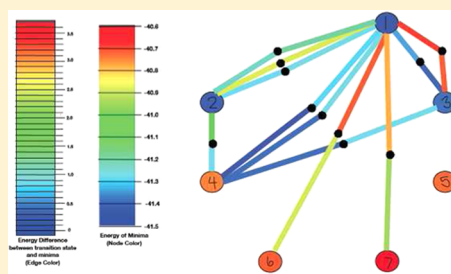


# Enrichment of Network Diagrams for Potential Surfaces

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**ABSTRACT:** Traditional network diagrams connect nodes with simple lines. When one uses them to help interpret complex potential surfaces, that information, the links between minima, is not sufficient to give insights into the dynamics that can occur on those surfaces. Here, we introduce a simple means to introduce more information into the network diagram. Specifically, since each node represents a local potential minimum, the line that links two nodes can be considered a representation of the minimum-energy path between those minima. Then one can add a point along the link, for example, the midpoint, so the link then consists of two segments, one from each minimum to the saddle point of the lowest-energy path connecting them. That makes it possible to represent the energy, at least in terms of energy bands, by coloring each segment from minimum to saddle. We here show examples of such color-coded network diagrams for two illustrative atomic clusters.



## I. INTRODUCTION

One of the frequent uses of network diagrams is its application to complex potential surfaces, the representations of the energy of an array of atoms as a function of the geometric arrangement of those atoms. The nodes of such a diagram represent the local energy minima and the links between nodes denote the link between adjacent minima, that is, minima separated by a single energy saddle. There may, of course, be additional single-saddle pathways between the same minima. However, the network diagram implicitly indicates the lowest-energy pathway. Such diagrams are useful for providing information about how many-atom systems can rearrange and sometimes relax to their lowest minima. However, there is no information in a traditional network diagram concerning the kinetics of rearrangements, isomerizations, or the time scales of passage among the minima. Here we introduce a way to include the key information that governs those kinetic processes, specifically, information regarding the energies of the minima and the energy barriers that separate them. Specifically, we illustrate how to color the links between minima to reveal the approximate heights of the energy barriers between local minima, by coloring each link in two segments. Each segment is a qualitative representation of the path from minimum to *saddle*. That way, the color of each link can indicate the energy difference between a minimum and a specific saddle. Thus, for example, two minima of equal energies connected through a saddle have a link of a single color in the enriched network diagram; minima of different energies and, hence, different minimum-to-saddle energy barriers have a bicolor link in the diagram.

There are more ways to increase the information in network diagrams for potential surfaces. The easiest is probably simply to add an index number to indicate the order in which the local minima occur, starting with the global minimum as “1” and continuing upward in energy from there. Or the energy of each node can be indicated to an approximate extent either by color or by the diameter of a circle representing each node.

This approach shares some characteristics with “disconnection diagrams”,<sup>1,2</sup> also called “lid diagrams”,<sup>3</sup> insofar as these diagrams reveal the energies of minima and the saddles that link them. Disconnection diagrams, however, have somewhat different information about the geometric structure of an energy landscape than does a network diagram. While network diagrams implicitly indicate minimum energy barriers between neighboring minima, they do not distinguish specific pathways between minima when multiple pathways exist. Network diagrams traditionally show pathways linking adjacent minima but do not indicate anything about the barrier heights of those links. Here we are showing a way to enrich the information in a network diagram to exhibit essentially all the content that one would find in a combination of a network and a disconnection diagram.

We show a few examples, none exhaustive of all the minima on a potential surface, but enough to display the method and the content of these enriched illustrations. In particular, we discuss the kinds of insights that this form of diagram reveals uniquely. We present this to open an approach to enriching a visualization device; the final discussion indicates natural directions to explore from here.

## II. 13-ATOM LENNARD-JONES CLUSTER

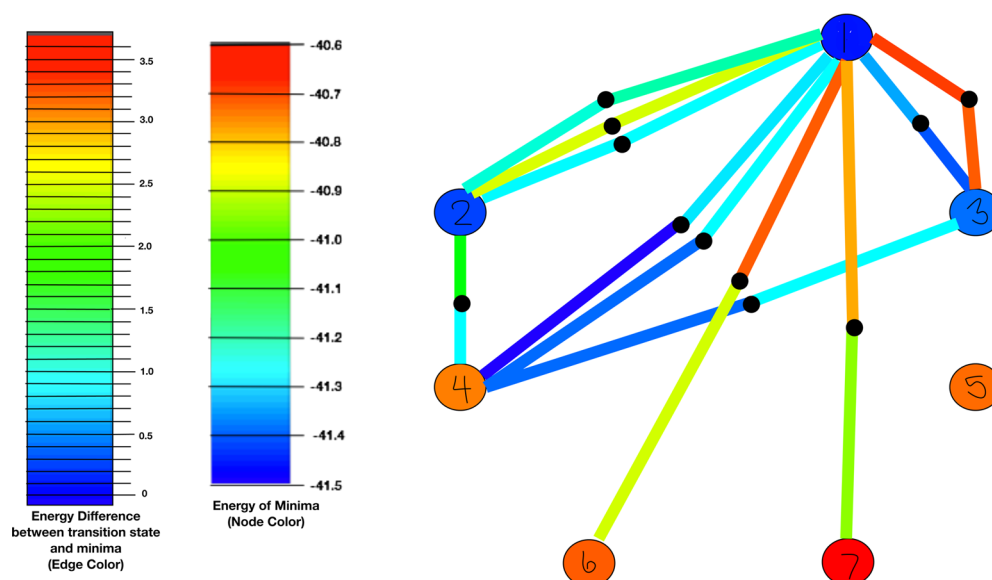
The cluster of 13 rare gas atoms, for example, Ar<sub>13</sub>, and its frequent model of 13 atoms bound by pairwise Lennard-Jones potentials, has long been recognized as a paragon model for systems exhibiting the stability associated with closed-shell structures. The rare gas clusters and their “L-J” models exhibit icosahedral geometries in their lowest-energy forms, with a few

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## Lowest 7 Minima of Lennard-Jones 13-Atom Cluster



**Figure 1.** Enhanced network for the lowest seven local minima of the 13-atom cluster bound by Lennard–Jones pairwise potentials. Energy units are the scale parameter  $\epsilon$  of the Lennard–Jones potential.

exceptions, such as the 38- and 75-atom systems.<sup>4</sup> Consequently, the clusters with closed-shell icosahedra show exceptional stability, and the binding energy per atom is higher for those closed-shell structures, with 13, 55, ..., atoms.

Here, we show in Figure 1 our first example, an “enriched” network diagram for the seven lowest-energy minima of the 13-atom cluster with Lennard–Jones pairwise interactions,  $LJ_{13}$ . The energies of the minima are indicated by the right-hand color scale, with the global minimum, #1, at the top, in darkest blue, minimum 2 at left in almost as dark blue, minimum 3 at the right, also blue, and minima 4 through 7 below. The links are also color-coded, but all in two segments. Each segment represents the path from a minimum to the saddle along a specific pathway to another minimum. The color scale at the left indicates the energy separation between the minimum and the saddle to which it connects. Hence, a blue link indicates that the minimum and saddle it connects have very similar energies, so that energy barrier is easily reached. An orange or red link indicates that the saddle has an energy much higher than the minimum. The saddle positions are arbitrarily placed at the midpoints of the links; it would be possible to include more information by placing the saddle positions to indicate relative distances from the minima, for example, or, as one reviewer suggests, at a position indicating the relative rates of forward and backward passages at a specific temperature. Alternatively, as another reviewer suggests, the nodes could be located at positions indicating the relative distances between nodes and saddles, as measured by principal coordinates.

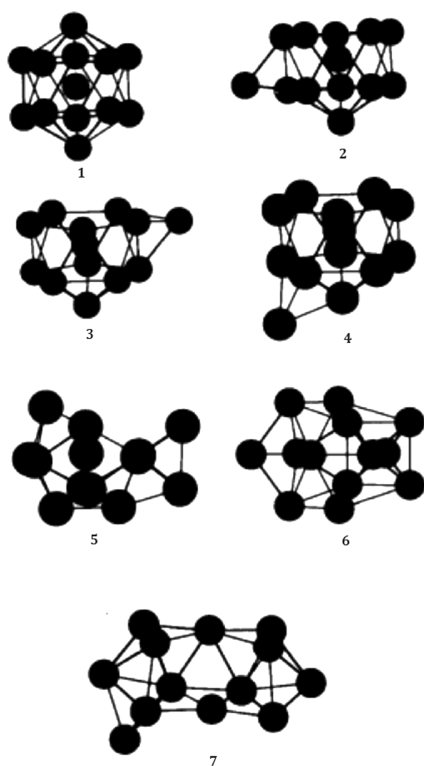
In some cases, there is only one direct pathway between two minima, as in the case of the link between minimum 1 and minimum 6, while minima 1 and 2 are linked by three separate pathways, all fairly symmetrical, as the similarity of colors on both sides of each link indicates. Minima 1 through 4 are fairly strongly interconnected, but minima 6 and 7 link only to minimum 1 among those shown in this set. Moreover, minimum 5 has no direct connection to any of the others of the seven lowest-energy structures.

It is just this kind of information that an “enriched” network diagram can provide. The disconnection diagram shows the lowest-energy barrier but not the multiplicity of pathways. The “enriched” network diagram is related to but goes beyond the information in disconnection diagrams by including more topography-specific information and, hence, additional semi-quantitative insight into kinetic mechanisms and dynamics. For example, we can infer from Figure 1 that, at temperatures that just allow isomerization, we can expect to see minima 3 and 4 more populated than minimum 2, despite their being at higher energies. Minimum 2 is simply less kinetically accessible than the next two in energy. However, at somewhat higher temperatures, the fact that there are three direct paths between minima 1 and 2 indicates that when isomerization between these two does occur, it can be expected to be facile. We know that when multiple pathways are accessible at sufficiently high temperature  $T$ , the kinetics deviates from the traditional rate dependence of transition state theory,<sup>5</sup> and the effective rate constant  $k$  increases beyond the classical proportionality between  $\log k$  and  $1/T$ .<sup>6</sup>

The geometric structures of those seven lowest-energy local minima were among those found by Wales and Berry;<sup>7</sup> they are reproduced in Figure 2. All can be related to the icosahedron that constitutes the global minimum, although minima 5, 6, and 7 are not so readily recognizable as such.

### III. WATER OCTAMER

We move to a more complex system, the cluster of eight water molecules,  $(H_2O)_8$ , represented by a TIP4P potential.<sup>8</sup> There are of course many simulations of water clusters, based on various interaction potentials. One example using TIP4P, from which we drew our diagram is the work of Wales and Hodges.<sup>9</sup> Figure 3 is the enhanced network diagram showing the lowest 16 local minima for this system. Note that only five of those minima have direct links between them and that the lowest minimum is not one of those five. Roughly, minima 1 and 2 lie rather deep on the potential energy surface; minima 3 through



**Figure 2.** Seven lowest-energy structures of  $LJ_{13}$ .

8 are somewhat higher, minimum 9 is higher still, and minima 10 through 16 are at the top of the energy scale of the figure.

Because this system is considerably more complex than the  $LJ_{13}$  cluster, it is not surprising that there are far fewer links directly connecting the low-lying minima of the water octamer. Hence, we can expect clusters of water molecules to exhibit a variety of structures, for example, in a mass-selected molecular beam, in this octamer case at least two, in contrast to the single icosahedron that we can expect for  $LJ_{13}$ .

## IV. SUMMARY AND CONCLUSIONS

By incorporating some of the semiquantitative information regarding a complex potential surface into a limited network diagram representing some of that surface, we can reveal useful insights into the kinetics and dynamics that the system of interest can exhibit. We can recognize pathways between specific local minima and see whether each pathway is steep or relatively flat and whether it is symmetric or very asymmetric. We can see whether multiple pathways link two connected minima and, from the heights of the upper pathways, get a sense of the energy or temperature range at which the kinetics linking those minima will deviate from transition state theory of Arrhenius.<sup>5</sup>

This approach does not attempt to express quantitatively how multiple pathways between nodes would affect the temperature dependence of rates; it merely indicates the existence of multiple direct pathways and their barrier heights. In that sense, it does not address the role of free energies of excitation, as addressed by Krivov and Karplus.<sup>10</sup>

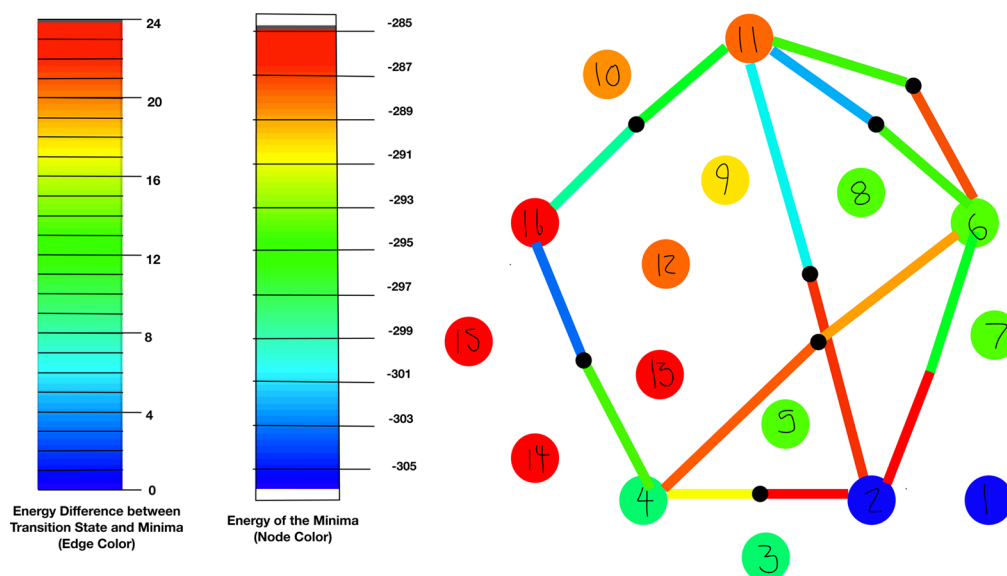
It remains to be seen how much information we would want to include in such diagrams. For example, would it be useful to include 10 or 30 minima, hence, 10 or 30 nodes, in a representation of a cluster of, say, 13 atoms? Clearly one would not want to construct an enhanced diagram for 100 minima. Closely related is the question of how large a system would be usefully described by an enhanced network diagram. One might, for example, want to determine how many nodes would have to be included in order to estimate the number of minima that could be connected, via multiple intermediate minima, to the global minimum, given a temperature or energy of the system. We shall not try to answer these questions here, but merely raise them. They are the challenges that one now faces if one wishes to apply “enriched network diagrams”.

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### Lowest 16 Minima of TIP4P Water Octamer



**Figure 3.** Enhanced network for the lowest 16 local minima of the water octamer, represented by the TIP4P potential. Energy units are kJ/mol.

## Notes

The authors declare no competing financial interest.

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