

Split-Step Eigenvector-Following Technique for Exploring Enthalpy Landscapes at Absolute Zero

John C. Mauro*

Science & Technology Division, Corning Incorporated, Corning, New York 14831, and NYS College of Ceramics, Alfred University, Alfred, New York 14802

Roger J. Loucks

Department of Physics & Astronomy, Alfred University, Alfred, New York 14802

Jitendra Balakrishnan

Science & Technology Division, Corning Incorporated, Corning, New York 14831

Received: November 23, 2005; In Final Form: January 4, 2006

The mapping of enthalpy landscapes is complicated by the coupling of particle position and volume coordinates. To address this issue, we have developed a new split-step eigenvector-following technique for locating minima and transition points in an enthalpy landscape at absolute zero. Each iteration is split into two steps in order to independently vary system volume and relative atomic coordinates. A separate Lagrange multiplier is used for each eigendirection in order to provide maximum flexibility in determining step sizes. This technique will be useful for mapping the enthalpy landscapes of bulk systems such as supercooled liquids and glasses.

1. Introduction

Recently, there have been many studies involving potential energy landscapes of molecular clusters,^{1–4} biomolecules,⁴ supercooled liquids,^{5–10} and glassy systems.^{4,11–13} Potential energy landscapes do not allow for changes in the volume of a system and are thus inadequate for understanding structural relaxation in inorganic glasses. A recent study by Middleton and Wales¹² introduced the concept of an enthalpy landscape and applied it to a model glass system under isobaric conditions. Exploration of an enthalpy landscape allows for changes in both particle positions and the total volume of the system. To separate the thermal and configurational components of energy, the enthalpy landscape is computed at absolute zero. This zero temperature landscape corresponds to an underlying surface that is sampled by a system at finite temperature in an isobaric ensemble.

In this paper, we derive a new eigenvector-following technique for locating minima and transition points in an enthalpy landscape. Our derivation is based on our previous study of potential energy landscapes,¹⁴ in which we used steepest descents to find minima and an eigenvector-following method to locate first-order transition points. However, for bulk systems with periodic boundary conditions, the method of steepest descent has convergence issues due to the tortuosity of the enthalpy landscape. To this end, we present a recursive algorithm for mapping enthalpy landscapes that incorporates eigenvector-following methods for locating both minima and transition points.

Our new eigenvector-following technique includes two steps at each iteration in order to independently vary system volume and relative atomic positions. The justification for this approach is discussed in sections 2–4, and the split-step technique itself is presented in sections 5 and 6. Finally, a recursive algorithm for mapping enthalpy landscapes is provided in section 7.

2. The Difficulty of Enthalpy Landscapes

The zero temperature enthalpy landscape of an N -particle system is

$$\mathcal{H} = E(x_1, x_2, \dots, x_{3N}, L) + PL^3 \quad (1)$$

where the potential (i.e., configurational) energy E is a function of $3N$ position coordinates, x_1, x_2, \dots, x_{3N} , and the length L of the simulation cell. The pressure P of the system is constant, and we assume a cubic cell volume of $V = L^3$. The enthalpy landscape therefore has a dimensionality of $3N + 1$, minus any constraints.

If the enthalpy of the system with initial positions x_i^0 , where $i = 1, 2, \dots, 3N$, and initial length L^0 is given by $\mathcal{H}(x_i^0, L^0)$, then we can approximate the enthalpy at a new position $x_i = x_i^0 + h_i$ and new length $L = L^0 + h_L$ using the Taylor series expansion

$$\begin{aligned} \mathcal{H}(x_i, L) \approx & \mathcal{H}(x_i^0, L^0) + \\ & \sum_{i=1}^{3N} \left. \frac{\partial \mathcal{H}}{\partial x_i} \right|_{x_i=x_i^0, L=L^0} h_i + \left. \frac{\partial \mathcal{H}}{\partial L} \right|_{x_i=x_i^0, L=L^0} h_L + \\ & \frac{1}{2} \sum_{i=1}^{3N} \sum_{j=1}^{3N} h_i \left. \frac{\partial^2 \mathcal{H}}{\partial x_i \partial x_j} \right|_{x_i=x_i^0, L=L^0} h_j + \frac{1}{2} \left. \frac{\partial^2 \mathcal{H}}{\partial L^2} \right|_{x_i=x_i^0, L=L^0} h_L^2 + \\ & \frac{1}{2} \sum_{i=1}^{3N} h_i \left. \frac{\partial^2 \mathcal{H}}{\partial x_i \partial L} \right|_{x_i=x_i^0, L=L^0} h_L + \frac{1}{2} \sum_{i=1}^{3N} h_L \left. \frac{\partial^2 \mathcal{H}}{\partial L \partial x_i} \right|_{x_i=x_i^0, L=L^0} h_i \quad (2) \end{aligned}$$

This can be written in matrix notation as

$$\mathcal{H}(\mathbf{q}) \approx \mathcal{H}(\mathbf{q}^0) + \mathbf{g}^T \mathbf{h} + \frac{1}{2} \mathbf{h}^T \mathbf{H} \mathbf{h} \quad (3)$$

where the position vectors are given by

$$\mathbf{q} = \begin{pmatrix} x_1 \\ x_2 \\ \vdots \\ x_{3N} \\ L \end{pmatrix}; \mathbf{q}^0 = \begin{pmatrix} x_1^0 \\ x_2^0 \\ \vdots \\ x_{3N}^0 \\ L^0 \end{pmatrix} \quad (4)$$

and the displacement vector $\mathbf{h} = \mathbf{q} - \mathbf{q}^0$ is

$$\mathbf{h} = \begin{pmatrix} h_1 \\ h_2 \\ \vdots \\ h_{3N} \\ h_L \end{pmatrix} \quad (5)$$

The gradient vector \mathbf{g} and the $(3N + 1) \times (3N + 1)$ Hessian matrix \mathbf{H} , evaluated at $\mathbf{q} = \mathbf{q}^0$, are given by

$$\mathbf{g} = \begin{pmatrix} \frac{\partial \mathcal{H}}{\partial x_1} \\ \frac{\partial \mathcal{H}}{\partial x_2} \\ \vdots \\ \frac{\partial \mathcal{H}}{\partial x_{3N}} \\ \frac{\partial \mathcal{H}}{\partial L} \end{pmatrix}_{\mathbf{q}=\mathbf{q}^0} \quad (6)$$

and

$$\mathbf{H} = \begin{pmatrix} \frac{\partial^2 \mathcal{H}}{\partial x_1^2} & \frac{\partial^2 \mathcal{H}}{\partial x_1 \partial x_2} & \cdots & \frac{\partial^2 \mathcal{H}}{\partial x_1 \partial x_{3N}} & \frac{\partial^2 \mathcal{H}}{\partial x_1 \partial L} \\ \frac{\partial^2 \mathcal{H}}{\partial x_2 \partial x_1} & \frac{\partial^2 \mathcal{H}}{\partial x_2^2} & \cdots & \frac{\partial^2 \mathcal{H}}{\partial x_2 \partial x_{3N}} & \frac{\partial^2 \mathcal{H}}{\partial x_2 \partial L} \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ \frac{\partial^2 \mathcal{H}}{\partial x_{3N} \partial x_1} & \frac{\partial^2 \mathcal{H}}{\partial x_{3N} \partial x_2} & \cdots & \frac{\partial^2 \mathcal{H}}{\partial x_{3N}^2} & \frac{\partial^2 \mathcal{H}}{\partial x_{3N} \partial L} \\ \frac{\partial^2 \mathcal{H}}{\partial L \partial x_1} & \frac{\partial^2 \mathcal{H}}{\partial L \partial x_2} & \cdots & \frac{\partial^2 \mathcal{H}}{\partial L \partial x_{3N}} & \frac{\partial^2 \mathcal{H}}{\partial L^2} \end{pmatrix}_{\mathbf{q}=\mathbf{q}^0} \quad (7)$$

respectively.

In our previous derivation of an eigenvector-following technique for potential energy landscapes,¹⁴ the Hessian matrix \mathbf{H} contained second derivatives with respect to position coordinates x_i only. Since the position coordinates are independent of each other, that Hessian matrix was symmetric. In the case of an enthalpy landscape, the Hessian matrix has one additional row and column including derivatives with respect to the simulation cell length L . The chief difficulty in extending our potential energy approach to enthalpy landscapes is that the position and length coordinates are not truly independent of each other. When implementing a change in length for a bulk system with periodic boundary conditions, it is standard to scale the atomic positions according to

$$\frac{\partial x_i}{\partial L} = \frac{x_i}{L} \quad (8)$$

since any change in length produces a corresponding “stretch-

ing” of atomic positions. This relationship leads to

$$\frac{\partial^2 \mathcal{H}}{\partial x_i \partial L} = \frac{\partial^2 \mathcal{H}}{\partial L \partial x_i} + \frac{1}{L} \frac{\partial \mathcal{H}}{\partial x_i} \quad (9)$$

and therefore the Hessian matrix \mathbf{H} for an enthalpy landscape is not symmetric. This poses a problem in computing the eigenvalues and eigenvectors of \mathbf{H} , since most eigenvector solvers assume a symmetric matrix; those that allow for asymmetric matrixes are much less efficient than symmetric eigenvector solvers. In addition, an asymmetric matrix can lead to complex eigenvalues.

We can take advantage of the relationship in eq 9 to symmetrize the Hessian. Substituting eq 9 into 2, we obtain

$$\begin{aligned} \mathcal{H}(x_i, L) \approx \mathcal{H}(x_i^0, L^0) + \\ \sum_{i=1}^{3N} \left(1 + \frac{h_L}{L} \right) \frac{\partial \mathcal{H}}{\partial x_i} \bigg|_{x_i=x_i^0, L=L^0} h_i + \frac{\partial \mathcal{H}}{\partial L} \bigg|_{x_i=x_i^0, L=L^0} h_L + \\ \frac{1}{2} \sum_{i=1}^{3N} \sum_{j=1}^{3N} h_i \frac{\partial^2 \mathcal{H}}{\partial x_i \partial x_j} \bigg|_{x_i=x_i^0, x_j=x_j^0, L=L^0} h_j + \frac{1}{2} \frac{\partial^2 \mathcal{H}}{\partial L^2} \bigg|_{x_i=x_i^0, L=L^0} h_L^2 + \\ \sum_{i=1}^{3N} h_L \frac{\partial^2 \mathcal{H}}{\partial L \partial x_i} \bigg|_{x_i=x_i^0, L=L^0} h_i \end{aligned} \quad (10)$$

which can be rewritten in matrix notation as

$$\mathcal{H}(\mathbf{q}) \approx \mathcal{H}(\mathbf{q}^0) + \left(1 + \frac{h_L}{L} \right) \mathbf{g}^T \mathbf{h} - \frac{h_L^2}{L} g_L + \frac{1}{2} \mathbf{h}^T \mathbf{H}' \mathbf{h} \quad (11)$$

where \mathbf{H}' is the symmetrized Hessian

$$\mathbf{H}' = \begin{pmatrix} \frac{\partial^2 \mathcal{H}}{\partial x_1^2} & \frac{\partial^2 \mathcal{H}}{\partial x_1 \partial x_2} & \cdots & \frac{\partial^2 \mathcal{H}}{\partial x_1 \partial x_{3N}} & \frac{\partial^2 \mathcal{H}}{\partial L \partial x_1} \\ \frac{\partial^2 \mathcal{H}}{\partial x_1 \partial x_2} & \frac{\partial^2 \mathcal{H}}{\partial x_2^2} & \cdots & \frac{\partial^2 \mathcal{H}}{\partial x_2 \partial x_{3N}} & \frac{\partial^2 \mathcal{H}}{\partial L \partial x_2} \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ \frac{\partial^2 \mathcal{H}}{\partial x_1 \partial x_{3N}} & \frac{\partial^2 \mathcal{H}}{\partial x_2 \partial x_{3N}} & \cdots & \frac{\partial^2 \mathcal{H}}{\partial x_{3N}^2} & \frac{\partial^2 \mathcal{H}}{\partial L \partial x_{3N}} \\ \frac{\partial^2 \mathcal{H}}{\partial L \partial x_1} & \frac{\partial^2 \mathcal{H}}{\partial L \partial x_2} & \cdots & \frac{\partial^2 \mathcal{H}}{\partial L \partial x_{3N}} & \frac{\partial^2 \mathcal{H}}{\partial L^2} \end{pmatrix}_{\mathbf{q}=\mathbf{q}^0} \quad (12)$$

To choose appropriate steps in the x_i and L dimensions, we define the Lagrange function

$$\begin{aligned} \mathcal{L} = -\mathcal{H}(x_i^0, L^0) - \\ \sum_{i=1}^{3N} \left(1 + \frac{h_L}{L} \right) \frac{\partial \mathcal{H}}{\partial x_i} \bigg|_{x_i=x_i^0, L=L^0} h_i - \frac{\partial \mathcal{H}}{\partial L} \bigg|_{x_i=x_i^0, L=L^0} h_L - \\ \frac{1}{2} \sum_{i=1}^{3N} \sum_{j=1}^{3N} h_i \frac{\partial^2 \mathcal{H}}{\partial x_i \partial x_j} \bigg|_{x_i=x_i^0, x_j=x_j^0, L=L^0} h_j - \frac{1}{2} \frac{\partial^2 \mathcal{H}}{\partial L^2} \bigg|_{x_i=x_i^0, L=L^0} h_L^2 - \\ \sum_{i=1}^{3N} h_L \frac{\partial^2 \mathcal{H}}{\partial L \partial x_i} \bigg|_{x_i=x_i^0, L=L^0} h_i + \frac{1}{2} \sum_{i=1}^{3N} \lambda_i (h_i^2 - c_i^2) + \\ \frac{1}{2} \lambda_L (h_L^2 - c_L^2) \end{aligned} \quad (13)$$

where $c_{i,L}$ are the desired step sizes in the various directions and $\lambda_{i,L}$ are Lagrange multipliers. Taking the derivative of \mathcal{L} with respect to an arbitrary step h_k and setting it equal to zero, we obtain

$$0 = -\sum_{i=1}^{3N} \left(1 + \frac{h_L}{L}\right) g_i \delta_{ik} - \sum_{i=1}^{3N} \frac{h_i}{L} g_i \delta_{kL} - g_L \delta_{kL} - \sum_{i=1}^{3N+1} \sum_{j=1}^{3N+1} h_i H_{ij}' \delta_{jk} + \sum_{i=1}^{3N+1} \lambda_i h_i \delta_{ik} \quad (14)$$

which can be rewritten as

$$0 = -g_k - \frac{h_L}{L} \sum_{i=1}^{3N} g_i \delta_{ik} - \frac{\delta_{kL}}{L} \sum_{i=1}^{3N} g_i h_i - \sum_{i=1}^{3N+1} H_{ik}' h_i + \lambda_k h_k \quad (15)$$

Unfortunately, the solution to eq 15 is difficult to obtain since the equations for h_i and h_L are coupled. This is actually a specific example of a more general optimization problem where the coordinates do not have a simple relationship but rather are related via partial derivatives.

3. A General Statement of the Problem

Suppose we want to minimize the function $f(a,b)$, where the coordinates a and b have no simple holonomic constraint, $\alpha(a,b) = 0$, but are related through the partial derivatives

$$\frac{\partial a}{\partial b} = c(a,b); \quad \frac{\partial b}{\partial a} = 0 \quad (16)$$

One solution of this problem involves decoupling of the a and b coordinates, which can be accomplished by introducing a new $\bar{a} = p(a,b)$ coordinate, where \bar{a} satisfies

$$\frac{d\bar{a}}{db} = 0 \quad (17)$$

Note that since a and b are not independent variables, we have a total derivative instead of a partial derivative. The problem then becomes determination of the restrictions on $p(a,b)$ such that eq 17 is satisfied.

The total differential of \bar{a} is

$$d\bar{a} = \left. \frac{\partial \bar{a}}{\partial b} \right|_a db + \left. \frac{\partial \bar{a}}{\partial a} \right|_b da \quad (18)$$

such that

$$\frac{d\bar{a}}{db} = \left. \frac{\partial \bar{a}}{\partial b} \right|_a + \left. \frac{\partial \bar{a}}{\partial a} \right|_b \frac{\partial a}{\partial b} = 0 \quad (19)$$

Hence

$$\left. \frac{\partial \bar{a}}{\partial a} \right|_b c(a,b) = - \left. \frac{\partial \bar{a}}{\partial b} \right|_a \quad (20)$$

Taking the special case where $c(a,b)$ and $p(a,b)$ are separable

$$c(a,b) = q(a) w(b); \quad p(a,b) = r(a) s(b) \quad (21)$$

Therefore

$$s(b) \left. \frac{\partial r(a)}{\partial a} \right|_b q(a) w(b) = -r(a) \left. \frac{\partial s(b)}{\partial b} \right|_a \quad (22)$$

Since there is no holonomic constraint between a and b , eq 22

can be split into separate equations of a and b

$$q(a) \frac{\partial r(a)}{\partial a} = r(a) \quad (23)$$

$$s(b) w(b) = - \frac{\partial s(b)}{\partial b} \quad (24)$$

These equations become

$$\frac{\partial \ln r(a)}{\partial a} = \frac{1}{q(a)} \quad (25)$$

$$\frac{\partial \ln s(b)}{\partial b} = -w(b) \quad (26)$$

and yield the solutions

$$r(a) = \exp\left(\int \frac{1}{q(a)} da\right) \quad (27)$$

$$s(b) = \exp\left(-\int w(b) db\right) \quad (28)$$

Thus, the coordinates can be decoupled by choosing

$$\bar{a} = \exp\left(\int \frac{1}{q(a)} da - \int w(b) db\right) \quad (29)$$

4. Application to Enthalpy Landscapes

In our case, the function $f(a,b)$ is the enthalpy function $\mathcal{H}(x_i, L)$, where a simple holonomic relation between x_i and L is not present. To see this point, consider a bulk system of atoms. If the length of the system changes, all of the x_i coordinates scale according to eq 8, but displacement of a single atom does not produce a measurable change in L . Thus, we have

$$\frac{\partial x_i}{\partial L} = x_i \frac{1}{L}; \quad \frac{\partial L}{\partial x_i} = 0 \quad (30)$$

From eq 29, we introduce the new coordinates \bar{x}_i as

$$\bar{x}_i = \exp\left(\int \frac{1}{x_i} \partial x_i - \int \frac{1}{L} \partial L\right) \quad (31)$$

which simplifies to

$$\bar{x}_i = C \frac{x_i}{L} = \frac{x_i}{L} \quad (32)$$

where the constant of integration C is set to unity. The normalized positions \bar{x}_i are independent of changes in L since

$$\frac{d\bar{x}_i}{dL} = \sum_{j=1}^{3N} \left(\frac{\partial \bar{x}_i}{\partial x_j} \right) \left(\frac{\partial x_j}{\partial L} \right) + \frac{\partial \bar{x}_i}{\partial L} = \frac{x_i}{L^2} - \frac{x_i}{L^2} = 0 \quad (33)$$

With this notation, the enthalpy landscape can be expressed as

$$\mathcal{H} = E(\bar{x}_1, \bar{x}_2, \dots, \bar{x}_{3N}, L) + PL^3 \quad (34)$$

and the Taylor expansion of enthalpy simplifies to

$$\mathcal{H}(\bar{\mathbf{q}}) \approx \mathcal{H}(\bar{\mathbf{q}}^0) + \bar{\mathbf{g}}^T \bar{\mathbf{h}} + \frac{1}{2} \bar{\mathbf{h}}^T \bar{\mathbf{H}} \bar{\mathbf{h}} \quad (35)$$

where the overbars denote use of the normalized \bar{x}_i coordinates.

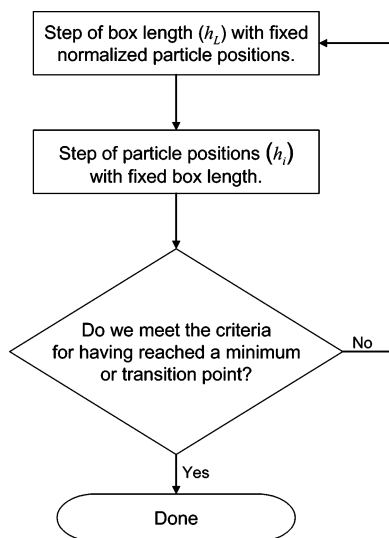


Figure 1. Flowchart of the split-step eigenvector-following technique for locating minima and transition points.

In principle, the step vector $\bar{\mathbf{h}}$ can be calculated following the same procedure as for potential energy landscapes¹⁴ since the \bar{x}_i and L coordinates are decoupled. However, this involves computation of first and second derivatives of enthalpy with respect to the normalized \bar{x}_i coordinates rather than the natural x_i coordinates. Since x_i and L have units of length, the elements, eigenvalues, and eigenvectors of the Hessian matrix would all have the same units. While in principle this is not an issue, it eases implementation since it is more computationally convenient to compute derivatives and the step vector in terms of the unnormalized coordinates x_i . This can be accomplished using a split-step eigenvector-following technique described in the next section.

5. Split-Step Eigenvector-Following Technique

The split-step eigenvector-following technique consists of iteratively stepping through the enthalpy landscape toward a minimum or transition point. Each iteration involves two steps: (1) step of the simulation box length L while maintaining constant normalized positions \bar{x}_i ; (2) Step of the positions x_i while maintaining constant L .

This procedure is shown graphically in Figure 1. In the first step of the iteration, the enthalpy can be written in terms of a Taylor series expansion

$$\mathcal{H}(\bar{x}_i^0, L) \approx \mathcal{H}(\bar{x}_i^0, L^0) + \left. \frac{\partial \mathcal{H}}{\partial L} \right|_{\bar{x}_i=\bar{x}_i^0, L=L^0} h_L + \frac{1}{2} \left. \frac{\partial^2 \mathcal{H}}{\partial L^2} \right|_{\bar{x}_i=\bar{x}_i^0, L=L^0} h_L^2 \quad (36)$$

We can now write a Lagrange function in one dimension

$$\mathcal{L}_L = -\mathcal{H}(\bar{x}_i^0, L^0) - \left. \frac{\partial \mathcal{H}}{\partial L} \right|_{\bar{x}_i=\bar{x}_i^0, L=L^0} h_L - \frac{1}{2} \left. \frac{\partial^2 \mathcal{H}}{\partial L^2} \right|_{\bar{x}_i=\bar{x}_i^0, L=L^0} h_L^2 + \frac{1}{2} \lambda_L (h_L^2 - c_L^2) \quad (37)$$

Taking the derivative with respect to h_L yields

$$\frac{\partial \mathcal{L}_L}{\partial h_L} = 0 = - \left. \frac{\partial \mathcal{H}}{\partial L} \right|_{\bar{x}_i=\bar{x}_i^0, L=L^0} - \left. \frac{\partial^2 \mathcal{H}}{\partial L^2} \right|_{\bar{x}_i=\bar{x}_i^0, L=L^0} h_L + \lambda_L h_L \quad (38)$$

Defining

$$F_L = \left. \frac{\partial \mathcal{H}}{\partial L} \right|_{\bar{x}_i=\bar{x}_i^0, L=L^0} = \left(\frac{\partial E}{\partial L} + 3PL^2 \right)_{\bar{x}_i=\bar{x}_i^0, L=L^0} \quad (39)$$

and

$$b_L = \left. \frac{\partial^2 \mathcal{H}}{\partial L^2} \right|_{\bar{x}_i=\bar{x}_i^0, L=L^0} = \left(\frac{\partial^2 E}{\partial L^2} + 6PL \right)_{\bar{x}_i=\bar{x}_i^0, L=L^0} \quad (40)$$

we have

$$h_L = \frac{F_L}{\lambda_L - b_L} \quad (41)$$

The change in enthalpy $\Delta \mathcal{H}_L$ for such a step h_L is

$$\Delta \mathcal{H}_L = \frac{F_L^2 \left(\lambda_L - \frac{b_L}{2} \right)}{(\lambda_L - b_L)^2} \quad (42)$$

Hence, the sign of the enthalpy change depends on both b_L and the choice of Lagrange multiplier λ_L .

The second step involves changes in the particle positions x_i with a fixed box length L . In this case, the gradient and second derivative terms reduce to

$$\frac{\partial \mathcal{H}}{\partial x_i} = \frac{\partial E}{\partial x_i}, \quad \frac{\partial^2 \mathcal{H}}{\partial x_i \partial x_j} = \frac{\partial^2 E}{\partial x_i \partial x_j} \quad (43)$$

Therefore, this step is exactly the same as with our previous analysis for potential energy landscapes in the canonical ensemble.¹⁴ The position step vector is given by

$$\mathbf{h}_x = \sum_{i=1}^{3N} \frac{F_i}{\lambda_i - b_i} \mathbf{V}_i \quad (44)$$

where b_i and \mathbf{V}_i are the eigenvalues and associated eigenvectors of the symmetric $3N \times 3N$ Hessian matrix \mathbf{H}

$$\mathbf{H} \mathbf{V}_i = b_i \mathbf{V}_i \quad (45)$$

and F_i is defined by

$$\mathbf{g} = \sum_{i=1}^{3N} F_i \mathbf{V}_i \quad (46)$$

The change in enthalpy associated with the position step vector \mathbf{h}_x is

$$\Delta \mathcal{H}_x = \Delta E_x = \sum_{i=1}^{3N} \frac{F_i^2 \left(\lambda_i - \frac{b_i}{2} \right)}{(\lambda_i - b_i)^2} \quad (47)$$

Again, the sign of the enthalpy change in a particular eigendirection \mathbf{V}_i depends on both the eigenvalue b_i and the choice of Lagrange multiplier λ_i .

6. Choice of Lagrange Multipliers

To locate transition points and minima in the enthalpy landscape, we must make an appropriate choice of Lagrange multipliers. In this section, we specify a suitable choice of Lagrange multipliers for both cases.

6.1. Locating Transition Points. A transition point is defined as a stationary point where exactly one of the eigenvalues of the Hessian matrix is negative. Thus, a transition point corresponds to an enthalpy maximum in one eigendirection and an enthalpy minimum in all other eigendirections. With the split-step technique, the single negative eigenvalue may be any one of b_i or b_L . Treating the length dimension as the $(3N + 1)^{\text{th}}$ dimension, as in eq 4, the eigenvector corresponding to $b_L = b_{3N+1}$ is

$$\mathbf{V}_L = \mathbf{V}_{3N+1} = \begin{pmatrix} 0 \\ 0 \\ \vdots \\ 0 \\ 1 \end{pmatrix} \quad (48)$$

As such, we may rewrite the total change in enthalpy as a summation of enthalpy changes in each of the $3N + 1$ eigendirections

$$\Delta\mathcal{H} = \sum_{i=1}^{3N+1} \Delta\mathcal{H}_i \quad (49)$$

where

$$\Delta\mathcal{H}_i = \frac{F_i^2 \left(\lambda_i - \frac{b_i}{2} \right)}{(\lambda_i - b_i)^2} \quad (50)$$

Suppose we wish to find a transition point by maximizing enthalpy in a particular \mathbf{V}_i eigendirection while minimizing in all of the orthogonal $\mathbf{V}_{j \neq i}$ directions. The eigendirection \mathbf{V}_i of interest may be associated with changes in either position or length. Due to the split-step nature of our approach, the eigenvector cannot have components of both position and length simultaneously. It follows from our previous analysis¹⁴ that a choice of $\lambda_i > |b_i|$ and $\lambda_j < -|b_j|$ would guarantee a step in the correct direction toward a transition point. However, this specifies neither the particular values of $\lambda_{i,j}$ nor the magnitude of the step.

We may simplify our analysis by assuming that a transition point search always starts from a local minimum in the enthalpy landscape. This is also the most practical case to consider from an applications point of view, since we are typically interested in finding the transition enthalpy between two stable configurations, e.g., two inherent structures using Stillinger's terminology.⁹ A minimum in the enthalpy landscape has the property $b_k > 0$ for all $k = 1, 2, \dots, N$. As we walk on the enthalpy landscape from the minimum to a transition point, we are essentially walking uphill along a valley or stream bed. If the direction of our walk up the stream bed is \mathbf{V}_i and the step size is sufficiently small, we should have $b_j > 0$ for all $j \neq i$ and be near the enthalpy minima in the $\mathbf{V}_{j \neq i}$ directions along the entire walk. In the case of an infinitesimal step size, we would exactly follow the stream bed; however, due to finite step sizes, we may have slight deviations from the stream bed. These deviations may be corrected by an appropriate choice of $\lambda_{j \neq i}$, which is accomplished by finding the nearest stationary point in the $\Delta\mathcal{H}_{j \neq i}$ contribution

$$\frac{\partial \Delta\mathcal{H}_{j \neq i}}{\partial \lambda_{j \neq i}} = 0 = - \frac{2F_{j \neq i}^2}{(\lambda_{j \neq i} - b_{j \neq i})^3} \left(\lambda_{j \neq i} - \frac{b_{j \neq i}}{2} \right) + \frac{F_{j \neq i}^2}{(\lambda_{j \neq i} - b_{j \neq i})^2} \quad (51)$$

leading to

$$\frac{2 \left(\lambda_{j \neq i} - \frac{b_{j \neq i}}{2} \right)}{\lambda_{j \neq i} - b_{j \neq i}} = 1 \quad (52)$$

Therefore, we have

$$\lambda_{j \neq i} = 0 \quad (53)$$

The choice of $\lambda_{j \neq i} = 0$ reduces our Lagrange approach to exactly the Newton–Raphson method in all $\mathbf{V}_{j \neq i}$ eigendirections, and it is in agreement with our previous condition of $\lambda_{j \neq i} < b_{j \neq i}/2$ for minimization with $b_{j \neq i} > 0$.¹⁴ Note that if we accidentally step outside of the regime where $b_{j \neq i} > 0$, a negative $\lambda_{j \neq i} < b_{j \neq i}$ should be chosen. (This also indicates that the chosen step size in the \mathbf{V}_i eigendirection is too large—so large that we have effectively stepped out of the stream bed and started climbing hills in an orthogonal direction.)

The magnitude of the step size along the \mathbf{V}_i eigendirection is given by

$$h_i^2 = c_i^2 = \frac{F_i^2}{(\lambda_i - b_i)^2} \quad (54)$$

This leads to the condition

$$\lambda_i = b_i \pm \left| \frac{F_i}{c_i} \right| \quad (55)$$

Since $\lambda_i > b_i$ is required for enthalpy maximization with $b_i > 0$, we choose

$$\lambda_i = b_i + \left| \frac{F_i}{c_i} \right| \quad (56)$$

for this case. If $b_i = 0$, we are at an inflection point and can simply take a step along \mathbf{V}_i in the uphill direction.

As we progress up the stream bed, eventually we will pass through an inflection point where b_i becomes negative. The condition for enthalpy maximization with $b_i < 0$ is $\lambda_i > b_i/2$. Since in this case the nearest stationary point is the transition point of interest with exactly one negative eigenvalue b_i , the most efficient choice of Lagrange multiplier is $\lambda_i = 0$, corresponding again to the Newton–Raphson step. Thus in the case of $b_i < 0$, the step size c_i is determined by the Newton–Raphson method.

Finally, we note that the first step from the initial minimum point must follow a different scheme than that given by eq 54 since $F_i = 0$ for all i . In this case, we choose a simple step of magnitude c_i in the \mathbf{V}_i eigendirection. There should be no components of \mathbf{h} in the other $\mathbf{V}_{j \neq i}$ eigendirections since we also have $F_{j \neq i} = 0$ and wish to remain in the stream bed.

6.2. Locating Minima. The steepest descent method fails to find minima in the tortuous enthalpy landscape of a bulk system. Thus, we may modify the above eigenvector-following approach with a different choice of Lagrange multipliers in order to locate minima accurately. To find a minimum, we wish to minimize enthalpy in all eigendirections. Therefore, from eqs 49 and 50 we see that for $b_i > 0$, a choice of $\lambda_i = 0$ ensures enthalpy minimization. For all $b_i < 0$, we require $\lambda_i < b_i/2$. If we assume a step size of c_i in the \mathbf{V}_i direction, then

$$c_i = \left| \frac{F_i}{(\lambda_i - b_i)} \right| \quad (57)$$

Therefore, we choose

$$\lambda_i = b_i - \left| \frac{F_i}{c_i} \right| \quad (58)$$

Finally, if $b_i = 0$, we are at an inflection point. In this case, we can simply take a step along \mathbf{V}_i in the downhill direction. We have found this technique to be much more effective than steepest descent for finding minima in a bulk system.

7. Recursive Algorithm for Mapping the Enthalpy Landscape

A recursive algorithm for mapping an enthalpy landscape using split-step eigenvector-following is given in Figure 2. The actual split-step eigenvector-following technique is executed every time a new minimum or transition point needs to be found. The split-step technique itself is outlined in Figure 1 and executed iteratively according to the following procedure:

1. If finding a transition point, choose the eigendirection of interest to follow. This may be along the parallel or antiparallel directions of the softest mode or along any of the harder modes of interest.

2. Execute a change in the length L of the simulation cell while maintaining constant normalized positions \bar{x}_i . Compute the first and second derivatives of enthalpy with respect to length, F_L and b_L , and choose a Lagrange multiplier according to the criteria put forth in section 6. Change the simulation cell length in three dimensions by the resulting step h_L .

3. Change the atomic positions x_i while maintaining constant L . Compute the gradient \mathbf{g} and Hessian \mathbf{H} , and determine the eigenvalues and normalized eigenvectors of the Hessian matrix. The eigenvectors form the columns of a $3N \times 3N$ unitary matrix

$$\mathbf{U} = (\mathbf{V}_1 \mathbf{V}_2 \cdots \mathbf{V}_{3N}) \quad (59)$$

Compute the vector $\mathbf{F} = \mathbf{U}^T \mathbf{g}$, where

$$\mathbf{F} = \begin{pmatrix} F_1 \\ F_2 \\ \vdots \\ F_{3N} \end{pmatrix} \quad (60)$$

Select the Lagrange multipliers λ_i according to the criteria in section 6 and compute the step vector \mathbf{h}_x . Update the atomic positions accordingly.

4. Repeat steps 2 and 3 until converged at a minimum or transition point. The criteria for convergence are (a) $|F_i| < \epsilon$, where ϵ is chosen to reflect the desired level of precision, and (b) all $b_i > 0$ for a minimum or exactly one $b_i < 0$ for a transition point.

We have implemented this algorithm and tested it for a 64-atom selenium system with periodic boundary conditions using the ab initio potentials of Mauro and Varshneya.¹⁵ The split-step eigenvector-following technique was able to correctly find both minima and transition states in the Se_{64} enthalpy landscape. Two example minima and the connecting transition state are shown in Figure 3. A partial disconnectivity graph of the Se_{64} enthalpy landscape is shown in Figure 4, with labels indicating the molar volumes of the inherent structures and transition states.

The algorithm above is different from that of Middleton and Wales¹² in our choice of Lagrange multipliers. Both our

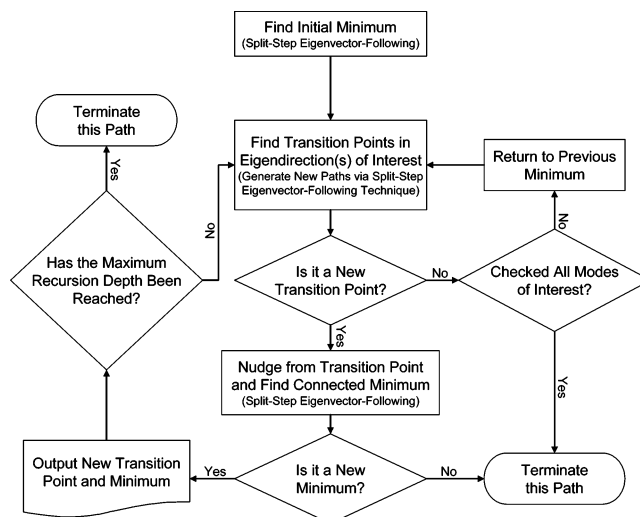


Figure 2. Flowchart of the recursive algorithm for mapping an enthalpy landscape.

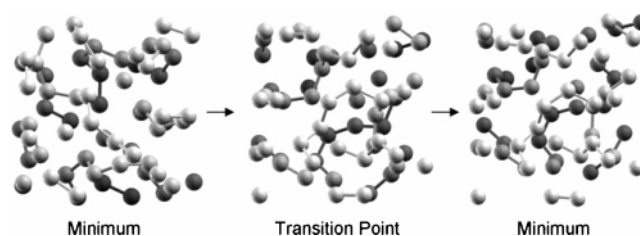


Figure 3. Example minima and transition point in the enthalpy landscape of Se_{64} , assuming periodic boundary conditions.

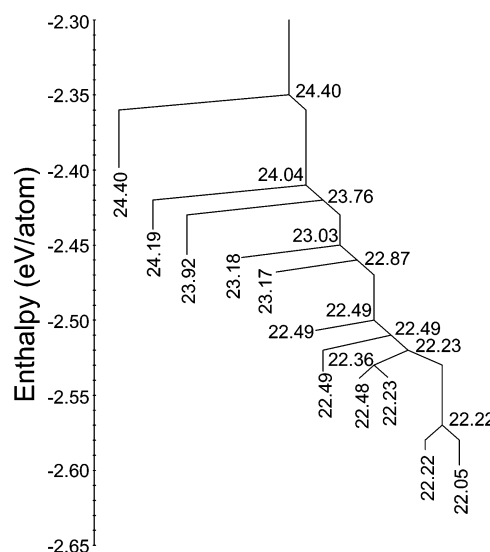


Figure 4. Partial disconnectivity graph for the enthalpy landscape of Se_{64} , assuming periodic boundary conditions. The labels indicate molar volumes of the inherent structures and transition states, in units of cm^3/mol .

approach and that of Middleton and Wales ensure that stationary points meet convergence criteria with respect to length and position coordinates, but our choice of Lagrange multipliers achieves this convergence in roughly 40–50% fewer iterations.¹⁴

8. Conclusions

We have developed a split-step eigenvector-following technique for locating minima and transition points in an enthalpy landscape at absolute zero. Each iteration is split into two steps in order to independently vary the size of the simulation cell

and the relative atomic coordinates. A separate Lagrange multiplier is used for each eigendirection in order to provide maximum flexibility in determining step sizes. This technique is useful for mapping the enthalpy landscapes of bulk systems such as supercooled liquids and glasses.

Acknowledgment. We acknowledge the valuable assistance of David J. Wales, who first suggested this line of study via e-mail. We also acknowledge the assistance and support of Catherine Abbott, Arun K. Varshneya, and Srikanth Raghavan.

References and Notes

- (1) Wales, D. J. *J. Chem. Phys.* **1994**, *101*, 3750–3762.
- (2) Miller, M. A.; Doye, J. P. K.; Wales, D. J. *J. Chem. Phys.* **1999**, *110*, 328–334.
- (3) Murrell, J. N.; Laidler, K. J. *J. Chem. Soc., Faraday Trans. 2* **1968**, *64*, 371–377.
- (4) Wales, D. J. *Energy Landscapes*; Cambridge University Press: Cambridge, 2003.
- (5) Debenedetti, P. G. *Metastable Liquids: Concepts and Principles*; Princeton University Press: Princeton, NJ, 1996.
- (6) Goldstein, M. *J. Chem. Phys.* **1969**, *51*, 3728–3739.
- (7) Stillinger, F. H. *J. Chem. Phys.* **1988**, *88*, 7818–7825.
- (8) Debenedetti, P. G.; Stillinger, F. H.; Truskett, T. M.; Roberts, C. *J. Phys. Chem. B* **1999**, *103*, 7390–7397.
- (9) Debenedetti, P. G.; Stillinger, F. H. *Nature* **2001**, *410*, 259–267.
- (10) Stillinger, F. H.; Debenedetti, P. G. *J. Chem. Phys.* **2002**, *116*, 3353–3361.
- (11) Middleton, T. F.; Wales, D. J. *Phys. Rev. B* **2001**, *64*, 024205.
- (12) Middleton, T. F.; Wales, D. J. *J. Chem. Phys.* **2003**, *118*, 4583–4593.
- (13) Hernández-Rojas, J.; Wales, D. J. *J. Non-Cryst. Solids* **2004**, *336*, 218–222.
- (14) Mauro, J. C.; Loucks, R. J.; Balakrishnan, J. *J. Phys. Chem. A* **2005**, *109*, 9578–9583.
- (15) Mauro, J. C.; Varshneya, A. K. *Phys. Rev. B* **2005**, *71*, 214105.