Locating stationary points of sorbate-zeolite potential energy surfaces using interval analysis

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(Dated: August 25, 2004)

Abstract

The diffusion of a sorbate molecule in a zeolite can be studied using transition-state theory. In this application, and other applications of transition-state theory, finding all local minima and saddle points of the potential energy surface is a critical computational step. A new strategy is described here for locating stationary points on a potential energy surface. The methodology is based on interval analysis, and provides a mathematical and computational *guarantee* that *all* stationary points will be found. The technique is demonstrated using potential energy surfaces arising in the use of transition-state theory to study the diffusion of three sorbates, xenon, methylene, and sulfur hexafluoride, at infinite dilution in silicalite.

Keywords: stationary points, transition states, zeolites, diffusion, interval-Newton method

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I. INTRODUCTION

Transition-state theory[1] is a well-established methodology which, by providing an approach for computing the kinetics of infrequent events, is useful in the study of numerous physical systems. Classically, it assumes that there exists a hypersurface in phase space which divides the space into a reactant region and a product region.[2] Although the theory was originally for interpretation of chemical reaction rates, it can be amended for non-reacting systems, including desorption/adsorption and diffusion processes in which no chemical bonds are broken or made. For a detailed background in transition-state theory, the reader is referred to the excellent reviews of Truhlar *et al.*[3,4]

Of particular interest here is the problem of computing the diffusivity of a sorbate molecule in a zeolite. This can be done using the methodology of transition-state theory, as described by June *et al.*[5] It is assumed that diffusive motion of the sorbate molecules through the zeolite occurs by a series of uncorrelated hops between potential minima in the zeolite lattice. A sorption state or site is constructed around each minimum of the potential energy hypersurface. A first order rate constant, k_{ij}, is then associated with the rate of transition between a given pair of neighboring sites, i and j. Any such pair of sites is then assumed to be separated by a dividing surface on which a saddle point of the potential energy hypersurface is located. The saddle point can be viewed as the transition state between sites, and a couple of steepest decent paths from the saddle point connect the minima associated with the i and j sites. After rate constants have been determined for all possible transitions between the sorption sites, a continuous-time/discrete-space Monte Carlo calculation can then be used to determine the self-diffusivity of the sorbate molecules. Obviously, in this application, and in other applications of transition-state theory, finding

all local minima and saddle points of the potential energy surface, $\mathcal{V}$, is critical. We describe here a new approach, based on interval mathematics, for finding all stationary points of a potential energy surface, and apply it to three sorbate-zeolite systems.

Stationary points satisfy the condition $\boldsymbol{g} = \nabla\mathcal{V} = \mathbf{0}$; that is, at a stationary point the gradient of the potential energy surface is zero. Using the eigenvalues of $H = \nabla^2\mathcal{V}$, the Hessian of the potential energy surface, stationary points can be classified into local minima, local maxima, and saddle points (of order determined by the number of negative eigenvalues). There are a number of methods for locating stationary points. A Newton or quasi-Newton method, applied to solve the nonlinear equation system $\nabla\mathcal{V} = \mathbf{0}$, will yield a solution whenever the initial guess is sufficiently close to a stationary point. This method can be used in an exhaustive search, using many different initial guesses, to locate stationary points. The set of initial guesses to use might be determined by the user (intuitively or arbitrarily) or by some type of stochastic multistart approach. Another popular approach is the use of eigenmode-following methods, as done, for example, by Tsai and Jordan.[6] These methods can be regarded as variations of Newton's method. In an eigenmode-following algorithm, the Newton step is modified by shifting some of the eigenvalues of the Hessian (from positive to negative or vice versa). By selection of the shift parameters, one can effectively find the desired type of stationary points. There are also a number of other approaches, many involving some stochastic component, for finding stationary points.

In the context of sorbate-zeolite systems, June *et al.*[5] use an approach in which minima and saddle points are located separately. A three step process is employed in an exhaustive search for minima. First, the volume of the search space (one asymmetric unit) is discretized by a grid with a spacing of approximately 0.2Å, and the potential and gradient vector are tabulated on the grid. Second, each cube formed by a set of nearest-neighbor grid nodes

is scanned, and the three components of the gradient vector on the eight vertices of the cube checked for changes in sign. Finally, if all three components are found to change sign on two or more vertices of the cube, a BFGS quasi-Newton minimization search algorithm is initiated to locate a local minimum, using the coordinates of the center of the cube as the initial guess. Two different algorithms are tried for determining the location of saddle points. One searches for global minimum points in the function $\boldsymbol{g}^{\mathrm{T}}\boldsymbol{g}$, i.e. the sum of the squares of the components of the gradient vector. The other algorithm, due to Baker,[7] searches for saddle points directly from an initial point by maximizing the potential energy along the eigenvector direction associated with the smallest eigenvalue and by minimizing along directions associated with all other eigenvalues of the Hessian.

All the methods discussed above, however, have a major shortcoming, namely that they provide no guarantee that *all* local minima and first order saddle points will actually be found. One approach to resolving this difficulty is given by Westerberg and Floudas,[8] who transform the equation-solving problem $\nabla\mathcal{V} = \mathbf{0}$ into an equivalent optimization problem that has global minimizers corresponding to the solutions of the equation system (i.e., the stationary points of $\mathcal{V}$). A deterministic global optimization algorithm, based on a branch-and-bound strategy with convex underestimators, is then used to find these global minimizers. Whether or not all stationary points are actually found depends on proper choice of a parameter (alpha) used in obtaining the convex underestimators, and Westerberg and Floudas do not use a method that guarantees a proper choice. However, there do exist techniques,[9,10] based on an interval representation of the Hessian, that in principle could be used to guarantee a proper value of alpha, though likely at considerable expense computationally.

We describe here a new approach in which interval analysis is applied directly to the

solution of $\nabla\mathcal{V} = \mathbf{0}$. This approach, based on an interval-Newton methodology, provides a mathematical and computational *guarantee* that *all* stationary points of the potential energy surface will be found (or, more precisely, enclosed within an arbitrarily small interval). In the next section we provide a brief background in interval analysis and give details of the interval-Newton methodology and some recent improvements in it. The potential energy model for the sorbate-zeolite systems studied is described in Section III. Section IV then presents the results of computational studies for three sorbates, xenon, methylene, and SF_6, in silicalite.

II. INTERVAL ANALYSIS

A real interval X is defined as the set of real numbers lying between (and including) given upper and lower bounds; that is, $X = [\underline{X}, \overline{X}] = \{x \in \Re \mid \underline{X} \leq x \leq \overline{X}\}$. Here an underline is used to indicate the lower bound of an interval and an overline is used to indicate the upper bound. A real interval vector $\boldsymbol{X} = (X_1, X_2, \ldots, X_n)^{\mathrm{T}}$ has n real interval components and can be interpreted geometrically as an n-dimensional rectangle or box. Note that in this context uppercase quantities are intervals, and lowercase quantities or uppercase quantities with underline or overline are real numbers.

Basic arithmetic operations with intervals are defined by $X \ \mathrm{op} \ Y = \{x \ \mathrm{op} \ y \mid x \in X, \ y \in Y\}$, where $\mathrm{op} = \{+, -, \times, \div\}$. Interval versions of the elementary functions can be similarly defined. It should be emphasized that, when machine computations with interval arithmetic operations are done, as in the procedures outlined below, the endpoints of an interval are computed with a directed (outward) rounding. That is, the lower endpoint is rounded down to the next machine-representable number and the upper endpoint is rounded up to the next machine-representable number. In this way, through the use of

interval, as opposed to floating-point arithmetic, any potential rounding error problems are avoided. Several good introductions to interval analysis, as well as interval arithmetic and other aspects of computing with intervals, are available.[11–14] Implementations of interval arithmetic and elementary functions are also readily available, and recent compilers from Sun Microsystems directly support interval arithmetic and an interval data type.

For an arbitrary function $f(\boldsymbol{x})$, the *interval extension*, $F(\boldsymbol{X})$, encloses all values of $f(\boldsymbol{x})$ for $\boldsymbol{x} \in \boldsymbol{X}$; that is, it encloses the *range* of $f(\boldsymbol{x})$ over $\boldsymbol{X}$. It is often computed by substituting the given interval $\boldsymbol{X}$ into the function $f(\boldsymbol{x})$ and then evaluating the function using interval arithmetic. This so-called "natural" interval extension is often wider than the actual range of function values, though it always includes the actual range. For example, the natural interval extension of $f(x) = x/(x-1)$ over the interval $X = [2,3]$ is $F([2,3]) = [2,3]/([2,3]-1) = [2,3]/[1,2] = [1,3]$, while the true function range over this interval is $[1.5,2]$. This overestimation of the function range is due to the "dependency" problem, which may arise when a variable occurs more than once in a function expression. While a variable may take on any value within its interval, it must take on the *same* value each time it occurs in an expression. However, this type of dependency is not recognized when the natural interval extension is computed. In effect, when the natural interval extension is used, the range computed for the function is the range that would occur if each instance of a particular variable were allowed to take on a different value in its interval range. For the case in which $f(\boldsymbol{x})$ is a single-use expression, that is, an expression in which each variable occurs only once, natural interval arithmetic will always yield the true function range. For example, rearrangement of the function expression used above gives $f(x) = x/(x-1) = 1+1/(x-1)$, and now $F([2,3]) = 1+1/([2,3]-1) = 1+1/[1,2] = 1+[0.5,1] = [1.5,2]$, the true range. For cases in which such rearrangements are not possible, there are a variety of other approaches

that can be used to try to tighten interval extensions.[11–14]

Of particular interest here is the *interval-Newton* method. Given an $n \times n$ nonlinear equation system $\boldsymbol{f}(\boldsymbol{x}) = \boldsymbol{0}$ with a finite number of real roots in some initial interval, this technique provides the capability to find tight enclosures of *all* the roots of the system that lie within the given initial interval. An outline of the interval-Newton methodology is given here. More details are available elsewhere.[12,13,15] It should be emphasized that this technique is *not* equivalent to simply implementing the routine "point" Newton method in interval arithmetic.

Given some initial interval $\boldsymbol{X}^{(0)}$, the interval-Newton algorithm is applied to a sequence of subintervals. For a subinterval $\boldsymbol{X}^{(k)}$ in the sequence, the first step is the *function range test*. An interval extension $\boldsymbol{F}(\boldsymbol{X}^{(k)})$ of the function $\boldsymbol{f}(\boldsymbol{x})$ is calculated. If there is any component of the interval extension $\boldsymbol{F}(\boldsymbol{X}^{(k)})$ that does not include zero, then the interval can be discarded, since no solution of $\boldsymbol{f}(\boldsymbol{x}) = \boldsymbol{0}$ can exist in this interval. The next subinterval in the sequence may then be considered. Otherwise, testing of $\boldsymbol{X}^{(k)}$ continues. During this step, other interval-based techniques (e.g., constraint propagation) may also be applied to try to shrink $\boldsymbol{X}^{(k)}$ before proceeding.

The next step is the *interval-Newton test*. The linear interval equation system

$$\boldsymbol{F}'(\boldsymbol{X}^{(k)})(\boldsymbol{N}^{(k)} - \boldsymbol{x}^{(k)}) = -\boldsymbol{f}(\boldsymbol{x}^{(k)}), \tag{1}$$

is solved for a new interval $\boldsymbol{N}^{(k)}$, where $\boldsymbol{F}'(\boldsymbol{X}^{(k)})$ is an interval extension of the Jacobian of $\boldsymbol{f}(\boldsymbol{x})$, and $\boldsymbol{x}^{(k)}$ is an arbitrary point in $\boldsymbol{X}^{(k)}$. It has been shown[12–14] that any root contained in $\boldsymbol{X}^{(k)}$ is also contained in the *image* $\boldsymbol{N}^{(k)}$. This implies that if the intersection between $\boldsymbol{X}^{(k)}$ and $\boldsymbol{N}^{(k)}$ is empty, then no root exists in $\boldsymbol{X}^{(k)}$, and also suggests the iteration scheme $\boldsymbol{X}^{(k+1)} = \boldsymbol{X}^{(k)} \cap \boldsymbol{N}^{(k)}$. In addition, it has also been shown[12–14] that, if $\boldsymbol{N}^{(k)} \subset \boldsymbol{X}^{(k)}$, then there is a *unique* root contained in $\boldsymbol{X}^{(k)}$ and thus in $\boldsymbol{N}^{(k)}$. Thus, after computation of $\boldsymbol{N}^{(k)}$

from Eq. (1), there are three possibilities: (1) $\boldsymbol{X}^{(k)} \cap \boldsymbol{N}^{(k)} = \emptyset$, meaning there is no root in the current interval $\boldsymbol{X}^{(k)}$ and it can be discarded; (2) $\boldsymbol{N}^{(k)} \subset \boldsymbol{X}^{(k)}$, meaning that there is *exactly* one root in the current interval $\boldsymbol{X}^{(k)}$; (3) neither of the above, meaning that no conclusion can be drawn. In the last case, if $\boldsymbol{X}^{(k)} \cap \boldsymbol{N}^{(k)}$ is sufficiently smaller than $\boldsymbol{X}^{(k)}$, then the interval-Newton test can be reapplied to the resulting intersection, $\boldsymbol{X}^{(k+1)} = \boldsymbol{X}^{(k)} \cap \boldsymbol{N}^{(k)}$. Otherwise, the intersection $\boldsymbol{X}^{(k)} \cap \boldsymbol{N}^{(k)}$ is bisected, and the resulting two subintervals are added to the sequence (stack) of subintervals to be tested. If an interval containing a unique root has been identified, then this root can be tightly enclosed by continuing the interval-Newton iteration, which will converge quadratically to a desired tolerance (on the enclosure diameter).

This approach is referred to as an interval-Newton/generalized-bisection (IN/GB) method. At termination, when the subintervals in the sequence have all been tested, either all the real roots of $\boldsymbol{f}(\boldsymbol{x}) = \boldsymbol{0}$ have been tightly enclosed, or it is determined that no root exists. Applied to nonlinear equation solving problems, this can be regarded as a type of branch-and-prune scheme on a binary tree. It should be emphasized that the enclosure, existence, and uniqueness properties discussed above, which are the basis of the IN/GB method, can be derived without making any strong assumptions about the function $\boldsymbol{f}(\boldsymbol{x})$ for which roots are sought. The function must have a *finite* number of roots over the search interval of interest; however, no special properties such as convexity or monotonicity are required, and $\boldsymbol{f}(\boldsymbol{x})$ may have transcendental terms.

Clearly, the solution of the linear interval system given by Eq. (1) is essential to this approach. To see the issues involved in solving such a system, consider the general linear interval system $\boldsymbol{A}\boldsymbol{z} = \boldsymbol{B}$, where the matrix $\boldsymbol{A}$ and the right-hand-side vector $\boldsymbol{B}$ are interval-valued. The solution set $\mathcal{S}$ of this system is defined by $\mathcal{S} = \left\{ \boldsymbol{z} \,\middle|\, \tilde{A}\boldsymbol{z} = \boldsymbol{b}, \tilde{A} \in \boldsymbol{A}, \boldsymbol{b} \in \boldsymbol{B} \right\}$.

However, in general this set is not an interval and may have a very complex, polygonal geometry. Thus to "solve" the linear interval system, one instead seeks an interval $\boldsymbol{Z}$ containing $\mathcal{S}$. Computing the interval hull (the tightest interval containing $\mathcal{S}$) is NP-hard,[16] but there are several methods for determining an interval $\boldsymbol{Z}$ that contains but overestimates $\mathcal{S}$. Various interval-Newton methods differ in how they solve Eq. (1) for $\boldsymbol{N}^{(k)}$ and thus in the tightness with which the solution set is enclosed. By obtaining bounds that are as tight as possible, the overall performance of the interval-Newton approach can be improved, since with a smaller $\boldsymbol{N}^{(k)}$ the volume of $\boldsymbol{X}^{(k)} \cap \boldsymbol{N}^{(k)}$ is reduced, and it is also more likely that either $\boldsymbol{X}^{(k)} \cap \boldsymbol{N}^{(k)} = \emptyset$ or $\boldsymbol{N}^{(k)} \subset \boldsymbol{X}^{(k)}$ will be satisfied. Thus, intervals that may contain solutions of the nonlinear system are more quickly contracted, and intervals that contain no solution or that contain a unique solution may be more quickly identified, all of which leads to a likely reduction in the number of bisections needed.

Frequently, $\boldsymbol{N}^{(k)}$ is computed component-wise using an interval Gauss-Seidel approach, preconditioned with an inverse-midpoint matrix. Though the inverse-midpoint preconditioner is a good general-purpose preconditioner, it is not always the most effective approach.[12] Recently, a hybrid preconditioning approach (HP/RP), which combines a simple pivoting preconditioner with the standard inverse-midpoint scheme, has been described by Gau and Stadtherr[17] and shown to achieve substantially more efficient computational performance than the inverse-midpoint preconditioner alone, in some cases by multiple orders of magnitude. However, it still cannot yield the tightest enclosure of the solution set, which, as noted above, is in general an NP-hard problem. Lin and Stadtherr[18,19] have recently suggested a strategy (LISS_LP) based on linear programming (LP) for solving the linear interval system, Eq. (1), arising in the context of interval-Newton methods. Using this approach, exact component-wise bounds on the solution set can be calculated, while

avoiding exponential time complexity. In numerical experiments,[18,19] LISS_LP has been shown to achieve further computational performance improvements compared with HP/RP. The methodology used here is the LISS_LP strategy for implementing the interval-Newton approach.

III. POTENTIAL ENERGY MODEL REPRESENTATION

Zeolites are materials in which AlO_4 and SiO_4 tetrahedra are the building blocks of a variety of complex porous structures characterized by interconnected cavities and channels of molecular dimensions.[20] Silicalite contains no aluminum and thus no cations; this has made it a common and convenient choice as a model zeolite system. The crystal structure of silicalite, well known from X-ray diffraction studies,[21] forms a three-dimensional interconnected pore network through which a sorbate molecule can diffuse. In this work, the phase with orthorhombic symmetry is considered and a rigid lattice model, in which all silicon and oxygen atoms in the zeolite framework are occupying fixed positions and there is perfect crystallinity, is assumed. One spherical sorbate molecule (united atom) will be placed in the lattice, corresponding to infinitely dilute diffusion. The system is comprised of 27 unit cells, each of which is $20.07 \times 19.92 \times 13.42$Å with 96 silicon atoms and 192 oxygen atoms.

All interactions between the sorbate and the oxygen atoms of the lattice are treated atomistically with a truncated Lennard-Jones 6-12 potential. That is, for the interaction between the sorbate and oxygen atom i the potential is given by

$$\mathcal{V}_i = \begin{cases} \frac{a}{r_i^{12}} - \frac{b}{r_i^6} & r_i < r_{\text{cut}} \\ 0 & r_i \geq r_{\text{cut}}, \end{cases} \tag{2}$$

where a is a repulsion parameter, b is an attraction parameter, r_{cut} is the cutoff distance,

and r_i is the distance between the sorbate and oxygen atom i. This distance is given by

$$r_i^2 = (x - x_i)^2 + (y - y_i)^2 + (z - z_i)^2, \tag{3}$$

where (x, y, z) are the Cartesian coordinates of the sorbate, and $(x_i, y_i, z_i), i = 1, \ldots, N$ are the Cartesian coordinates of the N oxygen atoms. The silicon atoms, being recessed within the SiO_4 tetrahedra, are neglected in the potential function.[22] Therefore, the total potential energy, $\mathcal{V}$, of a single sorbate molecule in the absence of neighboring sorbate molecules is represented by a sum over all lattice oxygens,

$$\mathcal{V} = \sum_{i=1}^{N} \mathcal{V}_i. \tag{4}$$

Interaction parameters for the attraction and repulsion terms of the Lennard-Jones potential, as well as cutoff distances, are given in Table I for the three sorbate-zeolite systems considered in the examples below.

The interval-Newton methodology will be applied to determine the sorbate locations (x, y, z) that are stationary points on the potential energy surface $\mathcal{V}$ given by Eq. (4), that is, to solve the nonlinear equation system $\nabla\mathcal{V} = \mathbf{0}$. To achieve tighter interval extensions of the potential function and its derivatives, and thus improve the performance of the interval-Newton method, the mathematical properties of the Lennard-Jones potential and its first- and second-order derivatives are exploited.

Each term in the potential function is of the standard Lennard-Jones form

$$\mathcal{V}_{LJ} = \frac{a}{r^{12}} - \frac{b}{r^6}, \tag{5}$$

in which the distance r appears twice. In this case, when interval arithmetic is applied to compute the interval extension, overestimation will occur due to the multiple occurrence of

r. However, a Lennard-Jones term can be rearranged into a single-use expression

$$\mathcal{V}_{LJ} = a\left(\frac{1}{r^6} - \frac{b}{2a}\right)^2 - \frac{b^2}{4a}. \tag{6}$$

in which distance appears only once. In this way, the exact interval extension $V_{LJ}(R)$ of a term $\mathcal{V}_{LJ}(r)$ can be calculated due to avoidance of the dependency problem.

The simplest expression relating r to (x, y, z) is in terms of r^2, as given by Eq. (3). Thus, for purposes of bounding the derivatives of $\mathcal{V}_{LJ}$, it is covenient to work in terms of r^2. The first-order derivative of a Lennard-Jones term with respect to r^2 is given by

$$\mathcal{V}'_{LJ} = -\frac{6a}{r^{14}} + \frac{3b}{r^8}. \tag{7}$$

In this case, no single-use rearrangement is possible. However, it is easily shown that $\mathcal{V}'_{LJ}$ is concave, and when

$$r^2 = \sqrt[3]{\frac{7a}{2b}} = r_1^2 \tag{8}$$

its maximum value

$$\mathcal{V}'^{*}_{LJ} = \frac{9b}{7r_1^8} \tag{9}$$

is obtained. Given a distance interval $R = [\underline{R}, \overline{R}]$, so that $R^2 = [\underline{R}^2, \overline{R}^2]$, we can then obtain the exact interval extension (range) $V'_{LJ}(R^2)$ of the first-order derivative $\mathcal{V}'_{LJ}$ over R^2 from

$$V'_{LJ} = \begin{cases} [\min\{\mathcal{V}'_{LJ}(\underline{R}^2), \mathcal{V}'_{LJ}(\overline{R}^2)\}, \mathcal{V}'^{*}_{LJ}] & \text{if } r_1^2 \in R^2 \\ [\mathcal{V}'_{LJ}(\underline{R}^2), \mathcal{V}'_{LJ}(\overline{R}^2)] & \text{if } r_1^2 > \overline{R}^2 \\ [\mathcal{V}'_{LJ}(\overline{R}^2), \mathcal{V}'_{LJ}(\underline{R}^2)] & \text{if } r_1^2 < \underline{R}^2. \end{cases} \tag{10}$$

Similarly, it can be shown that the second-order derivative of a Lennard-Jones term with respect to r^2,

$$\mathcal{V}''_{LJ} = \frac{42a}{r^{16}} - \frac{12b}{r^{10}}, \tag{11}$$

is convex, and when

$$r^2 = \sqrt[3]{\frac{28a}{5b}} = r_2^2 \tag{12}$$

its minimum value

$$\mathcal{V}_{LJ}^{''*} = -\frac{9b}{2r_2^{10}} \tag{13}$$

is obtained. Thus, we can then obtain the exact interval extension (range) $V_{LJ}''(R^2)$ of the second-order derivative $\mathcal{V}_{LJ}''$ over R^2 from

$$V_{LJ}'' = \begin{cases} [\mathcal{V}_{LJ}''^*, \max\{\mathcal{V}_{LJ}''(\underline{R}^2), \mathcal{V}_{LJ}''(\overline{R}^2)\}] & \text{if } r_2^2 \in R^2 \\ [\mathcal{V}_{LJ}''(\underline{R}^2), \mathcal{V}_{LJ}''(\overline{R}^2)] & \text{if } r_2^2 < \underline{R}^2 \\ [\mathcal{V}_{LJ}''(\overline{R}^2), \mathcal{V}_{LJ}''(\underline{R}^2)] & \text{if } r_2^2 > \overline{R}^2. \end{cases} \tag{14}$$

Note that, when evaluating $\mathcal{V}_{LJ}'(\underline{R}^2)$, $\mathcal{V}_{LJ}'(\overline{R}^2)$, and $\mathcal{V}_{LJ}'^*$ in Eq. (10) and $\mathcal{V}_{LJ}''(\underline{R}^2)$, $\mathcal{V}_{LJ}''(\overline{R}^2)$, and $\mathcal{V}_{LJ}''^*$ in Eq. (14), interval arithmetic needs to be used to bound rounding error.

Through the rearrangement of $\mathcal{V}_{LJ}$ and the use of the concavity of $\mathcal{V}_{LJ}'$ and the convexity of $\mathcal{V}_{LJ}''$, it is thus possible to determine the interval extensions of a Lennard-Jones term and its first- and second-order derivatives exactly (within round out). The total potential function $\mathcal{V}$, however, is a summation over a very large number of such terms, each representing a repeated occurrence of the independent sorbate position variables (x, y, z). Thus, overestimation in the interval extensions of $\mathcal{V}$ and its derivatives will still occur and may be quite substantial. Use of the bounding techniques described above for the terms of $\mathcal{V}$ and the terms of its derivatives will only lessen the overestimation not eliminate it.

IV. RESULTS AND DISCUSSION

The interval-Newton methodology described above is now applied to find the stationary points of the potential energy surface $\mathcal{V}$ for three sorbate-silicalite systems. Due to the

orthorhombic symmetry of the silicalite lattice, the search space is only one asymmetric unit, $[0, 10.035] \times [0, 4.98] \times [0, 13.42]$Å, which is one-eighth of a unit cell. This defines the initial interval for the interval-Newton method, namely $X^{(0)} = [0, 10.035]$Å, $Y^{(0)} = [0, 4.98]$Å, and $Z^{(0)} = [0, 13.42]$Å. Following June *et al.*,[5] stationary points with extremely high potential, such as $\mathcal{V} > 0$, will not be sought. To do this, we calculate the interval extension $V = [\underline{V}, \overline{V}]$ of $\mathcal{V}$ over the interval currently being tested, and if the lower bound $\underline{V} > 0$, then the current interval is discarded. All computations were performed on a Dell workstation running a 1.7 GHz Intel Xeon processor under Linux.

A. Xenon

The first system considered is that of a xenon sorbate in silicalite, as described by June *et al.*[5] Using the LISS_LP strategy for the interval-Newton method, a total of 15 stationary points were found in a computation time of 724 s, as summarized in Table II. The locations of the stationary points, their energy value, and their type are listed in Table III. Five local minima were found, along with 8 first-order saddle points and two second-order saddle points. June *et al.*[5] also tried to find all saddle points and minima of the potential energy surface. They report the same five local minima, as well as nine of the ten saddle points. They do not report finding the lower energy second-order saddle point (saddle point #14 in Table III).

For each first-order saddle point in Table III, we followed June *et al.*'s method[5] to associate the saddle point with the transition state between two specific minima. The saddle point first was perturbed by 10^{-5}Å in either direction along the eigenvector of the Hessian matrix associated with the negative eigenvalue. A steepest descent method using a step of 0.01Å was taken in the direction $-\boldsymbol{g}$. After 500 iterations, the steepest descent calculation was

terminated and a Newton method was used to locate the minima connected through the saddle point. The results of these calculations are given in the rightmost column of Table III. For example, the lowest energy saddle point (#6) can be viewed as connecting minima #1 and #3. In some cases the descent path from a saddle point led to a state outside the initial search box. Since the search box is one asymmetric unit, for each state found outside the search box, we can always find the equivalent state inside the search box through the symmetry operator and/or the periodic operator. In Table III this is indicated by marking the state number with a prime. Thus, saddle point #7 connects minimum #2 with an equivalent point in a neighboring asymmetric unit. As expected, the results found for the states connected by the first-order saddle points is consistent with the analysis of June *et al.*[5]

A similar procedure was used on the two second-order saddle points, but using both negative eigenvalues. For example, in the case of saddle point #15, beginning with perturbations in either direction along the eigenvector associated with the most negative eigenvalue leads to a connection between minima #2 and #3. Repeating with the least negative eigenvalue leads to a connection between minima #4 and #5. Thus, this saddle point can be viewed as providing a crossconnection involving these four points. However, there are lower energy connections between all except #2 and #3. Though June *et al.*[5] do not identify this point as a second-order saddle, they do identify it as associating minima #2 and #3. In their transition state analysis, they use this second-order saddle point, along with five of the eight first-order saddles. The other three first-order saddles (#6, #7 and #8) are very low-lying and separate relatively closely spaced minima by only a small energy barrier, across which rapid thermal equilibrium can be assumed.

The second-order saddle point #14, not reported by June *et al.*,[5] is very close to the

first-order saddle point #13, and slightly lower in energy. Apparently neither of the two methods tried by June *et al.*[5] was able to locate this point. The first method they tried uses the same grid-based optimization scheme used to locate local minima in $\mathcal{V}$, but instead applied to minimize $\boldsymbol{g}^{\mathrm{T}}\boldsymbol{g}$. However, stationary points #13 and #14 are approximately 0.1Å apart, while the grid spacing they used was approximately 0.2Å. This illustrates the danger in using grid-based schemes for finding all solutions to a problem. By using the interval methodology described here, one never needs to be concerned about whether or not a grid spacing is fine enough to find all solutions. The second method they tried was Baker's algorithm,[7] as described briefly above, but it is unclear how they initialized the algorithm. A key advantage of the interval method is that no point initialization is required. Only an initial *interval* must be supplied, here corresponding to one asymmetric unit, and this is determined by the geometry of the zeolite lattice. Thus, in this context the interval methodology is initialization independent.

B. Methylene

The second system considered is that of methylene in silicalite, as described by Maginn *et al.*[23] in the context of a larger study of *n*-alkanes in silicalite. In order to develop a coarse-grained picture of the zeolite consistent with the alkane-zeolite potential energy surface, Maginn *et al.*[23] put a single spherical methylene "test particle" in the silicalite asymmetric cell and then searched for the local minima in the potential energy surface given by Eq. (4). Subsequently, they developed a "wire frame" picture of the channels in the zeolite by considering only the repulsive part of the potential function and searching for local minima and first-order saddles. We consider here both of these problems, namely methylene-silicalite with the Lennard-Jones potential and methylene-silicalite with only the repulsive part of the

potential.

For the case of the Lennard-Jones potential, a total of 21 stationary points are found using the LISS_LP strategy for the interval-Newton method, in a computation time of 870 s. The locations of the stationary points, as well as their type and energy value, are given in Table IV. Five local minima are found, along with 9 first-order saddle points, 6 second-order saddle points, and one local maximum, are found. The results for the positions of the minima agree with those given by Maginn *et al.*,[23] which were obtained using a local solver with a multiple start scheme.[24] The energy values reported by Maginn *et al.*[23] are all slightly lower than those in Table IV, apparently because they reflect the untruncated Lennard-Jones potential (summation over all oxygen atoms in a unit cell and its neighboring unit cells). Maginn *et al.*[23] did not search for saddle points for the case of the Lennard-Jones potential.

For the first-order saddle points, the connectivity to local minima was again found using the procedure of June *et al.*,[5] and the results listed in Table IV. Note that in the case of stationary point #7, which lies near a corner of the initial search space (asymmetric unit), both connected states lie in neighboring asymmetric units.

For the case in which only the repulsive part of the potential was used, seven stationary points were found using the interval-Newton methodology, in a computation time of 265 s. These stationary points are listed in Table V; there are three local minima and four first-order saddle points. The locations of these points correspond to the results given by Maginn *et al.*[23]

C. Sulfur hexafluoride

The final system considered is that of SF_6 in silicalite, another system studied by June *et al.*[5] Using the LISS_LP strategy for the interval-Newton method, 9 stationary points were found in a computation time of 270 s. As shown in Table VI, four local minima and five first-order saddle points were found. No second-order saddle points or local maxima were found. June *et al.*[5] do not report values for the stationary points that they found; however, the results given in Table VI are consistent with their discussion of this problem.

V. CONCLUDING REMARKS

We have demonstrated a new methodology for reliably locating stationary points of sorbate-zeolite potential energy surfaces. The technique is based on interval analysis, in particular an interval-Newton/generalized-bisection algorithm in which a strategy[18,19] based on linear programming is used to solve the linear interval subproblems. The approach provides a mathematical and computational *guarantee* that *all* stationary points of potential energy surface will be found. As can be seen from the computational performance results summarized in Table II, the interval-Newton methodology used is also quite efficient in solving these problems. While we have concentrated here on problems involving transition-state analysis of diffusion in zeolites, we anticipate that the methodology will be useful in many other types of problems in which transition-state theory is applied.

For the problems studied here, the search space was three-dimensional and described by Cartesian coordinates. The interval-Newton methodology can also be applied to problems involving non-Cartesian coordinates, as well as to problems in which intramolecular coordinates are used. In the later case, the dimensionality of the search space may become

increasingly large. Because the underlying problem of finding *all* stationary points *deterministically* is NP-hard, we would expect that, as dimensionality increases, the methodology will eventually become ineffective due to excessive computation time requirements. The point at which this occurs will vary from problem to problem; however, it should be noted that, in other types of applications, this methodology has been used to solve problems with over 200 degrees of freedom.[25]

Acknowledgments

This work has been supported in part by the donors of The Petroleum Research Fund, administered by the ACS, under Grant 35979-AC9, and by the Indiana 21st Century Research & Technology Fund. We also thank Prof. Edward J. Maginn for his helpful comments and advice.

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TABLE I: Interaction parameters and cutoff distance for the truncated Lennard-Jones potential for oxygen with methylene[23], xenon[5] and sulfur hexafluoride.[5]

Interacting Pair	a (kcal Å^{12}/mol)	b (kcal Å^6/mol)	r_{cut} (Å)
O – CH_2	0.1399×10^7	965.3	13
O – Xe	0.3113×10^7	1836	15
O – SF_6	1.7776×10^7	4560	15

TABLE II: Summary of performance of LISS_LP on sorbate-silicalite problems

Sorbate	Stationary Points Found	CPU Time (s)
Xenon	15	724
Methylene (LJ)	21	870
Methylene (repulsive)	7	265
SF_6	9	270

TABLE III: Stationary points of the potential energy surface of xenon in silicalite

No.	Type	Energy(kcal/mol)	x(Å)	y(Å)	z(Å)	Connects
1	minimum	-5.9560	3.9956	4.9800	12.1340	
2	minimum	-5.8763	0.3613	0.9260	6.1112	
3	minimum	-5.8422	5.8529	4.9800	10.8790	
4	minimum	-5.7455	1.4356	4.9800	11.5540	
5	minimum	-5.1109	0.4642	4.9800	6.0635	
6	1st order	-5.7738	5.0486	4.9800	11.3210	(1, 3)
7	1st order	-5.6955	0.0000	0.0000	6.7100	(2′, 2)
8	1st order	-5.6060	2.3433	4.9800	11.4980	(1, 4)
9	1st order	-4.7494	0.1454	3.7957	6.4452	(2, 5)
10	1st order	-4.3057	9.2165	4.9800	11.0110	(3, 4)
11	1st order	-4.2380	0.0477	3.9147	8.3865	(2, 4)
12	1st order	-4.2261	8.6361	4.9800	12.8560	(3, 5′)
13	1st order	-4.1405	0.5925	4.9800	8.0122	(4, 5)
14	2nd order	-4.1404	0.5883	4.8777	8.0138	(4,5),(4,4′)
15	2nd order	-4.1027	9.1881	4.1629	11.8720	(2,3),(4,5)

TABLE IV: Stationary points of the potential energy surface of methylene in silicalite (Lennard-Jones potential)

No.	Type	Energy(kcal/mol)	x(Å)	y(Å)	z(Å)	Connects
1	minimum	-3.2899	3.9646	4.9800	12.3390	
2	minimum	-3.2584	0.4698	0.9394	5.9826	
3	minimum	-3.2442	5.9467	4.9800	10.7240	
4	minimum	-3.2040	1.3411	4.9800	11.6990	
5	minimum	-2.8766	0.5876	4.9800	5.9724	
6	1st order	-3.1502	4.9528	4.6283	11.2790	(1, 3)
7	1st order	-3.1052	9.6439	0.1264	0.1205	(2′, 2″)
8	1st order	-3.0811	2.3978	4.9800	11.6240	(1, 4)
9	1st order	-2.6233	0.2187	3.7405	6.3635	(2, 5)
10	1st order	-2.3674	9.2169	4.9800	10.8810	(3, 4′)
11	1st order	-2.3264	0.0743	3.7977	8.4413	(2, 4)
12	1st order	-2.3151	8.5300	4.9800	12.9170	(3, 5′)
13	1st order	-2.2739	8.7862	4.0664	12.5150	(2′, 3)
14	1st order	-2.2618	0.7135	4.9800	8.0321	(4, 5)
15	2nd order	-3.1384	4.8522	4.9800	11.3950	
16	2nd order	-3.0892	10.0350	0.0000	13.4200	
17	2nd order	-3.0892	10.0350	0.0000	0.0000	
18	2nd order	-3.0892	0.0000	0.0000	6.7100	
19	2nd order	-2.2724	8.7828	4.1858	12.6960	
20	2nd order	-2.2301	9.1246	4.0744	11.8350	
21	maximum	-2.0354	9.6221	4.9800	12.2630	

TABLE V: Stationary points of the potential energy surface of methylene in silicalite (repulsive potential only)

No.	Type	Energy(kcal/mol)	x(Å)	y(Å)	z(Å)	Connects
1	minimum	0.1559	9.6357	4.9800	12.3614	
2	minimum	0.6451	4.1318	4.9800	11.6298	
3	minimum	0.6705	0.0491	0.6783	6.5541	
4	1st order	0.6786	0.0000	0.0000	6.7100	(3, 3′)
5	1st order	0.7508	10.0334	1.9828	0.0086	(1′, 3′)
6	1st order	0.7844	2.6474	4.9800	11.3282	(1′, 2)
7	1st order	0.8721	6.7084	4.9800	11.3923	(1, 2)

TABLE VI: Stationary points of the potential energy surface of SF_6 in silicalite

No.	Type	Energy(kcal/mol)	x(Å)	y(Å)	z(Å)	Connects
1	minimum	-9.8923	4.1159	4.9800	11.6820	
2	minimum	-9.4079	0.0773	0.7267	6.4898	
3	minimum	-8.8814	9.9462	4.9800	13.3750	
4	minimum	-8.6880	1.6351	4.9800	11.0670	
5	1st order	-9.2736	0.0000	0.0000	6.7100	(2, 2′)
6	1st order	-8.2341	2.5043	4.9800	11.3270	(1, 4)
7	1st order	-7.7591	0.8381	4.9800	9.9748	(3′, 4)
8	1st order	-7.5698	10.0040	2.4616	13.3320	(2′, 3)
9	1st order	-6.6658	7.1559	4.9800	11.4830	(1, 3)