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Monte Carlo Studies of Motions in Molecular Crystals

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Computer simulations of thermal motions in molecular solids have been made using a Monte Carlo MC program. Certain results of the simulations are best shown by means of computer movies, as will be noted when appropriate. Problems studied to date which will be emphasized here are: relaxation around porphyrin substitutional defects and vacancy defects in *n*-octane matrices, rotational motions in solid benzene[1] and growth of benzene microcrystals.

The MC technique[2] does not provide a true time history of a system, but rather, it yields a Markov chain of configurations which are reasonably close in phase space and have the proper Boltzmann distribution. Thus the sequence is primarily designed to obtain ensemble averages of physical quantities.

Nevertheless, studies of a sequence of configurations can give an indication of the likely course of a real event even though the sequence itself does not correspond precisely to a real time event. Such studies can be used to investigate relaxation phenomena or to search for stable or metastable configurations. In particular, the end result of a long enough MC calculation at 0 K will always be a configuration which is at least a local minimum in the potential energy.

This has proved to be a productive way to use the MC program, because direct calculation of statistical quantities is difficult due to the computer time requirements for evaluating intramolecular interactions during a run long enough to be statistically significant. In addition, computer movies made from a sequence of Monte Carlo configurations have been found to be a very efficient way of extracting information about dynamical phenomena from the numerical results.

The intermolecular interactions are modeled by the well known atom–atom potential[3] method. For phenomena which are primarily steric, the particular choice of potential parameters is not too important. The molecular geometry was taken from x-ray data[4–5] except that the C—H bond lengths were set to 1.08 Å to agree with the length used in the determination of the parameters. The nitrogens were treated according to the suggestion of Fyfe and Harold-Smith.[6] The rigid molecule approximation was also used, which might be questionable in the case of the *n*-octane molecules. However, a justification for this will be given later.

More details about the problems mentioned earlier follow:

Porphyrin substitution defects in n-*octane matrices.* There is much information available about the orientation of porphyrin substitutional defects (Shpolskii sites) in *n*-alkane hosts from the work of van der Waals and collaborators.[7,8] In *n*-octane, there are two prominent sites, called the *A* site and the *B* site, whose orientations have been determined by ESR measurements. There is other information about these sites, which will be mentioned later. However, direct information about whether the porphyrins displace two or three *n*-octanes is not available, although space filling models provide some guidance. An atom–atom potential calculation should be able to determine this point more reliably and, in turn, comparison of theoretical and experimental orientational information will be a good check on the reliability of the potential model for calculating the structure of defect sites.

From simple size considerations, it appeared that the most likely defect structures would be a porphyrin molecule substituted for two or three *n*-octane molecules which were neighbors along the crystallographic *a* or *b* axes. In the calculations, such sites were first established and the porphyrin was oriented in such a way that the overlap between it and any matrix molecules was not too great. Then a 1000 step MC run at 0 K in which only the porphyrin was allowed to move was performed. This was followed by a run in which the porphyrin and all of its nearest neighbors could move. The net effect was as though this group of molecules was allowed to relax in an infinite, frozen *n*-octane matrix. The calculations were carried through essentially to completion for orientations which appeared to be true minima, they were terminated much earlier for orientations which were obviously not optimal.

Several orientations in two or three molecule defects along the crystal *a* and *b* axes were tried. Three possibilities for sites were found as follows.

There was a unique choice for the *A* site—one in which the porphyrin was almost, but not exactly, oriented with its plane in the *b–c* crystal plane with the molecular direction $x + y$ of Ref. 7 being parallel to the long axis of the octane chains. The molecular *z*-axis made an angle of 28° with the crystal *a*-axis, which agrees with ESR data.[8]

For the *B* site, two possibilities were found. Both were three molecule vacancies along the crystallographic *a* axis. The optimum was one in which the porphyrin was exactly in the crystal *a*–*c* plane with the molecular $x + y$ direction oriented as above. This also agrees with ESR data. The other site *b'* was about 400 K higher in energy than the optimum one. This seems like quite a bit, but energy changes of greater magnitude were found during the relaxations and energies of the discarded sites were several thousands of degrees higher. The *B* site was carried into the *B'* site by a rotation of the porphyrin about its *z* axis by about 45° followed by a rotation about an axis through the center of the molecule and parallel to the long *n*-octane axis by about 10°.

The defect models which result from this calculation provide a pleasing, intuitive explanation for several other experimental observations. The two vacancy *A* site is a tighter fit than the three vacancy *B* site so its librational frequencies should be higher. The theoretical values are of 50 cm^{-1} and 25 cm^{-1} respectively for the lowest librational modes. Experimentally,[9] the values are 34 cm^{-1} and 17 cm^{-1}. The agreement in magnitude is satisfactory and the trend is quite good. The *A* site is thermodynamically stable both theoretically and experimentally.[9] Even though the B site is a tighter fit than the *A*, both are quite good and the binding energies of the porphyrin to the matrix are similar for both. However, the additional binding energy of one whole *n*-octane molecule is lost in going from a two to a three molecule vacancy and the latter, with or without the substituted porphyrin, is much higher in energy. It is also observed[9] that the spectral lines for the *B* site are slightly narrower than for the *A* site. This effect is also consistent with the model, as will be discussed in the following section.

Relaxation around a vacancy defect related to the Shpolskii effect in crystalline n-*octane*. One of the motivations behind the experimental study of this system is that it exhibits the Shpolskii effect: the spectral lines of the guest molecule are narrow and well defined, which indicates a weak coupling of it to the host lattice. Here, early in the course of the porphyrin substitutional defect work it was noted that the *n*-octane matrix did not relax very much around the defect. This was still true after long relaxation runs for the *A*, *B* and *B'* sites; the maximum center of mass displacement of an octane was less than 0.2 Å for an *A* site and 0.1 Å for a *B* site.

Thus one is lead to a hypothesis that vacancy defects in this system might be quite stable because of a very interlocking form of crystal packing which becomes apparent in stereographic projections. If so, such defects could provide non-collapsible cages for substitutional defects and the latter could reside in the lattice without interacting too strongly with it. This would be a possible explanation of the Shpolskii effect in this matrix.

So far one study at 0 K has given very little relaxation around a two molecule vacancy defect oriented in the *b* direction. Based on experience with the substitutional defect calculations, it is unlikely that much relaxation will occur in similarly structured vacancy defects. Nevertheless, calculations to test this will be performed.

In addition to being stable against collapse, the vacancy cages have another feature which supports the experimental Shpolskii effect observations: the cage is large enough so that the carbon skeleton of the porphyrin is farther away from the matrix than a typical interplanar spacing in aromatic crystals. Thus the π-orbital system of the porphyrin should be somewhat shielded from matrix effects. Here, the *A* site should be less shielded than the *B* site and, in accord with this line of reasoning, its spectral line should be broader. This is in agreement with experiment, as noted previously.

Rotational motions in solid benzene. Here, the motivation was to see if a well defined mechanism was responsible for the rotation. After an extensive search, no specific mechanism was found, indicating that the rotations are thermally stimulated, random, unlikely events. In particular, no evidence of cooperativity between the motions of a rotating molecule and its neighbors was found.

The search was facilitated by a computer movie of four rotational events in a run at 200 K. The temperature was dictated by the technical requirements of the MC calculation and is not immediately connected with the temperature at which rotation would begin to be observed in an NMR experiment. Here, the temperature had to be high enough so a rotation was at least probable during a reasonable length computer run in the small (64 molecule) crystal that was used and low enough so general thermal motion did not obscure the mechanism that was sought.

It was found that, during a rotation, there was a concentration of energy in the rotating molecule and a particular set of four nearest neighbors. It was possible to extract a dynamical rotational barrier for this packet whose height was consistent with previous static calculations[10] in being of the same general shape and somewhat lower.

Growth of benzene microcrystals. Eight to sixteen benzene molecules were spatially and rotationally oriented at random with a mean spacing of about 20 Å. They were allowed to come together at 0 K so that a minimum or metastable state was reached. Some interesting orientational effects during the formation of dimers, trimers and tetramers were found, although clusters which would give some ab initio hint about the true crystal have not been seen. These effects also are best illustrated by a computer movie.

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