Asymmetric coexistence curves in an exactly-solvable model of binary liquid mixtures

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Abstract – An exactly-solvable lattice-gas model for binary liquid mixtures is proposed which describes not only complex miscibility effects, such as closed-loop phase diagrams, but also asymmetry in the coexistence curves. A key feature of the model is the inclusion of lattice vacancies, allowing density fluctuations in the system. In fact, density fluctuations are found to be essential if the asymmetries in the underlying microscopic interactions are to be expressed in the coexistence curves. The phase diagrams that result from this model are in accord with the qualitative features observed experimentally, and also indicate that other more novel forms of the coexistence curves await discovery.

INTRODUCTION

All binary liquid mixtures display coexistence curves that have at least some degree of asymmetry under interchange of the two components, a reflection of underlying microscopic differences in the component molecules. Even so, both theory and experiment (ref. 1) show that the critical solution points of binary liquid mixtures are in the same universality class as the simple, symmetric Ising ferromagnet, which thus serves as a suitable starting point in studying such systems. With the addition of further degrees of freedom and further interactions to the basic Ising model, such as orientation-dependent bonding, many of the complexities of real mixtures may be understood, including such novel phenomena as closed-loop phase diagrams. Incorporating asymmetry in such a model description, however, has proven to be a much more challenging task.

Recent theories for complex miscibility behavior in binary mixtures have included calculations using decorated-lattice models (refs. 2 and 3), position-space renormalization-group theory (ref. 4), and partial-trace approximations (ref. 5). As successful as the above models and calculations have been, they all share the drawback of having phase diagrams that are perfectly symmetric about concentration one half. The problem in each case is with the model itself, rather than with the means of calculation. In fact, these models may be extended to encompass asymmetric phase diagrams by simply incorporating density fluctuations in the system, as has been demonstrated using the partial-trace approximation (ref. 6). It is the purpose of this paper to show that asymmetry via density fluctuations may also be obtained without resorting to approximation methods at all, by using an exactly–solvable lattice model presented below.

ISING MODEL REPRESENTATION FOR BINARY LIQUID MIXTURES

In the simplest case, a binary liquid mixture may be represented by an Ising lattice-gas model, defined by the Hamiltonian

$$-\beta H_I = K_I \sum_{<ij>} s_i s_j + H_I \sum_i s_i \, , \tag{1}$$

where $s_i = \pm 1$, the first sum is over all nearest neighbors on the lattice, and the second sum is over all lattice sites. With the usual mixture-magnet correspondence the two values of s_i are identified with the two components, A and B, of the mixture, K_I represents the difference in van der Waals interaction between like and unlike molecules, and H_I is directly related to the chemical potential difference between the components. Note that with this model the energy of interaction for an AA nearest-neighbor pair ($s_i = +1$, $s_j = +1$) is the same as that for a BB nearest-neighbor pair ($s_i = -1$, $s_j = -1$), so that the two types of molecules are handled symmetrically.

To produce an asymmetric model it would seem only natural that one simply let the two energies mentioned above be different; that is, define E_{AA} to be different from E_{BB}. In terms of the model, this is accomplished by including an additional magnetic field, H, with a nonzero value. The problem is that to obtain coexistence it is necessary that the total magnetic field in the system be zero, thus one must set $H_I = -H$. This completely undoes the asymmetry inherent originally in $E_{AA} \neq E_{BB}$, and the resultant phase diagram is symmetric as before. The net effect has simply been a shift in the coexistence condition from $H_I = 0$ to $H_I = -H$.

LATTICE-GAS MODEL WITH BONDING INTERACTIONS

A reasonable way to extend the Ising model description given above, with the possibility of achieving asymmetry, is to introduce additional degrees of freedom in the model. For example, many binary mixtures have molecules that can hydrogen bond to one another, depending on whether the two molecules in question have the correct relative orientation. This possibility may be modeled with orientational degrees of freedom, σ_i, associated with each site of

the lattice gas. Now in reality a molecule's orientation is continuous, just as is its position in space, but just as space is partitioned into discrete cells in a lattice-gas model, imagine partitioning the solid angle surrounding a molecule into "cells" of solid angle. Each solid angle cell will be roughly the size of the solid angle associated with hydrogen bonding. Since hydrogen bonds have an angular width of roughly 10° (ref. 7), the solid angle surrounding a given molecule should be divided into something on the order of 500 cells. Thus, let $\sigma_i = 1, 2, 3, ..., q$, with $q \sim 500$.

A model designed along these lines is

$$-\beta H = \sum_{<ij>} \left[K_1(1 - \delta_{s_i s_j})\delta_{\sigma_i \sigma_j} + K_2(1 - \delta_{s_i s_j})(1 - \delta_{\sigma_i \sigma_j}) \right] , \tag{2}$$

which was first studied by Walker and Vause (ref. 4), and shown to agree well with experiments on closed-loop phase diagrams with $q = 500$. Note first that the zero of interaction is taken to be the energy associated with nearest-neighbor molecules of the same type, that is, $s_i = s_j$. Next, if unlike molecules are nearest neighbors, they may either bond or not depending on their relative orientation. This is taken into account by assigning $\sigma_i = \sigma_j$ as the condition for correct orientations, and $\sigma_i \neq \sigma_j$ corresponding to any other orientations. Thus K_1 is the energy of bonding, and K_2 is the energy associated with nonbonding.

The above model has been studied with position-space renormalization-group methods, but an exact solution is not possible. A very similar model, however, may be solved exactly. Consider the following Hamiltonian

$$-\beta H_S = \sum_{<ij>} V_{ij}^S , \tag{3}$$

where

$$V_{ij}^S = K_1(1 - \delta_{s_i s_j})P(\sigma_{ij}) + K_2(1 - \delta_{s_i s_j})(1 - P(\sigma_{ij})) + K_3 \delta_{s_i s_j} P(\sigma_{ij}) , \tag{4}$$

and

$$P(\sigma_{ij}) = \sum_{k=1}^{q} \delta_{\sigma_{ij}, k} \tag{5}$$

with $\sigma_{ij} = 1, 2, 3, ..., q^2$. This interaction potential is symmetric since it treats the two components the same, hence the sub- and superscripts S, and it also allows for bonding between like molecules with the K_3 term. The really new features here, however, are the bond variables σ_{ij} which replace the site variables σ_i and σ_j in equation (2), and the projection operator $P(\sigma_{ij})$ which is unity (zero) for bonding (nonbonding) relative orientations. Note that the q^2 values of σ_{ij} correspond to the q^2 orientations originally associated with σ_i and σ_j .

This model can be solved exactly because each bond variable is independent of all other bond variables on the lattice, and hence the σ_{ij} may be summed over without approximation, mapping the model onto the three-dimensional Ising model, for which exact results are known. Note that this is not possible with the site variables σ_i in equation (2) since these variables interact directly with one another. Another way of saying this is that equation (3) defines a decorated lattice model, where the bonds are decorated with the variables σ_{ij}. In typical decorated models (ref. 2) the bonds are decorated with both the Ising and orientational variables, which means that some Ising variables are treated differently than others. Here this is not the case. Each Ising variable occupies a lattice site, and the decorated bonds carry only information regarding the relative orientations associated with the sites they connect.

The model just described is similar to that studied by Huckaby (ref. 3). Furthermore, it can be shown (ref. 8) that the exact solution to the decorated-lattice model of equation (3) is precisely the same as the partial-trace approximation to the Hamiltonian of equation (2). Clearly then, given the success of the partial-trace approximations (ref. 5), this model provides a good starting point for further exact studies.

Asymmetric interactions

It is now of interest to explore asymmetry within the richer context provided by the inclusion of bonding interactions. In particular, consider the following asymmetric interaction potential

$$V_{ij}^A = \frac{1}{2} h_1(s_i + s_j)P(\sigma_{ij}) + \frac{1}{2} h_2(s_i + s_j)(1 - P(\sigma_{ij})) , \tag{6}$$

where again $P(\sigma_{ij})$ is the bonding projection operator, and where the s_i are taken to be ± 1. From this expression it is clear that h_1 is the energy splitting between AA and BB nearest-neighbor bonding pairs, and similarly, that h_2 is the energy splitting for AA and BB nonbonding nearest-neighbor pairs. With an asymmetric Hamiltonian defined by

$$-\beta H_A = \sum_{<ij>} V_{ij}^A , \tag{7}$$

the full Hamiltonian of interest is

$$-\beta H = -\beta H_S - \beta H_A . \tag{8}$$

Notice that in this model the asymmetric effects depend on temperature, since the amount of bonding in the system varies as the temperature is changed. As a result, it is certainly not the case that the condition for coexistence is simply shifted to a different value of the magnetic field, as happened with the simple Ising model, but rather the magnetic field must vary dynamically with temperature. In spite of this, the phase diagrams are still completely symmetric. We find that by satisfying the condition for coexistence, we at the same time force the system back to a symmetric condition–the parameter space we are working in is simply not large enough to permit coexistence and asymmetry to be specified separately. The only possible solution lies in enlarging the parameter space to include features of the system other than just bonding.

EXACTLY SOLVABLE LATTICE-GAS MODEL WITH ASYMMETRIC COEXISTENCE CURVES

In looking more carefully at the lattice models described above one oversimplification is immediately evident; namely, all lattice sites are occupied so that the system always has the same density, even as temperature is varied. Since the density clearly should vary, it is reasonable on physical grounds to include vacancies in the lattice models. Though lattice vacancies by themselves have nothing to do with asymmetry–that is, the vacancies are not placed preferentially near one type of molecule or the other, the presence of vacancies allows additional flexibility in the system permitting the underlying microscopic asymmetry to be expressed.

Lattice vacancies

To include lattice vacancies in the description of the system a new variable must be introduced in the Hamiltonian. We choose to associate this variable with the bonds, in a fashion similar to that described for σ_{ij}, so that the model is still of the decorated-lattice type and hence exactly solvable in terms of the known results for the three-dimensional Ising model. Let the variable describing vacancies be T_{ij}, with ij denoting the bond connecting sites i and j. T_{ij} must assume four values, corresponding to the following four conditions: site i empty and site j occupied; both sites empty; site i occupied and site j empty; both sites occupied. The values of T_{ij} for these four conditions are defined to be $T_{ij} = -1, 0, 1,$ and 2, respectively.

The Hamiltonian describing the system will include the terms given in the previous section when both sites associated with a bond are occupied ($T_{ij} = 2$). On the other hand, if either site is empty ($T_{ij} = -1, 1$), or if both sites are empty ($T_{ij} = 0$), then the interactions of the previous section do not occur at all. This may be obtained by writing the interactions in the form

$$\left[V_{ij}^S + V_{ij}^A \right]\left[\tfrac{1}{6} T_{ij}\left(T_{ij}^2 - 1\right) \right] .$$ (9)

Note that the second square bracket vanishes for $T_{ij} = -1, 0,$ and 1, and gives unity for $T_{ij} = 2$, as desired.

Similar consideration apply to magnetic field terms. That is, if only site i is occupied then only it contributes to the Hamiltonian, if both sites are occupied they both contribute, and so on. Thus, the Hamiltonian contains the terms

$$h\ s_i\left[\left(-\tfrac{1}{6}\right)T_{ij}\left(2T_{ij}^2 - 3T_{ij} - 5\right)\right] + h\ s_j\left[\tfrac{1}{2} T_{ij}(T_{ij} - 1)\right] .$$ (10)

Finally, there must be a term in the Hamiltonian determining the energy difference Δ associated with the presence of a vacancy. This term must give 2Δ if both sites are occupied, Δ if only one site is occupied, and zero if neither site is occupied. All these conditions are satisfied by the expression

$$\Delta\left[\left(-\tfrac{1}{3}\right) T_{ij}\left(T_{ij}^2 - 3T_{ij} - 1\right)\right] .$$ (11)

Putting this together results in the total Hamiltonian for our exactly-solvable model

$$-\beta H = \sum_{<ij>} \left\{ \left[V_{ij}^S + V_{ij}^A \right]\left[\tfrac{1}{6} T_{ij}\left(T_{ij}^2 - 1\right) \right] + h\ s_i\left[\left(-\tfrac{1}{6}\right)T_{ij}\left(2T_{ij}^2 - 3T_{ij} - 5\right)\right] + h\ s_j\left[\tfrac{1}{2} T_{ij}(T_{ij} - 1)\right] \right\}$$

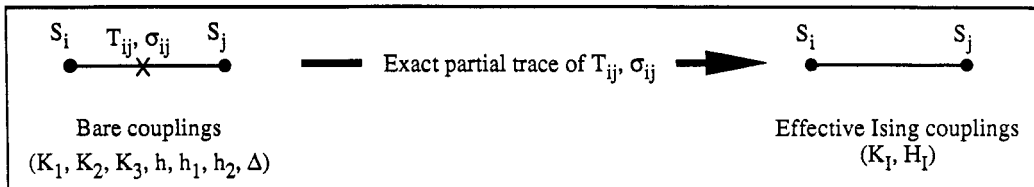$$+ \sum_{<ij>} \Delta\left[\left(-\tfrac{1}{3}\right) T_{ij}\left(T_{ij}^2 - 3T_{ij} - 1\right)\right] .$$ (12)

Figure 1 – Schematic representation of the exact transformation used to study the model defined by equation (12). The variables T_{ij} and σ_{ij} are associated with the bond connecting sites i and j, and since they interact with no other bond variables, may be summed over exactly.

Exact calculation

As illustrated in figure 1, the calculation now takes on the form of an exact trace over the T_{ij} and σ_{ij} variables for each bond, in the process generating effective Ising couplings between the Ising variables that still remain on every site. Since each bond is handled separately the transformation is really quite straightforward. In fact, the details are essentially the same as for the calculations already given in reference 5, and thus they will not be repeated here.

Briefly, the results are that the reduced free energy per site of the model defined by equation (12), $f = -\beta F/N$, is given by

$$f(\{J_i\}) = g(\{J_i\}) + f_I(K_I(\{J_i\}),\ H_I(\{J_i\})) ,$$ (13)

where $\{J_i\}$ refers to the set of couplings $(K_1, K_2, K_3, h, h_1, h_2, \Delta)$, g is an analytic function of the couplings, and K_I and H_I are the effective Ising coupling and magnetic field which enter into the free energy per site of the Ising model, f_I. The coexistence condition, of course, is simply that $H_I = 0$, and this condition determines the magnetic field h in terms of the other microscopic interactions. To obtain the phase diagram it is necessary to compute the mole fraction of A molecules–that is, the concentration–for both the left-hand (–) and right-hand (+) branches of the coexistence curves. This is obtained from $x_\pm = (1 \pm m)/2$, where $m = <s_i> = \partial f/\partial h$. Using the above relation this becomes

$$x_\pm = \tfrac{1}{2}\left[1 + \left(\partial g/\partial h + e_I \partial K_I/\partial h \pm m_I \partial H_I/\partial h\right)_{coex} \right] .$$ (14)

In the above, $e_I = \partial f_I/\partial K_I$ is the nearest-neighbor correlation and $m_I = \partial f_I/\partial H_I$ is the magnetization of the three-dimensional Ising model in the limit $H_I \rightarrow 0^+$. Results for these quantities may be found in the work of Scesney (ref. 9).

To complete the calculation, we note that

$$K_I = \frac{1}{4} \ln\left(\frac{Z_{+\,+}Z_{-\,-}}{Z_{+\,-}^2}\right) \;,\;\; H_I = \frac{1}{4} \ln\left(\frac{Z_{+\,+}}{Z_{-\,-}}\right)$$

$$g = \frac{1}{4}\ln(Z_{+\,+}Z_{-\,-}) - dK_I + \Delta \;, \tag{15}$$

where d is the dimension of the hypercubic lattice on which the model is defined (in the present case, of course, $d = 3$) and the Z's are partial partition functions defined as follows:

$$Z_{+\,+} = qe^{K_3 + h_1 + 2h + 2\Delta} + q(q-1)e^{h_2 + 2h + 2\Delta} + 2q^2e^{h+\Delta} + q^2$$

$$Z_{-\,-} = qe^{K_3 - h_1 - 2h + 2\Delta} + q(q-1)e^{-h_2 - 2h + 2\Delta} + 2q^2e^{-h+\Delta} + q^2$$

$$Z_{+\,-} = qe^{K_1 + 2\Delta} + q(q-1)e^{K_2 + 2\Delta} + q^2e^{h+\Delta} + q^2e^{-h+\Delta} + q^2 \;. \tag{16}$$

RESULTS

Figures 2 through 4 show typical results from this model. In particular, fig. 2(a) shows an asymmetric closed loop above an ordinary miscibility dome. The dashed line shows the diameter; that is, the average of the concentration of the left–hand and right–hand branches of the coexistence curve. In fig. 2(b) the magnetic field h required for coexistence is shown as a function of temperature. The circles on the curve show the locations of the three critical solution points. In a system such as this the concentration of vacancies is increasing with temperature, thus the density is decreasing as one would expect. With vacancies increasingly prevalent in the system the underlying microscopic asymmetries become more evident. At low temperature, with few vacancies but the same asymmetric interactions, the system is almost perfectly symmetric.
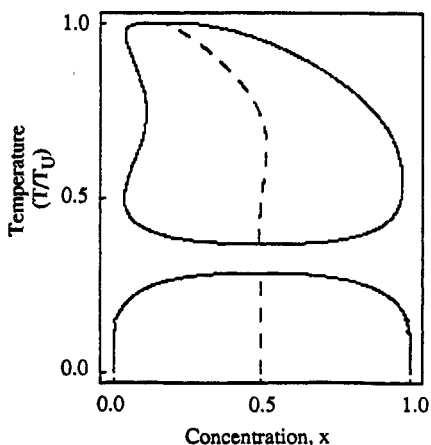

Figure 2(a) – Temperature $(-1/K_2)$ versus concentration phase diagram for the model of equation (12), with $-K_1/K_2 = 4.86$, $-K_3/K_2 = 5$, $-h_1/K_2 = 0.85$, $-h_2/K_2 = 1.75$, $-\Delta/K_2 = 1$, and $q = 500$. The temperature scale is normalized by the temperature of the upper critical solution point. Note that the asymmetry is much more evident at higher temperatures, due to the increased concentration of vacancies.
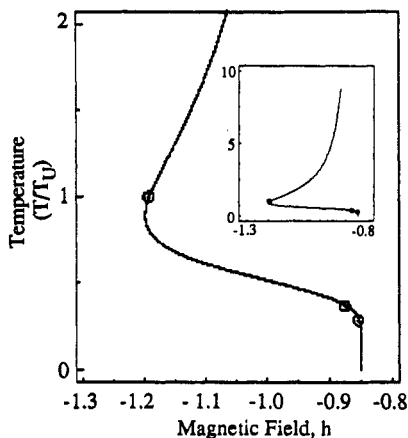

Figure 2(b) – Magnetic field h required for coexistence, as a function of temperature, for the system shown in figure 2(a). The circles indicate critical solution points.

Figure 3(a) and 3(b) show two phase diagrams that form a sequence leading to the diagram of fig.2. In particular, as the bonding between unlike molecules is made more favorable the miscibility dome pinches in, finally breaking off to allow a region of intermediate-temperature miscibility as in fig.2.
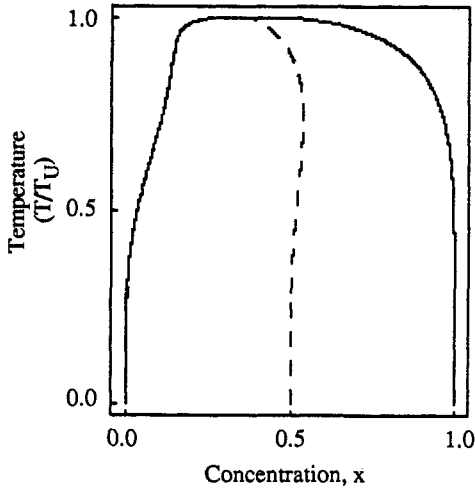
Figure 3(a) – Temperature $(-1/K_2)$ versus concentration phase diagram for the model of equation (12), with $-K_1/K_2 = 4.8$, $-K_3/K_2 = 5$, $-h_1/K_2 = 5$, $-h_2/K_2 = 0.3$, $-\Delta/K_2 = 1$, and $q = 500$. The temperature scale is normalized by the temperature of the upper critical solution point. This is an example of asymmetry in an otherwise ordinary miscibility dome.
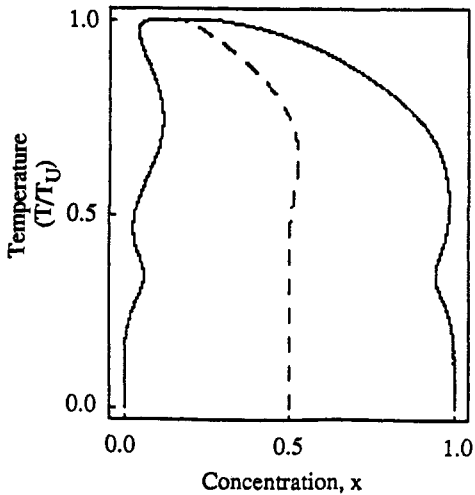

Figure 3(b) – Temperature $(-1/K_2)$ versus concentration phase diagram for the model of equation (12), with $-K_1/K_2 = 4.8$, $-K_3/K_2 = 5$, $-h_1/K_2 = 0.85$, $-h_2/K_2 = 1.75$, $-\Delta/K_2 = 1$, and $q = 500$. The temperature scale is normalized by the temperature of the upper critical solution point. In this case like-molecule bonding is causing the miscibility dome to "pinch in". With stronger like-molecule bonding the phase diagram would be like that shown in fig. 2(a).

In fig. 4 the unlike molecule bonding is energetically more favorable than the like molecule bonding, thus at low temperature the system is miscible. These figures show results that are very similar to phase diagrams seen in experimental systems. In fig. 4(a) the phase diagram bows out toward the high concentration side, whereas in fig. 4(b) the closed loop is almost symmetric about its center line, but it has been translated toward low concentrations.
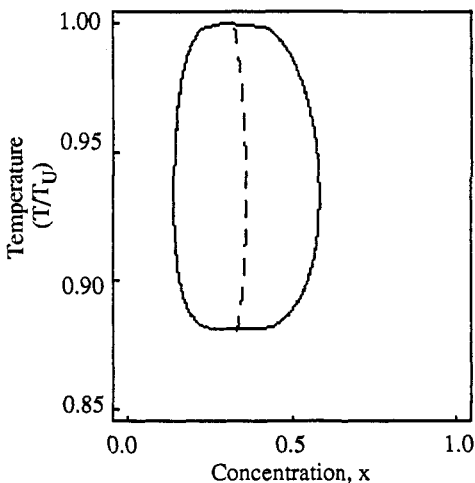

Figure 4(a) – Temperature $(-1/K_2)$ versus concentration phase diagram for the model of equation (12), with $-K_1/K_2 = 10$, $-K_3/K_2 = 0$, $-h_1/K_2 = 7.1$, $-h_2/K_2 = 0.3$, $-\Delta/K_2 = 0.75$, and $q = 500$. The temperature scale is normalized by the temperature of the upper critical solution point. A simple closed loop in this case, slightly bowed out toward the high concentration side.
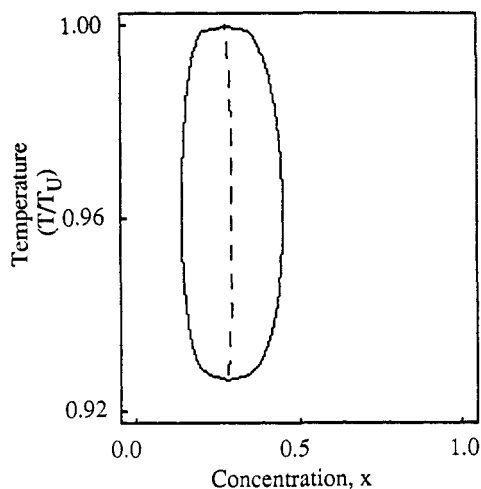
Figure 4(b) – Temperature $(-1/K_2)$ versus concentration phase diagram for the model of equation (12), with $-K_1/K_2 = 10$, $-K_3/K_2 = 0$, $-h_1/K_2 = 7.5$, $-h_2/K_2 = 0.7$, $-\Delta/K_2 = 0.75$, and $q = 500$. The temperature scale is normalized by the temperature of the upper critical solution point. The closed loop in this case is translated toward low concentration. Note that the entire loop exists to one side of $x = 0.5$.

These are just a few examples of the types of phase diagrams produced by the model introduced in this paper. The phase diagrams are physically reasonable, and point the way toward further study of asymmetric effects. In conclusion, we find that asymmetry is a more subtle feature than one might at first suppose, and that vacancies can play a necessary role in its expression.

REFERENCES

1. A. Kumar, H. R. Krishnamurthy and E. S. R. Gopal, Phys. Rep. 98, 57 (1983) and references therein.
2. G. R. Andersen and J. C. Wheeler, J. Chem. Phys. 69, 2082 (1978).
3. D. A. Huckaby, J. Chem. Phys. 81, 3691 (1984).
4. J. S. Walker and C. A. Vause, Phys. Lett. A 79, 412 (1980); J. S. Walker and C. A. Vause, J. Chem. Phys. 79, 2660 (1983).
5. C. A. Vause and J. S. Walker, Phys. Lett. A 90, 419 (1982);,R. E. Goldstein and J. S. Walker, J. Chem. Phys. 78, 1492 (1983).
6. J. S. Walker and R. E. Goldstein, Phys. Lett. A 112, 53 (1985).
7. L. Pauling, The Nature of the Chemical Bond, third edition, Cornell University Press, NY (1960).
8. J. S. Walker, to be published
9. P. E. Scesney, Phys. Rev. B1, 2274 (1970).