$ of 0.0064, 0.0014, and -0.0182 of Table II. This means that the formation volume $(\Delta V)_P$ predicted using $(\Delta P_\phi)_L$, or $(\Delta P_\phi)_\Omega$, comes out to be much too large. In fact, in the static approximation it is found that $(\Delta V)_P = 1.24\Omega$ and 1.50Ω at $T \sim 60$ and 80 K instead of 1.00 and 0.92! Even the sign of the relaxation volume is wrong. This huge discrepancy of the static approximation to $(\Delta V)_P$ from the LD value is probably the most noticeable effect of neglecting P_ω and represents a very important discovery in the work of De Lorenzi *et al.* (1984c) described here. Although argon (and its models) is expected to be badly behaved in this respect, because of the relatively high value of its Grüneisen parameter, from now on the effect of P_ω on defect properties cannot be disregarded light heartedly.

The results of the static treatment are thermodynamically consistent only if read at $P_{ex} = P_\phi$ and $T = 0$, where they are also exact in the classical framework. Values corresponding to different lattice parameters will then refer to different external pressures at $T = 0$. Attempts to interpret the data in terms of different temperatures assuming thermal volume expansion are bound to meet with inconsistencies, because of the neglect of the contribution of S to F, or of $\partial S/\partial V$ to P, or both. For instance, Eq. (11) holds exactly at $T = 0$ in the classical static model, with $P \equiv P_\phi$ given by Eq. (7), for any given lattice parameter:

$$(\Delta U)_{P_\phi} + P_\phi(\Delta V)_{P_\phi} = (\Delta U)_\Omega \qquad (13)$$

If one now desires to use the same data, obtained from knowledge of ϕ_0, ϕ_v, and their volume derivatives, to exploit or check Eq. (11) in full, i.e., at finite temperature T, one must alter both sides to include entropy contributions. In the left-hand side $P = P_\phi + P_\omega$ will replace P_ϕ throughout, and in the right-hand side the term $T(\Delta S_P - \Delta S_\Omega)$ will be added. Performing only one such modifications will, of course, unbalance Eq. (13). An approximate treatment consistently neglecting P_ω, but properly including S, produces $(\Delta F)_\Omega \simeq 8.06$ and $(\Delta G)_P \simeq -1.86$ at $T \simeq 80$ K in complete disregard of Eq. (10) and grave prejudice of the stability of the lattice held at constant external pressure!

The moral of these findings is that now is a good time to stop fooling the experimentalists. Predictions from unreliable procedures cannot be sold as reliable with the only excuse that they are the best one can do. The calculation of defect properties has turned out to be a very difficult task, and the use of approximations is seldom forgiving. Most of these approximations now can and should be dropped. Remaining sources of indeterminations must be spelled out and their effect analyzed carefully.

The only source of indeterminations of the LD treatment of the LJ model presented above sits in the residual anharmonic effects already mentioned for the case of the regular lattice. These will be treated below, apart from cutoff and finite size effects, for which the reader is referred to the original work.

D. COMPARISON WITH MC RESULTS

The free energy of formation of lattice vacancies in LJ crystals was first measured by Squire and Hoover (1969) using MC and a path integration method. The calculation was repeated by Jacucci and Ronchetti (1980) using the acceptance ratio method, and has been recently extended to include the evaluation of the formation volume (De Lorenzi *et al.*, 1984c). In these calculations one measures the free energy Δf associated with reversibly removing a particle from a perfect crystal, keeping the lattice parameter constant. The free energy contribution G/N of reintroducing the particle in the bulk of the system must be accounted for separately. This is commonly done by using MC energies and pressures, and experimental excess entropies. Eventually, the excess free energy should also be measured by MC in the model system.[1]

The formation Gibbs free energy is obtained as (Squire and Hoover, 1969; De Lorenzi *et al.*, 1984c).

$$(\Delta G)_{\mathrm{F}} = \Delta f + G/N \tag{14}$$

The formation volume requires a finite difference evaluation of the derivative of Δf with respect to volume. A small statistical uncertainty on Δf must therefore be achieved. Furthermore, this delicate difference operation may be spoiled by problems connected with cutoff of the interaction potential. In the work of De Lorenzi *et al.* (1984c) LD results for various system sizes and cutoff distances were compared, providing an indirect check of the adequacy of the MC procedure used to measure $\Delta\Omega_{\mathrm{F}}$ in a 108 particle system.

The LD value of the pressure is large and positive along the experimental equation of state of rare gas solids, while the MC pressure is fairly low. Since a term PV directly enters in G, and hence in $(\Delta G)_{\mathrm{F}}$ through G/N, the comparison of the two sets of data (MC and LD) should be done disregarding its contribution. Larger discrepancies are unnecessarily obtained otherwise. The comparison is then done on the quantity $(\Delta G)_{\mathrm{F}} - P\Omega$.

The LD value of this quantity exceeds the MC value by 6% at 60 K and 10% at 80 K (these deviations double if the term $P\Omega$ is not subtracted). Since the difference in the Helmholtz free energy per particle (~0.07 at 60 K, see above) is only one fifth of this, almost all the large explicit anharmonic contribution to (ΔG) comes from Δf, i.e., from the lattice relaxation around the defect. The conclusion is easily checked by a direct comparison of Δf values. The effect of anharmonicity is to lower the free energy of formation, with an increase by a factor ~4 of the number of lattice vacancies at 80 K in Ar.

An interesting result of the work of De Lorenzi *et al.* (1984c) is that the MC value of the formation volume, $\Delta\Omega_{\mathrm{F}}/\Omega = 1.21 \pm 0.05$ for $T \sim 60\ K \div 80\ K$, is intermediate between LD and LS values, LD being too low and LS too high, by over 20%.

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[1] Lowercase f is used to stress the difference of the quantity Δf presently in hand, which refers to the comparison of two crystals, with and without defects, i.e., consisting of different numbers of atoms $N - 1$ and N, and ΔF defined previously, which referred to the same number of atoms.

E. RELEVANCE FOR LD CALCULATIONS IN METALS

The test of approximations performed above is particularly interesting with respect to the case of alkali metals, for which lattice statics calculations that use accurate interaction potentials exist (Jacucci and Taylor, 1979). The relevance of the entropic term of Eq. (11) is clearly recognized in that work, and its contribution evaluated using experimental values for compressibility and thermal expansion. The contribution P_{ω} of vibrations to the pressure was, however, neglected so that all calculated volumes are confined to the LS model. Despite the presently described evidence that the latter approximation is indeed very bad for rare gas crystals, LS results for alkali metals met with precise agreement with careful experimental data. For Na and K adding the migration energy, obtained by MD by Da Fano and Jacucci (1977), to the static formation energies one can derive the temperature dependence of the self diffusion coefficient. Strikingly good agreement found for both metals with the slope of the best-fit formula of Mundy's data (Mundy, 1971; Mundy *et al.*, 1971) points to the fact that monovacancies can explain the curvature of the Arrhenius plot of Na.

TABLE IV

THE TEMPERATURE DEPENDENCE OF ΔH_{F} (MIGRATION) FOR AL CALCULATED USING $V(R, \Omega)$ TRUNCATED AT 1.8 A (LATTICE SPACING)

T	ΔU	$T(\Delta S_{\mathrm{F}} - \Delta S_{\mathrm{V}})$	ΔH_{F} (migration)
75	0.45	0	0.45 (0.41)[a]
350	0.40	0.11	0.51
450	0.38	0.16	0.54
705	0.34	0.27	0.61
860	0.31	0.38	0.69 (0.60)[a]
960	0.29	0.48	0.77

[a] The values in parentheses were obtained by using $V(R, \Omega)$ properly summed.

On the basis of this evidence, one is inclined to think that the approximation involved in neglecting P_ω in alkali metals will prove to be much better than in Ar. This is in accord with expectations on the role of anharmonic effects in these materials.

On the other hand, the other LS approximation of neglecting $T(\Delta S_P - \Delta S_V)$ in calculating finite temperature enthalpies from constant volume energies is always bad. A striking example is given for Al (Jacucci, *et al.*, 1981) by calculations of the migration enthalpy (see Table IV). From the LJ study of this section we can infer that if the volume changes are evaluated using only P_ϕ, as in this case, the correction is probably overestimated.

IV. Vacancy Migration

A. RATE THEORY FORMULAS

In the limit of classical mechanics rate theory is used to calculate the vacancy jump frequency. Calling S the saddle surface, or "watershed," separating the regions τ and τ' in configuration space corresponding to the defect being located at two neighboring lattice sites, one writes the jump rate as (Vineyard, 1957)

$$\Gamma = \sqrt{\frac{k_B T}{2\pi}}\,\frac{\int_S \exp(-\phi/k_B T)\,dS}{\int_\tau \exp(-\phi(k_B T)\,d\tau} \qquad (15)$$

The integral in the denominator extends over one of the two equivalent regions. In using Eq. (15), it is assumed that no memory of previous jumps is kept, so that the equilibrium distribution is established before each jump, and that no recrossings occur, i.e., that the surface S is crossed only once during the jump event. In the quasi-harmonic approximation Γ is written as (Vineyard, 1957)

$$\Gamma_0 = \frac{1}{2\pi}\frac{\prod_\alpha^{3N-3}\omega_\alpha}{\prod_\alpha^{3N-4}\omega_{s\alpha}}\exp\left[-\frac{\phi_s - \phi_v}{k_B T}\right] \qquad (16)$$

where again the center of mass motion has been excluded. The $\omega_{s\alpha}$ are the normal mode frequencies at the saddle point, and $\alpha = 3N - 3$ is the index of the imaginary frequency relative to the reaction coordinate, that has been left out from the product at the denominator. In this approximation S is replaced by the hyperplane S_0 tangent to S at the saddle point. We choose to rewrite Eq. (16) as

$$\Gamma_0 = (\bar{\omega}/2\pi)\exp(\Delta S/k_B)\exp(-\Delta U/k_B T) \qquad (17)$$

with

$$(\bar{\omega})^{3N-3} = \prod_\alpha^{3N-3}\omega_\alpha, \qquad \Delta S = k_B\sum_\alpha^{3N-4}\ln\frac{\bar{\omega}}{\omega_{s\alpha}} \qquad \text{and} \qquad \Delta U = \phi_s - \phi_v$$

Values of ΔU, ΔS, and $\bar{\omega}$ can be calculated by LD in the quasi-harmonic approximation, as for vacancy formation quantities. Results obtained by De Lorenzi *et al.* (1984c) are listed in Table V.

The calculations are done at constant Ω and at constant P. These conditions refer to the saddle point configuration with respect to the equilibrium one, i.e., they are chosen to be at values of P and Ω appropriate to the formation of the defect at constant pressure. Building $(\Delta G)_P$ and $(\Delta F)_\Omega$ from ΔU, ΔS, and $(\Delta U)_P$, Eq. (10) is seen to be again rather well-obeyed.

Results of Table V warrant a discussion similar to that presented for the formation data of Table II, that will not be repeated here. As in that case, the cutoff value was $r_c = 4.5\sigma$ and the data have not been corrected for long-range cutoff effects.

B. ANHARMONIC CONTRIBUTIONS TO THERMODYNAMICS

The calculation of Γ in Eq. (15) is essentially a free energy difference problem. It can therefore be approached by using methods based on sampling of the type encountered earlier for the calculation of the free energy of formation of defects. In fact Bennett (1975) has invented one such method to

TABLE V

VARIATIONS OF LD THERMODYNAMIC QUANTITIES OF AN LJ CRYSTAL CONTAINING A VACANCY UPON RAISING FROM EQUILIBRIUM TO THE SADDLE FOR VACANCY MIGRATION[a]

$k_B T$	0	0.3339 (~40 K)	0.4932 (~60 K)	0.6678 (~80 K)
$(\Delta S)_\Omega$	−1.1950	−1.2284	−1.2742	−1.3506
$(\Delta S)_P$	3.1612	3.1575	3.4404	3.9543
$(\Delta U)_\Omega$	5.2652	4.8035	4.3064	3.6314
$(\Delta U)_P$	6.3061	6.3192	6.4588	6.6048
$(\Delta P)_\Omega$	0.2402	0.2008	0.1669	0.1242
$(\Delta\Omega)_P/\Omega$	0.4897	0.4847	0.5098	0.5542
$(\Delta F)_\Omega$	5.2652	5.2137	4.9348	4.5333
$(\Delta G)_P$	5.2094	5.1666	4.9209	4.5078
$(\Delta H)_P$	5.2094	6.2209	6.6178	7.1485
$\bar{\omega}$	15.7509	14.8043	13.7263	12.3219

[a] From De Lorenzi *et al.* (1984). Definitions of ΔS and ΔU are in the text. Values of the geometrical mean $\bar{\omega}$ of the normal mode frequencies at equilibrium are also given (in reduced units $\sqrt{\varepsilon/m\sigma^2}$).

evaluate Γ. For LJ at $T \sim 60$ and 80 K, Bennett finds $\ln[\Gamma(m\sigma^2/\varepsilon)^{1/2}] = -7.5 \pm 1.0$ and -5.0 ± 0.5. The LD estimates from Table IV are -9.2 and -6.1, showing a rather large discrepancy between the quasi-harmonic approximation and fully anharmonic rate theory predictions. Because in Bennett's work direct jump frequency measurements were also made and gave the value of -5.3 ± 0.2 for the logarithm of the jump frequency at $T \sim 80$ K, in agreement with his anharmonic rate theory prediction, we conclude that (i) rate theory is reliable, while (ii) LD evaluations at high temperature may not be. In this case LD predictions are low by a factor anywhere from 2 to 15.

It should be noted that previous evaluations of Γ_0 using lattice statics values of $(\Delta U)_\Omega$ and an effective attack frequency ν^* in the place of the LD factor $(\bar{\omega}/2\pi)\exp(\Delta S)_\Omega$ accidentally yielded better agreement with anharmonic jump rates (Bennett, 1975). The LD value for $(\Delta S)_\Omega/k_B$ is larger than unity in modulus and negative in sign. This somewhat unexpected fact lowers the value of the LD prediction for Γ below previous estimates, thus destroying the apparent agreement between static predictions and dynamical results.

This is the first accurate comparison between harmonic and anharmonic rate theory predictions. That LD overestimates the barrier to atomic jumps may in fact be a general feature (Jacucci *et al.*, 1981; De Lorenzi *et al.*, 1982). The extension to metallic and ionic crystals is very desirable.

C. Dynamical Corrections Due to System Memory

Molecular dynamics studies of vacancy migration have revealed that memory effects are indeed present (Bennett and Alder, 1968; Bennett, 1975; Bennett, 1976a; Da Fano and Jacucci, 1976, 1977) as a tendency of the vacancy to persist in the direction of motion in successive jumps closely spaced in time. The most relevant consequence of this fact can be described as the occurrence of *multiple jump* processes in which the vacancy is displaced by more than one lattice spacing in one complex dynamical event. These events are clearly separated from regular single jumps in the distribution of time delays between successive jumps (see Fig. 2). In fact, the average delay allowed in multiple jumps is only about 10% of the Debye period. One may consider the second jump to be a dynamical consequence of the first. The distribution of time delays for longer delays closely follows an exponential distribution of time delays for longer delays closely follows an exponential decrease appropriate to randomization of the system memory between successive jump events. The contribution to diffusion of multiple jump events must be evaluated separately.

Double jumps have been observed in fcc and bcc lattices. They appear to be a general feature of solid-state diffusion, quite independent from the model

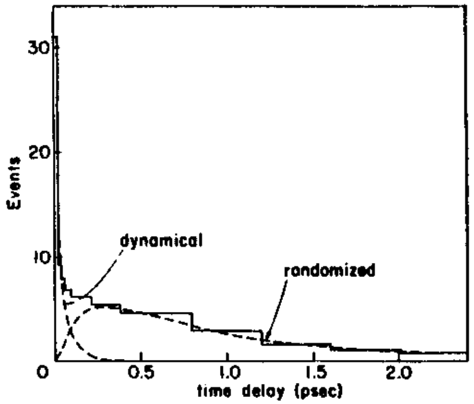


Fig. 2. Time delay between successive jumps of a vacancy; dashed lines indicate the separation of double events into the exponential long-time behavior of the randomized system and short-time behavior due to dynamical correlations. [From Da Fano and Jacucci (1976) and Flynn and Jacucci (1982).]

potential employed. The question is rather what fraction of double jumps occur at the melting point of crystals, than if they in fact exist. The activation energies (E_2) for double jumps are much higher than those (E_1) for single jumps, possibly higher than the double of it. Da Fano and Jacucci (1977) found the values (in electron volts) for E_1 and E_2 in Na, K, and Al to be 0.12, 0.08, 0.42 and 0.55, 0.40, and ~2, respectively, although it must be pointed out that multiple jumps involving more than two atoms were broken down into double jumps in the bookkeeping.

Because of their high activation energy double jumps do not contribute appreciably to atomic diffusion except in the close neighborhood of the melting point T_M. Even if they rise to 25% of the total jump events in Na, where they have been observed in greater number, when $T \approx 0.9\ T_M$ their relevance is much reduced. For instance, in K they drop from 17% at 330 K to 9% at 310 K. As a consequence, the double jump is not a possible candidate to explain the curvature of Arrhenius plots over large temperature intervals. Failure to clearly state this point in the original work has perhaps mislead some authors. Double jumps are most probably responsible (Bennett, 1976a; Da Fano and Jacucci; 1977) for the notorious "premelting phenomenon," e.g. in Na, i.e., an anomalous sudden increase in diffusivity accompanied, also in Na, by an anomalous decrease of the isotope effect factor.

The double jump must be regarded as a second diffusion channel available to the vacancy. In fact, there are many such channels for the various possible angles between the two atomic displacements, plus multiple jumps involving more than two atoms. In addition, vacancy jumps involving the displacement of only one atom to a second nearest-neighbor site have been also observed in Na (5% at T_M!) and in K.

Another observation of peculiar dynamical events in vacancy jumps (Bennett, 1975) refers to the fact that the system trajectory in configuration space may cross more than once, in a short time, the hyperplane S_0 tangent to the "watershed" S at the saddle point. Here S_0 is orthogonal to the direction of the eigenvector η_ξ having negative eigenvalue, and it is easily identified in the simulation by the vanishing of the reaction coordinate ξ. Because Eq. (16) gives an estimate of Γ_0 on the assumption that all crossings of S_0 are successful, these immediate recrossings are an additional source of error of the quasi-harmonic formula.

The problem of the recrossings is more general, however. Also, the watershed S in configuration space does not exactly separate trajectories falling in the two neighboring minima. This would happen only for purely viscous motion with no inertia, but not for newtonian motion. In the latter case, S can indeed be crossed more than once within a short time (Flynn, 1975) just because it is curved. Therefore, a more correct way of writing the jump frequency is

$$\Gamma = \Gamma' c \tag{18}$$

with Γ' given by Eq. (15), and c a conversion factor representing the fraction of forward crossing of S for which the jump is successfully completed. Equation (18) is more general than hitherto implied. Here Γ' and c can, in fact, be defined with reference to any convenient hypersurface between τ and τ' (Bennett, 1977); S_0 can be used to this end. The watershed S has the only advantage to maximize c. In any case a correct estimate of Γ requires an evaluation of c.

In summary, evidence gathered by MD studies indicates that dynamical events at variance with the assumptions of randomization and single crossings are restricted to short times. On the basis of this observation, an analysis of the origin of dynamical correlation effects has suggested (Flynn and Jacucci, 1982) a way to correct the predictions of diffusion coefficients from rate theory. The basic idea is that since these dynamical effects are restricted to short times, they can be related to local geometrical properties of the potential energy surface.

The rate at which return jumps occur may be calculated directly as the outcome of trajectories almost parallel to S that cross S twice because S is curved. This happens if the momentum along the trajectory is high enough to ensure a radius of curvature of the trajectory larger then that of S (see Fig. 3). Similarly, the frequency of multiple jumps can be evaluated from the thermal expectation rate of trajectories that cut the relevant dividing hypersurfaces

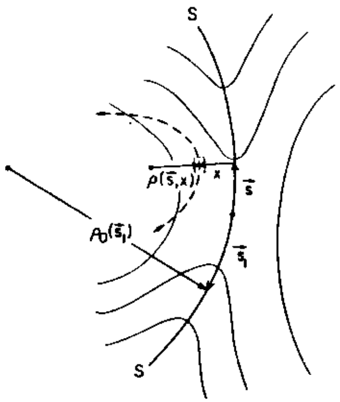


Fig. 3. Schematic representation of a curved saddle surface and the potential energy at neighboring points. The location of a volume element at x, s is indicated, together with a trajectory which is parallel to S inside the volume element. Return jumps occur when the radius of curvature $\rho(s, x)$ of the trajectory is greater than the radius of curvature $\rho_0(s)$ of the saddle surface at the same value of s, so that the trajectory cuts S twice. [From Flynn and Jacucci (1982).]

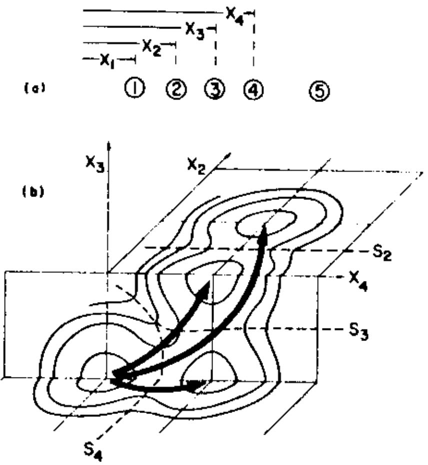


Fig. 4. (a) A row of atoms with a vacant site. (b) Schematic diagram of the potential energy contour for motion of atoms 2, 3, and 4, and the saddle surfaces S_4, S_3, and S_2 for successive jumps of atoms 4, 3, and 2 into the vacancy. Progressively longer heavy arrows indicate the jump of atom 4 from the initial configuration, the double jump of atoms 4 and 3, and the triple jump of atoms 4, 3, and 2 in a single dynamical event. It is possible, in principle, to calculate the rate at which multiple events occur and hence to correct errors in the rate theory predictions. [From Flynn and Jacucci (1982).]

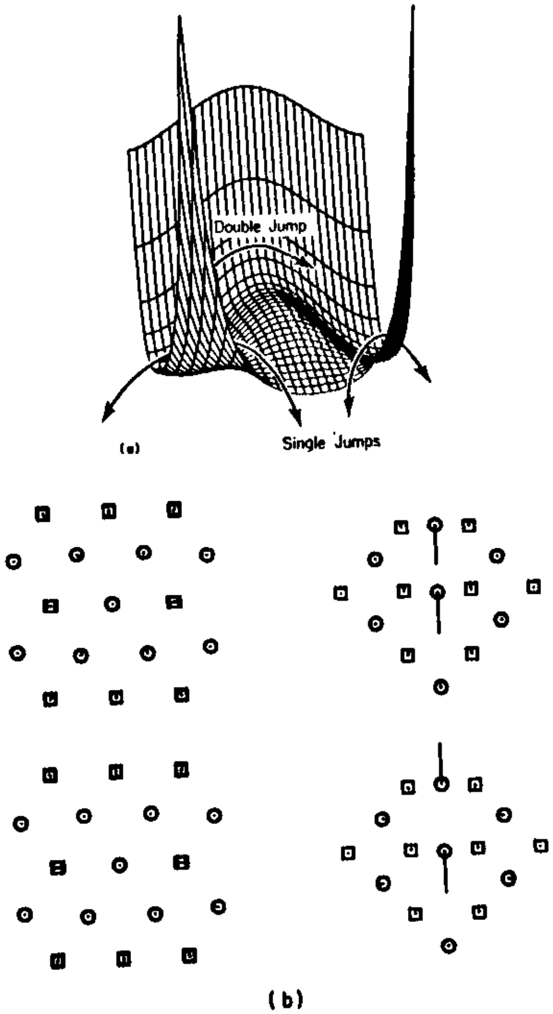


Fig. 5. Potential energy surface showing the path to double jumps of the vacancy in the fcc LJ crystal. (a) V plotted along two normal mode directions, ζ_1 and ζ_2, from the inflection point; ζ_1 (running from right to left) is the unstable mode corresponding to double jumps; ζ_2 is the decomposition mode for the jumping pair: it has zero frequency and exhibits a flexus of nonvanishing slope. Along this direction the potential falls from high values to the equilibrium configuration corresponding to the vacancy being in the middle. Usual saddle points for single jumps connect this configuration to the neighboring ones. The plot spans 1.4σ in ζ_1 and 0.6σ in ζ_2, resulting in a maximum variation of V of about 15ε. (b) Atomic displacements involved in modes ζ_1 and ζ_2 are projected in (i) the (110) plane normal to the atomic jump and (ii) the parallel (100) plane. Circles denote atoms in the central plane, squares denote atoms belonging to the two adjacent planes above and below. [From De Lorenzi *et al.* (1984d).]

in direct succession (see Figs. 4 and 5a,b). In both calculations local properties of ϕ (e.g., curvatures of S at the saddle point) are used to evaluate the first correction term in a T expansion of these anharmonic contributions. This analytic program can produce predictions useful also at high T if the Taylor series converges quickly.

The calculation of the isotope effect in tracer diffusion is also affected by dynamical contributions. The dependence of Γ on the mass of the jumping atom comes both from Γ' and c. If Γ' is defined with respect to the hyperplane S_0, the contribution of Γ' to the isotope effect is equal to the harmonic ΔK, and the only source of anharmonic contribution is c. Bennett (1975) has deviced a difference method to evaluate dc/dm by MD with reference to the planar S_0. Again, it has been proposed to use knowledge of the curvature of S at the saddle point to evaluate anharmonic contributions to the isotope effect to lowest order in a T expansion (Flynn, 1975).

It should be emphasized that a coherent program using modern calculations based on sampling, i.e., MC and MD, can be carried out to evaluate Γ' of Eq. (15) and c, as well as their mass dependence, at least with reference to S_0 (Bennett, 1976a). This last limitation is dictated by the necessity of having a simple criterion available to decide whether a given point is on the surface of interest. No such simple criterion, based on local properties of ϕ, is known to exist for S itself. Furthermore, MD can be employed to measure jump frequencies directly. However, all these calculations are still rare.

V. Analytical Treatment of Anharmonic Jump Frequency

If the analytical approach based on the Taylor expansion of ϕ to third order were successful, it would provide a theory of dynamical effects, the predictions of which would be valid for different materials and different temperature and pressure, given analytically in terms of potential energy and atomic masses. The structure of the theoretical results would make intuitively clear what factors cause rate theory to break down, and which physical systems are most likely to exhibit these effects. Therefore, analytical calculations of first order corrections to rate theory, including the fraction of return jumps, anharmonic isotope effect, and deviation of the flux Γ' through S or S_0 from Eq. (15) because of higher-order terms in the variation of the potential energy ϕ (see parts a, b, and c of Fig. 6), should be carried out numerically on realistic models. These first-order corrections could, in turn, be compared with available MD observations. This work is in progress (Jacucci *et al.*, 1984; De Lorenzi *et al.*, 1984a; De Lorenzi *et al.*, 1984b) and a partial description of it will be anticipated here.

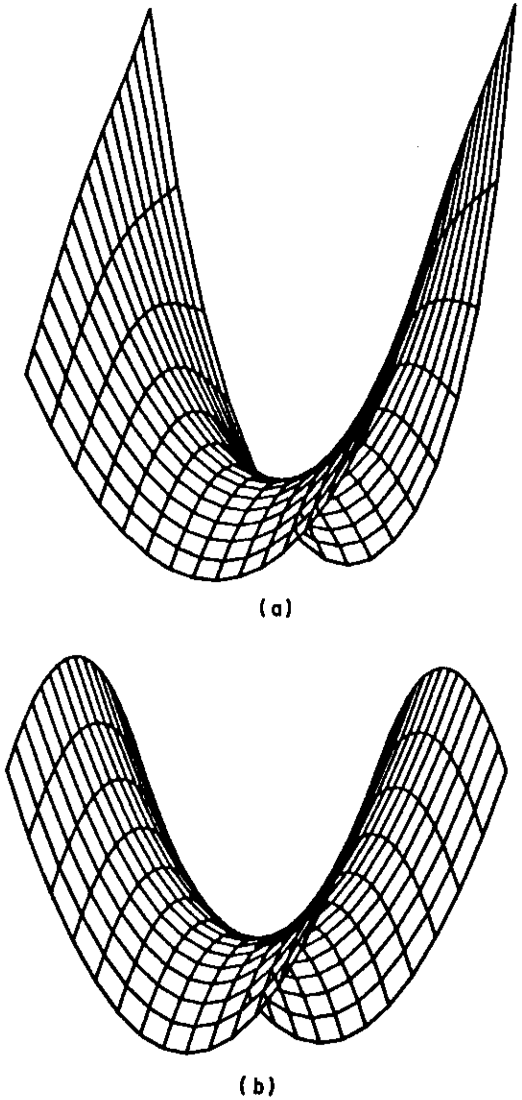
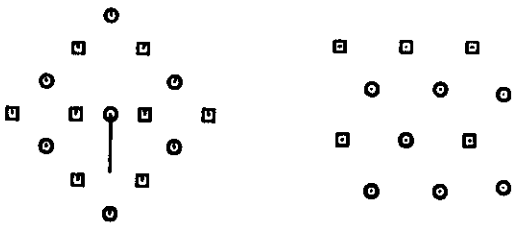


Fig. 6. Curved saddle for vacancy jumps in the fcc LJ crystal (a) compared to the osculating quadratic saddle and (b) plotted along the direction of the reaction coordinate z and along the direction of the saddle plane corresponding to maximum curvature of the saddle surface, v_1. The plot spans 0.4σ in both directions, resulting in a maximum variation of V of about 4ε for (a) and 3ε for (b). The atomic displacements involved in the reaction mode are shown in (c). [From De Lorenzi *et al.* (1984b).] (*Figure continues on next page.*)



(c)

Fig. 6. (*Continued*)

A. THE SADDLE SURFACE S

Consider the potential energy function ϕ; the gradient $\nabla\phi \equiv (\partial\phi/\partial x_1 \cdots \partial\phi/\partial x_{3N})$ defines a vector field in configuration space. Constant ϕ contours consists of $3N - 1$ dimensional hypersurfaces, everywhere orthogonal to $\nabla\phi$. The vector field has singular points where $\nabla\phi = 0$. Among these we are particularly interested in stable minima, where all the eigenvalues of $\Delta\phi$ are positive. Consider two nearby local minima, along with all possible trajectories in configuration space linking the two. To each trajectory one can associate the maximum value taken by ϕ on it. The point identified by the lowest value of these maxima will be called the saddle point P_0. In P_0, $\nabla\phi = 0$ and all but one eigenvalue of $\Delta\phi$ are positive. We wish to define a suitable "watershed" hypersurface dividing the space around P_0 into two regions surrounding the two local minima. These regions have the property that any curve everywhere tangent to the vector field $\nabla\phi$ belongs entirely either to one or to the other region and terminates in the corresponding local minimum, *unless* it belongs entirely to the watershed and terminates in the saddle point P_0. The watershed hypersurface shall be named the saddle surface S.

The $3N - 1$ dimensional hypersurface S is everywhere orthogonal to constant ϕ contours, and its normal $\mathbf{n}$ obeys the equation

$$\mathbf{n} \cdot \nabla\phi = 0 \tag{19}$$

in all points.

Furthermore, S contains the saddle point P_0. Its normal $\mathbf{n}_0$ in P_0 coincides with the direction of the eigenvector of $\Delta\phi$ having negative eigenvalue. The hyperplane through P_0 and normal to $\mathbf{n}_0$ is therefore tangent to S in P_0. It is called the saddle plane S_0.

B. TAYLOR EXPANSION FORM FOR S

We wish to find the Taylor expansion form for the equation of S about P_0. From now on we shall use the reference system with origin in P_0 having the principal axis parallel to the eigenvectors of $\Delta\phi$ at P_0. Call z the coordinate in the direction of the unstable normal mode, or reaction coordinate. The saddle plane is described by the equation

$$z = 0 \tag{20}$$

The equation of an hyperplane through a point P with normal $\mathbf{n} \equiv (n_1, \ldots, n_i, \ldots, n_{3N-1}, n_z)$ is

$$z - z(P) = -\sum_{i=1}^{3N-1} \frac{n_i}{n_z}[x_i - x_i(P)] \tag{21}$$

We can verify that the saddle plane has a normal $\mathbf{n}_0$ of components, $n_i(P_0) = 0$, $n_z(P_0) = 1$, as it should have.

The equation for S is of the type

$$z = F(\{x_i\}) \tag{22}$$

with $F(P_0) = 0$ and $\partial F(P_0)/\partial x_i = -n_i(P_0)/n_z(P_0) = 0$. The first nonvanishing terms in a Taylor expansion of the function F in powers of the displacements x_i are of second order. To this order, S is approximated by the quadratic form

$$z = \frac{1}{2}\sum_{i,j=1}^{3N-1} F_{ij}x_i x_j$$

Now

$$\frac{\partial^2 F}{\partial x_j\,\partial x_i} = \frac{\partial}{\partial x_j}\left(\frac{\partial F}{\partial x_i}\right) = \frac{\partial}{\partial x_j}\left(-\frac{n_i}{n_z}\right) = \frac{1}{n_z}\left(\frac{n_i}{n_z}\frac{\partial n_z}{\partial x_j} - \frac{\partial n_i}{\partial x_j}\right)$$

so that

$$F_{ij} = \left(\frac{\partial^2 F}{\partial x_i\,\partial x_j}\right)_{P_0} = \left(\frac{\partial^2 F}{\partial x_j\,\partial x_i}\right)_{P_0} = -\left(\frac{\partial n_i}{\partial x_j}\right)_{P_0} = -\left(\frac{\partial n_j}{\partial x_i}\right)_{P_0} \tag{23}$$

Note that the coefficients F_{ij} are the opposite of the elements of the curvature matrix

$$\mathbf{c} \equiv \begin{bmatrix} \dfrac{\partial n_1}{\partial x_1} & \cdots & \dfrac{\partial n_1}{\partial x_N} \\ \vdots & & \vdots \\ \dfrac{\partial n_N}{\partial x_1} & \cdots & \dfrac{\partial n_N}{\partial x_N} \end{bmatrix} \tag{24}$$

calculated in P_0. They can be related to derivatives of ϕ using the fact that S if a solution of $\nabla\phi \cdot \mathbf{n} = 0$, or

$$n_z\phi_z + \sum_{i=1}^{3N-1} n_i\phi_i = 0 \tag{25}$$

where $\phi_i = \partial\phi/\partial x_i$ and $\phi_z = \partial\phi/\partial z$. Equation (25) holds for all points of S. Therefore, we can impose the condition that the derivative of the left-hand side of the equation along any direction in space contained in S_0 must vanish in P_0. Iterating the procedure twice, we find after some algebra that

$$\phi_{zij} + \frac{\partial n_i}{\partial x_j}\phi_{ii} + \frac{\partial n_j}{\partial x_i}\phi_{jj} = 0 \tag{26}$$

or, remembering Eq. (23),

$$F_{ij} = \phi_{zij}/(\phi_{ii} + \phi_{jj} - \phi_{zz}) \tag{27}$$

all quantities being evaluated in P_0.

Equation (27) is the main result of this section and it shall be used in Section C as the base for the description of S_0 with a second order Taylor expansion of ϕ about P_0. Needless to say, the procedure used to obtain Eq. (27) can be iterated any number of times to get higher-order coefficients in the Taylor expansion (De Lorenzi *et al.*, 1984a).

An additional important feature of S being present in many different circumstances can be derived by symmetry arguments. Imagine that the saddle point geometry is equivalent looking from a positive or negative value of z. Then the derivatives, with respects to displacements along the unstable normal mode, of the eigenvalue ϕ_{ii} must be zero, viz.,

$$\phi_{zii} = \phi_{-zii} = 0 \tag{28}$$

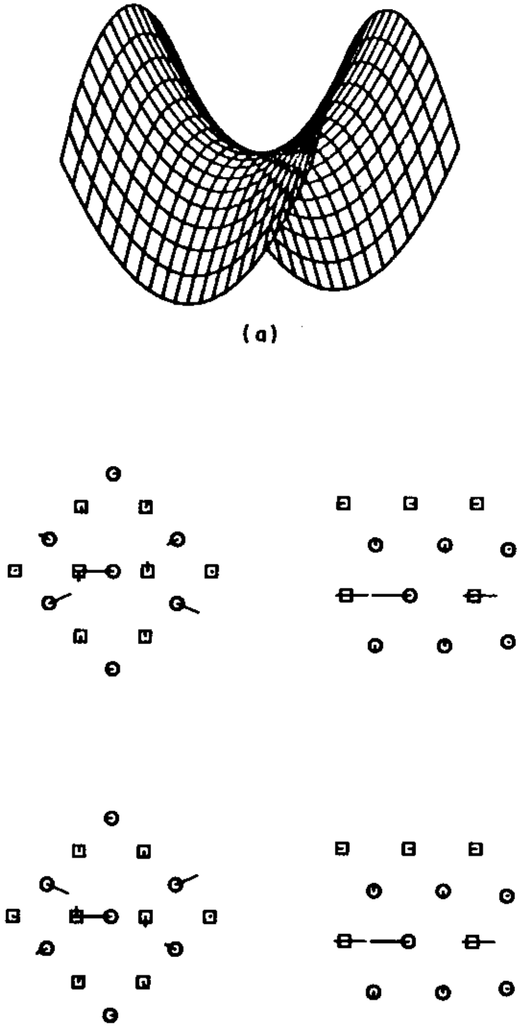
No such requirement exists on ϕ_{zij} for $i \neq j$, since the symmetry $\phi_{z-ij} = \phi_{-zij} = -\phi_{zij}$ is sufficient for the two sides of S to be equivalent. This symmetry property is to be found in many important instances of solid state diffusion, e.g., vacancy diffusion in fcc crystals. In all these cases Eq. (22) becomes

$$z = \frac{1}{2}\sum_{i=1}^{3N-1}\sum_{j\neq i=1}^{3N-1} F_{ij}x_i x_j \tag{29}$$

because $F_{ii} = 0$. The matrix $\mathbf{c}(P_0)$ has diagonal elements that are all zero. It can be diagonalized by finding normal modes of the saddle surface quadratic form having eigenvalues $-\rho_i^{-1}$, i.e., the inverse of the radii of curvature. The equation for S becomes

$$z = -\frac{1}{2}\sum_{i=1}^{3N-1} \rho_i^{-1}\xi_i^2 \tag{30}$$

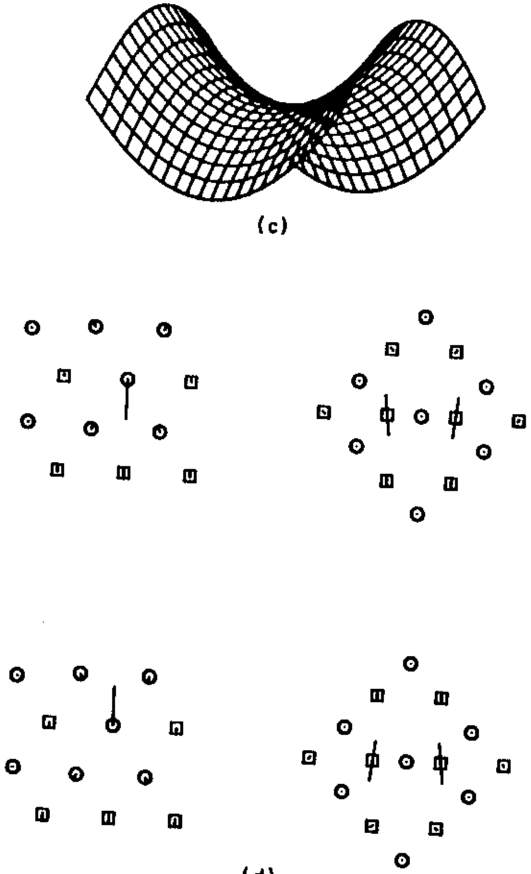
Because of the invariance of the trace, the sum of the principal curvatures $-(\rho_i)^{-1}$ must vanish, so that $\sum_{i=1}^{3N-1}(\rho_i)^{-1} = 0$. The eigenvalues of $\mathbf{c}$ are in



(a)

(b)

Fig. 7. (a) Plot of the *saddle-shaped* saddle surface for vacancy jumps in the fcc LJ crystal along the twin directions of maximum principal curvature (v_1); the plot spans 2σ along v_1^+ and v_1^-, and 1.1σ along z. (b) Projections of atomic displacements involved in v_1^+ and v_1^-. (c) Surface along the twin directions of principal curvature v_2 showing the second largest curvature; the plot spans 2σ along v_2^+ and v_2^-, and 0.75σ along z. (d) Projections of atomic displacements involved in v_2^+ and v_2^-. [From De Lorenzi *et al.* (1984b).] (*Figure continues on next page.*)



(c)

(d)

Fig. 7. (*Continued*)

fact seen to come in pairs having opposite sign. As a consequence the saddle surface S has itself the shape of a many-dimensional saddle (Figs. 7 and 8)!

In conclusion, a quadratic description of S in powers of the displacements from P_0 is simply done in terms of third-order derivatives of ϕ at P_0 of the type ϕ_{zij} and of the eigenvalues of the dynamical matrix also at P_0, the coefficients F_{ij} being given by Eq. (27). In practical cases, numerical knowledge of these coefficients will permit to take into account, to lowest order, corrections due to the curvatures of S, in diffusion processes. The extension to higher orders is, in principle, also possible.

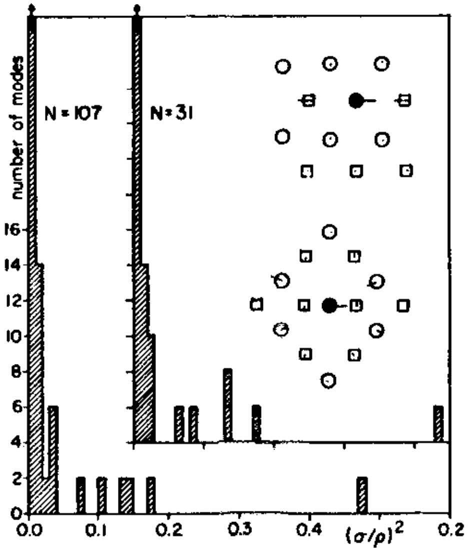


Fig. 8. Distributions of squared principal curvatures of the saddle surface for vacancy jumps in Lennard-Jones 31 and 107 atom cyclically repeating crystals. The atomic displacements in a direction of highest principal curvature are shown again. The twin directions of identical principal curvature are related by mirror reflection from the (110) plane through the central atom. [From Jacucci *et al.* (1984).]

C. A NUMERICAL PROCEDURE FOR EXTRACTING THE COEFFICIENTS F_{ij}

Given $\Delta\phi(P_0)$, its eigenvectors in cartesian coordinates, and the respective eigenvalues, and given the possibility of evaluating $\nabla\phi$ at any point P, a numerical procedure has been developed to obtain the normal coordinates derivatives ϕ_{zij} entering the coefficients F_{ij} (Jacucci *et al.*, 1984). This problem cannot be approached analytically in general for $N \approx 100$. Imagine having computed all third-order derivatives of ϕ in cartesian coordinates. The problem of transforming this matrix to normal coordinate derivatives is a formidable computational task. One must adopt a numerical procedure that yields ϕ_{zij} directly.

Starting from P_0 consider a displacement δ along the direction $\mathbf{x}_i$, and evaluate $\phi_z(x_i = \delta, x_j = z = 0, j \neq i) \equiv v_1$. Then consider a displacement 2δ also along $\mathbf{x}_i$, and evaluate $\phi_z(x_i = 2\delta, x_j = z = 0, j \neq i) \equiv v_2$. If δ is small enough, we shall pick up only the leading term in the power expansion of ϕ_z with respect to x_i. Calling n the order of this leading term, we write

$$\phi_z(x_i, x_j = z = 0, j \neq i) = \alpha x_i^n \qquad \text{and} \qquad v_2 = v_1(2)^n \tag{31}$$

(39)

We can get n simply as

$$n = \ln(v_2/v_1)/\ln 2 \tag{32}$$

If we find $n = 2$, then we can evaluate ϕ_{zii}, because near P_0 it must be

$$\phi_z(x_i, x_j = z = 0, j \neq i) = \tfrac{1}{2}\phi_{zii}x_i^2 \tag{33}$$

If we find $n = 3$, then ϕ_{zii} must be zero. Let us extend the discussion to include cross derivatives entering F_{ij} for $i \neq j$. For simplicity we shall consider the important case in which $\phi_{zii} = 0$. Consider a displacement δ from P_0 along $\mathbf{x}_i$, and at the same time a displacement δ along $\mathbf{x}_k$.

From displacements δ and 2δ we get v_1 and v_2 and from Eq. (32) n. If $n = 2$, we have

$$\begin{aligned}\phi_z(x_i = x_k, x_j = z = 0, j \neq i \neq k) &= \tfrac{1}{2}(\phi_{zii}x_i^2 + 2\phi_{zik}x_ix_k + \phi_{zkk}x_k^2)\\ &= \phi_{zik}x_ix_k \end{aligned} \tag{34}$$

Again, if we find $n = 3$, then ϕ_{zik} is zero. In practice the procedure is repeated for $3N(3N-1)/2$ times to fill the symmetrical ϕ_{zij} matrix, and hence $F_{ij} = -c_{ij}$. The stability of the results with respect to the parameter δ is found in typical applications to span several order of magnitude. Once the saddle point is well located within the precision of the computer, results for the various quantities of interest (listed below) are stable to one part in ten thousand (Jacucci *et al.*, 1984).

D. DYNAMICAL CORRECTIONS TO RATE THEORY DUE TO A CURVED S

Knowledge of the coefficients F_{ij} permits the calculation of dynamical corrections to rate theory due to the curvature of the saddle surface S, as proposed by Flynn (1975) and Flynn and Jacucci (1982), and carried out by Jacucci *et al.* (1984). The procedure is to construct the "watershed" corresponding to the energy barrier to atomic jumps, calculate the gross flux across it by rate theory, and subtract dynamical return jumps (coming from both sides!) to get the net flux. These calculations involve thermal averaging over the appropriate surface, which can be done part analytically and part by MC once S is approximated by Taylor expansion including third-order terms in ϕ.

The expression of the return jump fraction R'/R through the saddle surface S is (De Lorenzi *et al.*, 1984a)

$$\left(\frac{R'}{R}\right)_S = \frac{k_BT}{-\phi_{zz}}\sum_{i=1}^{3N-1}\frac{1}{\rho_i^2} = \frac{k_BT}{-\phi_{zz}}\sum_{i\neq j=1}^{3N-1}F_{ij}^2 \tag{35}$$

in terms of normal coordinate derivatives of ϕ, or in terms of principal radii

(40)

of curvature of S. Similarly, the fraction of immediate return jumps through the saddle plane S_0 is found to be (De Lorenzi *et al.*, 1984a)

$$\left(\frac{R'}{R}\right)_{S_0} = \frac{k_B T}{-4\phi_{zz}} \sum_{i \neq j = 1}^{3N-1} \frac{\phi_{zij}^2}{\phi_{ii}\phi_{jj}} \tag{36}$$

In both calculations only U-turns are considered; S-shaped trajectories crossing three and more times are disregarded, although they may exist. Furthermore, since the derivation is based on local differential properties (up to second order), trajectories that change their mind before recrossing may be spuriously included. Both errors tend to overestimate the fraction of return jumps.

Another quantity of interest is the anharmonic correction to the gross rate Γ through the free energy related configurational integrals appearing in Eq. (15). Unfortunately, a complete evaluation of this correction term to lowest order in T demands the inclusion of fourth-order terms in the expansion of ϕ. This task is out of reach of today's computational capacity if attacked analytically, but can be approached by MC. Third-order terms of the form $\phi_{zij} z x_i x_k$ do not contribute to the flux through S_0, where $z = 0$, but contribute to S. Third-order terms like $\phi_{ijk} x_i x_j x_k$ do not contribute to thermal averages, on symmetry grounds. The contribution to the flux through S of the former third-order term is (De Lorenzi *et al.*, 1984a)

$$\left(\frac{R''}{R}\right)_S = \frac{-k_B T}{4} \sum_{i \neq j = 1}^{3N-1} \frac{\phi_{zij}^2}{\phi_{ii}\phi_{jj}(\phi_{ii} + \phi_{jj} - \phi_{zz})} \tag{37}$$

so that the net flux Γ_S through S in this approximation is

$$\Gamma_S = \Gamma_0(1 - (R'/R)_S + (R''/R)_S) \tag{38}$$

while the net flux Γ_{S_0} through S_0 in the same approximation is

$$\Gamma_{S_0} = \Gamma_0(1 - (R'/R)_{S_0}) \tag{39}$$

In these equations Γ_0 is the harmonic flux of Eq. (16).

Γ_S and Γ_{S_0} are inescapably different, as is easily verified by substitution. The topological argument that all trajectories going from a minimum of ϕ, say, A, to one of the neighbor minima B must cut any suitable dividing surface does not apply here. However, it should be realized that this result pertains to the highly idealized hamiltonian of potential energy ϕ_3 given by

$$\phi_3 = -\frac{1}{2}\phi_{zz}z^2 + \frac{1}{2}\sum_{i=1}^{3N-1} \phi_{ii}x_i^2 + \frac{1}{2}z \sum_{i \neq j = 1}^{3N-1} \phi_{zij}x_i x_j \tag{40}$$

In fact, ϕ_3 bears no resemblance to ϕ away from P_0, and the minima of ϕ are not reproduced in ϕ_3. As a consequence, trajectories may exist that are solutions of the equation of motion under ϕ_3 and cross S but not S_0, whereas the corresponding trajectory through S does also cross S_0 under the action of ϕ. The ratio of the flux of the "missing" trajectories, over the total magnitude of the anharmonic contribution to the flux, is independent of the temperature, i.e., this problem is present in the lowest-order perturbation. A second source of discrepancy in Γ_S and Γ_{S_0}, as evaluated by the formulas above, consists in contributions from complicated trajectories undergoing several recrossings. This point will receive further attention below. Here we wish to underline that dynamical recrossings of S and S_0 have a quite different origin. Those of S are related to high momentum trajectories almost parallel to S. Those of S_0 are related to low-energy trajectories reaching S_0, but not the somewhat higher watershed S.

In conclusion, the net fluxes through S and S_0 can be evaluated by using ϕ_3. Γ_S is found to be somewhat larger than Γ_{S_0}, the discrepancy being a fixed fraction of contributions to order $k_B T$. The predictions for Γ_S are believed to be more reliable, and should be employed, e.g., in the evaluation of the isotope effect factor ΔK, in place of Γ_{S_0}. Numerical evaluation of the fluxes for specific cases, e.g., vacancy migration in model fcc crystals, can show the magnitude of these anharmonic corrections in typical solid-state diffusion instances and indicate whether terms of lowest order in $k_B T$ may be expected to be sufficient to accurately describe jump rates close to the melting point. A detailed comparison of the predicted fluxes with MD data would be of great help in drawing these conclusions. The remaining sources of anharmonic corrections, not included in this treatment, are (i) fourth-order terms in ϕ contributing to order $k_B T$ to Γ', and (ii) higher order terms in $k_B T$.

Before closing this section, we note that two anharmonic contributions affect the isotope effect factor ΔK (Flynn, 1975). One comes from the variation of the direction of the normal $\mathbf{n}$ to S, the other from the mass dependence of the fraction R'/R of return jumps. The first term is absent when calculating ΔK using the saddle plane, because $\mathbf{n}$ is always equal to $\mathbf{n}_0$ on S_0. Furthermore, by using $(R'/R)_{S_0}$ from ϕ_3, the fraction of return jumps from S_0 is found to be mass-independent (De Lorenzi *et al.*, 1984*a*).

In the case of the watershed S, the anharmonic expression of ΔK contains both contributions, neither of which vanishes. We see here effects of the observed difference of the two fluxes: $\Gamma_S \neq \Gamma_{S_0}$.

E. NUMERICAL RESULTS AND COMPARISON WITH MD

Numerical results on model systems appropriate to Al, Ar, and Cu were obtained by Jacucci *et al.* (1984). The investigation included a careful check of cutoff and size dependences, as well as calculations for various densities and temperatures (De Lorenzi *et al.*, 1984a).

TABLE VI

RETURN JUMP RATES CLOSE TO THE MELTING POINT

Metal	Jump rate (%)		
	$N = 31$	$N = 107$	$N \to \infty$
Al	5.1	4.6	4.4
Ar	3.5	4.3	4.6
Cu	4.0	—	—

The main results can be summarized as follows:

(i) The mean curvature of the saddle surface is similar for the various potential functions used (Lennard–Jones and Morse) and comes from only a few directions in the saddle plane.

(ii) $(R'/R)_S$ is invariably of the order of 5% at melting, so that statistical theories of diffusion are indeed valid, and the first order in k_BT should be quite sufficient (see Table VI).

(iii) The temperature-dependent correction $-K_TT_M$ to ΔK related to the variation of the direction of **n** is very small, less than 2% (see Table VII).

(iv) The correction term originating from the mass dependence of the return jumps is large and positive, and unambiguously predicts unphysical results upon mass substitution. This isotope effect "catastrophe" points to a basic flaw in the formulation of rate theory.

TABLE VII

HARMONIC AND ANHARMONIC ($\Delta K = K_0 - K_TT_M$) ISOTOPE EFFECT FACTORS

Metal	N	K_0	$-K_TT_M$	ΔK
Al	31	0.9229	−0.0188	0.9041
	107	0.9133	−0.0194	0.8939
	255	0.9125	—	—
	$\to\infty$	0.9124	−0.0196	0.8929
Ar	31	0.9609	−0.0139	0.9470
	107	0.9774	−0.0167	0.9607
	$\to\infty$	0.9789	−0.0178	0.9611
Cu	31	0.9365	−0.0153	0.9212
	107	0.9363	—	—

These results are of central importance for the theory of diffusion in solids. Their confirmation in MD studies is of great interest. Let us focus on the results for LJ at ~80 K: $(R'/R)_S \sim 0.05$ and $(R'/R)_{S_0} \approx 0.09$. Careful measurements of R'/R and ΔK were done by Bennett (1975) by using specially devised MD techniques. Both quantities were measured with respect to S_0, for the present case of vacancy migration in fcc LJ crystals.

The reported results are $R'/R = 10\%$ and $\Delta K = 0.89 \pm 0.05$. In the harmonic case these values are 0 and 0.98, so that anharmonic contributions are appreciable. The agreement of the two evaluations for $(R'/R)_{S_0}$ is particularly rewarding, in view of the fact that Bennett sees *all* return jumps, while the calculation of Jacucci *et al.* (1984) estimates only immediate return jumps related to the curvature of S. These, therefore, represent substantially all return jumps.

One further step is needed, however, to clear up the situation for the isotope effect. Complicated trajectories that cross the watershed three or more times, or start heading for a return jump and then change their mind, have not been accounted for, as mentioned above. Albeit very small, the number of these trajectories may be so strongly mass-dependent that the isotope effect cannot be accurately evaluated within the above analytical scheme, while the conclusions for Γ_S remain essentially unaltered in practical cases.

It is obvious that the possible cure of the errors in the bookkeeping of recrossings rests in the implementation of an exact jump condition that eliminates immediate return jumps. The existence of invariant manifolds in phase space that cannot be crossed by trajectories provides a critical jump condition that can be used in this context. A $(6N - 2)$-dimensional surface can be defined in phase space, called the *center manifold*, made up of trajectories indefinitely trapped in the saddle neighborhood. These trajectories are, of course, highly unstable and, if perturbed, fall into one of the two wells. In the harmonic approximation, the equation of the center manifold is $z = 0$; $\dot{z} = 0$, and the trajectories on it correspond to many dimensional harmonic motion. Presence of the term $\frac{1}{2} z \sum_{i \neq j=1}^{3N-1} \phi_{zij} x_i x_j$ displaces the center manifold from the watershed, and the two surfaces are quite unrelated.

The center manifold can be used to calculate the flux in such a way that there are no immediate return jumps (Jacucci *et al.*, 1984), as shown in Fig. (9). It is found in this way that the anharmonic jump frequency Γ_{CM} is only slightly larger than Γ_S, as expected because of the overestimation of return jumps. Furthermore, no isotope effect catastrophe is met. Calculations using these ideas are being carried out (De Lorenzi *et al.*, 1984d).

In conclusion, accurate jump rates can be calculated by using the notion of anharmonic saddle and geometrical constructions like the watershed and the center manifold in phase space. An improved, and for certain aspects new, conceptual basis for jump theories is achieved, and the validity of statistical jump theories is demonstrated for diffusion in solids. The path is

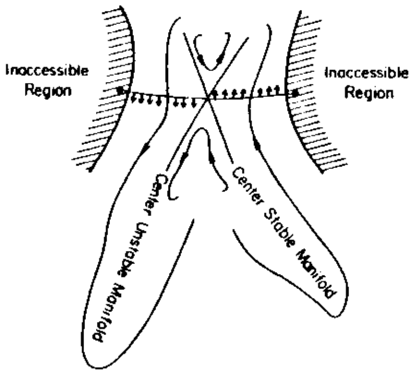


Fig. 9. Crossing surface in phase space with no immediate returns. The center *stable* and *unstable* manifolds cannot be crossed by trajectories. They meet on the *center manifold* and precisely separate trajectories crossing the dividing surface in opposite senses. Returns must go around these invariant manifolds and cannot be immediate. The flux toward one of the two sides is obtained by integrating over half of the dividing surface. The latter can be chosen rather arbitrarily as long as it is bounded by inaccessible high-energy regions. [From De Lorenzi *et al.* (1984).]

therefore open to precise future calculations of jump rates and of related thermodynamic parameters for model systems using realistic interatomic forces.

VI. Conclusions

Important results have been achieved. Comparison of Monte Carlo data with accurate quasi-harmonic lattice dynamics results for formation and migration of lattice vacancies demonstrates reliably, for the first time, that the *harmonic model overestimates* both contributions to the *free energy of activation* of diffusion in rare gases.

In addition, it has been analytically shown that the fraction of unsuccessful crossings of the "watershed" saddle surface in fcc crystals does not exceed 5% at melting. *Jump frequencies are therefore accurately given by rate theory* and may be corrected for dynamically inevitable immediate return jumps. This result is obtained by extending to third order the Taylor expansion of the potential energy in the analytical approach to rate theory.

The very success of the perturbation approach is possibly the most important new finding. It reopens the analytical path to the understanding of diffusion in solids, a path that appeared for some time bypassed by computer simulation. Reentering the stage, analytical mechanics seeks its revenge with elegance: The critical jump condition in phase space is effectively provided by invariant manifolds at the singular point, and the expression of these manifolds to first order in anharmonic perturbation is sufficient.

Further development and implementation of machine calculation methods, as they are coming within the reach of existing computers, for the investigation of point defect formation and migration in crystals will no doubt constitute one of the major areas of activity in this field during the coming years (see also Jacucci, 1984). A substantial advance in the understanding of point defect diffusion is to be expected as a result of using well handled statistical mechanics methods.

Challenging calculations to be confronted next, along the lines exposed in this chapter, are:

(i) formation free energies, enthalpies, and volumes using MC and MD in metals, starting from the alkalis for which excellent ab initio pair potentials exist, and in simple ionic solids;

(ii) jump rates for vacancy migration in bcc crystals; here the conformation of the saddle region should be more complex than in the fcc case, possibly featuring a metastable transition state;

(iii) multiple jump rates in various circumstances from knowledge of local properties of the N-body potential energy surface;

(iv) extension to highly disordered systems, e.g., superionic conductors (Flynn, 1979) and liquids (Stillinger and Weber, 1983), of method and concepts developed for point defect diffusion in crystalline solids.

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