From Eq. (6), a finite discontinuity in $C_{N,A}$ accompanied by (i) a finite compressibility discontinuity (*vis-à-vis* first-order transitions) and (ii) a well-behaved $(\partial\varphi/\partial T)_{N,A}$ yields a finite discontinuity in $C_{N,\varphi}$. In addition, since $a(\partial\varphi/\partial T)_{N,A}$ is the difference between the mean and partial entropies per atom of the monolayer,

$$\Delta C_{N,\varphi}=\Delta C_{N,A}+\frac{N}{aT}\Delta[(q_{\rm st}-l)^2K_{2T}], \tag{7}$$

where $l$ is the equilibrium heat of adsorption $T(s_v - s)$ involving only the mean entropies of vapor and film. For the present system, since the mean entropies are continuous at the transition, $l$ must be continuous and a finite discontinuity in $C_{N,A}$ resulting from finite discontinuities in $q_{\rm st}$ and $K_{2T}$ indicates a finite discontinuity in $C_{N,\varphi}$. We conclude that if the observed transition in the nitrogen monolayers is indeed characterized by discontinuities, as suggested by the data and quantitative analysis, then the transition is of the classical second-order type. Whether the present behavior is a specific property of nitrogen on graphite or a more general property of monolayers of heavy atoms adsorbed on relatively homogeneous surfaces with small lateral translation barriers (lateral variations across the basal plane of graphite are less than 40 K for all the noble gases[11]) is an intriguing question. In this regard, we note that recent precision isotherm studies of krypton on graphitized carbon black[3] appear to exhibit finite discontinuities in the compressibility at corresponding coverages slightly below monolayer capacity.

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# New Results for the Isotope Effect in Diffusion*

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An exact expression is derived for the isotopic difference of jump rates in diffusion processes and is used to examine several topical difficulties in the theory.

The dependence of diffusion on isotope mass provides an important method for identifying the mass-transport mechanism.[1] Chemically identical isotopes possessing masses $M''$ and $M'$ complete jumps at differing rates $w''$ and $w'$ such that

$$w''/w'=K[(M'/M'')^{1/2}-1]+1. \tag{1}$$

It has been widely believed[2,3,1] for many years that the many-body factor $K$ (often written $\Delta K$

and obviously unity for particles in independent motion) can be expressed in terms of a harmonic, normal-mode analysis of the diffusion saddlepoint as "the fraction of the kinetic energy in the unstable (diffusion-causing) mode possessed by the diffusing atom." In this Letter we derive a simple, exact expression for $w''/w'$ that bears no general relationship to kinetic-energy components. More speculative remarks about several outstanding problems are then offered on the basis of this new result.

The probability with which members of a classical equilibrating ensemble occupy points $(\vec{r}, \dot{\vec{r}})$ of their phase space[4] is $\rho(\vec{r}, \dot{\vec{r}}) = \rho_v(\vec{r})\rho_k(\dot{\vec{r}})$. Here, $\vec{r}$ for $N$-atom systems has $3N$ dimensions $x_{i\alpha}$ that locate Cartesian coordinates $i$ of particles $\alpha$, mass $M_\alpha$. $\rho_v(\vec{r}) = \rho_{v0}\exp[-V(\vec{r})/kT]$ depends only on the many-particle potential function $V(\vec{r})$ and is independent of the velocity distribution $\rho_k(\dot{\vec{r}}) = \rho_{k0}\exp[\sum_{i\alpha} - M_\alpha \dot{x}_{i\alpha}{}^2/2kT]$. The constants $\rho_{v0}$ and $\rho_{k0}$ normalize $\rho_v$ and $\rho_k$. To obtain the exact analog of Eq. (1), we first calculate inside this framework the rate at which representative points pass in one direction through a surface $S$ in $\vec{r}$ space. The rate per unit area through a surface at $\vec{r}$ with normal $\vec{n}$, components $n_{i\alpha}$, is evidently

$$w(\vec{n}) = \int_{\vec{n}\cdot\dot{\vec{r}}>0} d^3\dot{r}(\vec{n}\cdot\dot{\vec{r}})\rho(\vec{r}, \dot{\vec{r}})$$
$$= [2kT\textstyle\sum_{i\alpha} n_{i\alpha}{}^2/M_\alpha]^{1/2}\rho_v(\vec{r})/2\sqrt{\pi}. \qquad (2)$$

The relative rates $w''$ and $w'$ for two ensembles, identical except that atom 1 having mass $M''$ in the first is replaced in members of the second ensemble by $M'$, thus obey

$$\frac{w''(\vec{n})}{w'(\vec{n})} = \left\{\frac{\sum_i n_{i1}{}^2/M'' + \sum_{i,\alpha\neq1} n_i{}^2/M_\alpha}{\sum_i n_{i1}{}^2/M' + \sum_{i,\alpha\neq1} n_i{}^2/M_\alpha}\right\}^{1/2}, \qquad (3)$$

since the mass-independent factors $\rho_v$ cancel.

Equation (3) is the central result of this paper. The remainder comprises applications, and elaborations on its use.

(1) *Simple examples.*—Any specific saddle surface $S(\vec{r})$ employed to count jump frequencies is defined by $V$ and is thus $M$ independent, so that Eq. (3) applies to diffusion. When $S$ is planar, $\vec{n}$ is constant over $S$ and Eq. (3) provides the final jump frequencies to be compared with Eq. (1). For a monatomic host with $M_\alpha = M$, $\alpha \neq 1$, we find

$$w''/w'$$
$$= \{[1+\kappa(M/M''-1)]/[1+\kappa(M/M'-1)]\}^{1/2}, \qquad (4)$$

with $\kappa = \sum_i n_{i1}{}^2$. This exact result holds *regardless of anharmonicities,* provided $S$ remains planar, and *does* reduce, as $M'', M' \to M$, to Eq. (1) with $\kappa$ the fraction of kinetic energy possessed by atom 1 in motion along $\vec{n}$. Even isotopic disorder of the host spoils the simple interpretation, however; in general, $w''/w'$ is specified by the reciprocal effective mass along $\vec{n}$ rather than by kinetic energy.[5] For example, in a diatomic solid with sublattice masses $M_a$ and $M_b$, $a$ isotopes of mass $M''$ and $M'$ have, from Eq. (3), rates specified by

$$\kappa_1 = \textstyle\sum_i n_{i1}{}^2, \quad \kappa_2 = \sum_{i,b} n_{ib}{}^2,$$
$$1 - \kappa_1 - \kappa_2 = \textstyle\sum_{i,a\neq1} n_{ia}{}^2,$$

and the analog of Eq. (4) bears no simple relationship to kinetic energy.

(2) *Application to rocksalt crystals.*—Our proof, to the contrary, that $w''/w'$ is determined by $\vec{n}$, leads to the following provocative speculation: In some lattices (e.g., fcc, rocksalt) the saddlepoint locations of the migrating atom and its saddlepoint neighbors are determined largely by atomic size and symmetry (they fall in a plane). It therefore seems likely in these cases that $S$, and hence $\vec{n}$ also, depend mostly on crystal structure and is not very sensitive to the particular atomic species forming the lattice. For the monatomic fcc case this merely implies that $K$ takes similar values for all fcc crystals, which is approximately true.[6] For the rocksalt structure we can probably neglect $1 - \kappa_1 - \kappa_2$, which depends only on second and further-distant saddlepoint neighbors, to obtain

$$w''/w' = (1 + \kappa\Delta M/M_a)^{1/2},$$
$$\kappa = \kappa_1 M_b/(\kappa_1 M_b + \kappa_2 M_a). \qquad (5)$$

Arbitrarily choosing $\kappa_1 = 9\kappa_2$ we find the fit to the sparse existing data on pure rocksalt lattices[6] shown in Fig. 1. New data on pure rocksalt compounds, particularly those with widely dissimilar sublattice masses, would clearly be of great interest in clarifying the degree to which $S$ in compounds is indeed independent of all parameters except lattice structure.

(3) *Effects of nonplanar S: Temperature dependence.*—We now emphasize that $S$ is not generally planar and its curvature modifies the isotope effect. The $w(\vec{n})$ from Eq. (3) require thermal averaging over $S$ to give

$$\frac{w''}{w'} = \left\{\frac{\sum_i \langle n_{i1}{}^2\rangle/M'' + \sum_{i,\alpha\neq1}\langle n_{i\alpha}{}^2\rangle/M}{\sum_i \langle n_{i1}{}^2\rangle/M' + \sum_{i,\alpha\neq1}\langle n_{i\alpha}{}^2\rangle/M}\right\}^{1/2} \qquad (6)$$

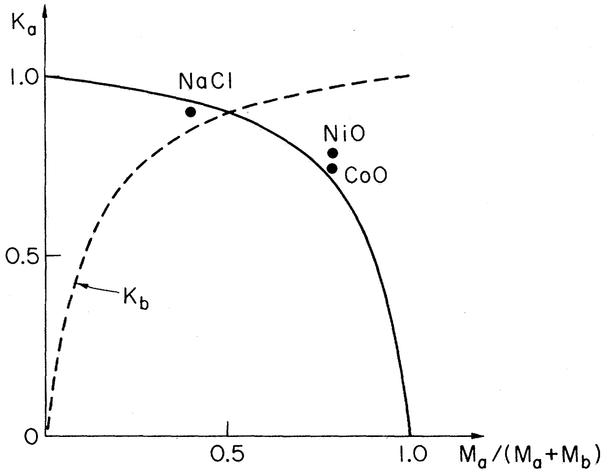

FIG. 1. The predicted $\kappa$ for rocksalt structures according to Eq. (5), with $\kappa_1=9\kappa_2$, compared with experimental results for NaCl, CoO, and NiO. $\kappa_a$ and $\kappa_b$ are the $\kappa$ of Eq. (4) for *a* and *b* isotopes.

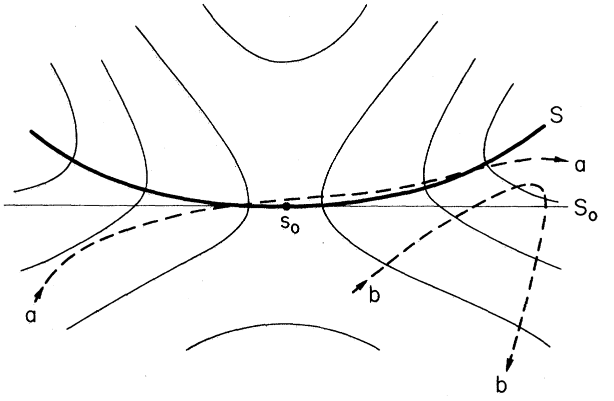

FIG. 2. Sketch showing potential contours, the curved saddle surface $S$, and the saddlepoint plane $s_0$ tangent to $S$ at the saddlepoint $\vec{s}_0$. Only an almost tangential trajectory (*a*) can cut $S$ twice, but a wide variety of trajectories (e.g., *b*) cut $s_0$ twice.

in which angular brackets signify $\int dS\,\rho_v(\vec{r})$ over $S$.

A possible resolution can now be seen for major difficulties encountered in recent theoretical treatments of the isotope effect. Most important is that computer studies by Bennett[7] of a Lennard-Jones crystal at high temperature conform rather well to experimental results for real fcc crystals[5] in predicting $K=0.89\pm0.05$ for $T\simeq T_m$, yet careful theoretical studies of $\vec{n}$ at the fcc saddlepoint $\vec{s}_0$ give a value 0.98 that is much too near unity.[8] This discrepancy can be explained as follows by a temperature dependence of $K$: As $\vec{s}_0$ is by definition a symmetry point of $V$, $\rho_v(\vec{r}-\vec{s}_0)$ is locally symmetric and odd powers vanish from the Taylor expansion of $n_{i\alpha}^2$ when inserted in Eq. (6). For $\kappa=1$ at the saddlepoint $\vec{s}_0$ one then finds

$$\kappa(T)=1-\gamma_1T+\gamma_2T^2+\dots, \tag{7}$$

in which $\gamma_1$ is positive. The choice $\gamma_1\sim0.1T_m^{-1}$ can obviously reconcile experiment, computer simulation, and the theoretical $\kappa$ at $\vec{s}_0$, since only at $T\to0$ does $\vec{n}(\vec{s}_0)$ determine $\kappa$. An explicit study of $S$ near $\vec{s}_0$ using computer models in conjunction with Eq. (6) could yield the required values of the $\gamma$ and hence $\kappa(T)$, and it is partly for the purpose of stimulating such efforts that this paper is written. Neither molecular dynamics nor experiment throughout the range $0<T<T_m$ seems feasible at present. Interpretations of a $T$-dependent $\kappa$ in terms of multiple-diffusion mechanisms[1] must be regarded with caution until these questions are clarified.

(4) *Return jumps.*—At the same time, a nonplanar $S$ renders unreliable the usual connection $D''/D'-1=f(w''/w'-1)$ between isotope diffusion coefficients and jump rates.[9] Here $f$ is the factor introduced by Bardeen and Herring[10] to describe defect-correlated random walks. This relationship holds only when each jump counted in $w$ causes a dynamically independent diffusion step. But for a curved $S$, and certain almost tangential trajectories (see Fig. 2), a return intersection is inherent in the lattice dynamics; and, since these intrinsic return paths are isotope dependent, they modify $D''/D'$. We must therefore write

$$D''/D'-1=f(w_0''/w_0'-1), \tag{8}$$

with $w_0$ the value of $w$ corrected for multiple crossings of $S$. Note that our concern is focused here on multiple crossings of $S$, rather than those much more frequent, but largely irrelevant, multiple crossings of the *plane* $S_0$, tangent to $S$ at $\vec{s}_0$ (see Fig. 2), that have been examined in recent molecular-dynamical work.[7]

Calculations of $w/w_0$ for trajectories nearly tangential to $S$ can be completed analytically in terms of the radii of curvature describing $S$, the value of $(\partial^2V/\partial n^2)_{\vec{s}_0}$, and the effective masses for motion perpendicular and parallel to $S$. The results are not given here as the required coefficients are not yet available for any model crystal. They could, however, become accessible from the model studies of $S$ urged above. The *dynamical correlation factor*, $g=w_0''w'/w_0'w''$, by which these effects are described, obeys $g > 1$ ($<1$) for $(\partial^2 V/\partial n^2)_{\vec{s}_0}$ positive (negative) and $M''/M' > 1$. Ordinary saddlepoints with $(\partial^2 V/\partial n^2)_{\vec{s}_0}$ negative thus enhance the mass sensitivity of $D$ whereas potential troughs at the saddlepoints (perhaps in bcc lattices) reduce the mass dependence.

(5) *Fast diffusion.*—In this same context we note finally that dynamical correlations increase for ultrafast diffusion (e.g., in liquids and superionic conductors) in which the distinction between vibrational and diffuse motions becomes blurred. The correlations increase as the saddlepoint energy decreases, and the notion of a saddlepoint surface tends to lose its utility. Recourse must eventually be made to an explicit calculation of the correlation functions $\langle \dot{x}_{i\alpha}(0)\dot{x}_{i\alpha}(t)\rangle$ for the various isotopic species.

(6) *An exact classical prediction.*—The exact results (2) and (6) offer a precise test of the classical theory. Newtonian trajectories in the configuration space of an impurity $M'$ in pure host $a$, mass $M_a$, are fixed by $V(\vec{r})$ and the mass ratio $\mu_a' = M'/M_a$ alone. All correlation effects therefore depend only on $T$ and $\mu$, so that there exists from Eq. (2) at $T$ a unique function $\varphi(\mu)$ such that

$$\varphi(\mu_a') = D_a'[A/M_a + (1-A)/M']^{-1/2}, \tag{9}$$

with $D_a'$ the diffusion coefficient of $M'$ in $a$, and $A$ independent of $\mu$. $\varphi$ can depend only weakly on $\mu$ through ordinary correlation effects[3] and curvature of $S$. If impurity isotopes $M''$ and $M'$ are diffused into two isotopically pure forms $a$ and $b$ of a single host (e.g., $\mathrm{Li}^6$ and $\mathrm{Li}^7$) a unique $A$ in Eq. (9) must, in the classical theory, bring the four $D$ onto a smooth curve that exhibits the weak $\mu$ dependence of $\varphi$. A failure of this relationship among correctly established $D$ would point unambiguously to a breakdown of the classical theory, and hence to quantum effects in diffusion. The similar but more complicated results that can be developed for compounds will be reported elsewhere.

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