Symmetry effects and equivalences in lattice models of hydrophobic interaction

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Abstract

We establish the equivalence of a recently introduced discrete model of the hydrophobic interaction, as well as its extension to continuous state variables, with the Ising model in a magnetic field with temperature-dependent strength. In order to capture the effect of symmetries of the solvent particles we introduce a generalized multistate model. We solve this model – which is not of the Ising type – exactly in one dimension. Our findings suggest that a small increase in symmetry decreases the amplitude of the solvent-mediated part of the potential of mean force between solute particles and enhances the solubility in a very simple fashion. High symmetry decreases also the range of the attractive potential. This weakening of the hydrophobic effect observed in the model is in agreement with the notion that the effect is entropic in origin.

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1 Introduction

The hydrophobic interaction is a property of aqueous solutions which has a long and multi-faceted history of study \[1, 2\]. We focus here on one particular issue, viz. the solvent-mediated interaction between solute particles. The balance between an energetically favorable accommodation of a solute particle between solvent particles and the entropically unfavorable necessity to place these solvent molecules in some particular orientation leads to an increase in free energy which is believed to be the basic mechanism of the hydrophobic effect. Since this increase of free energy becomes weaker with smaller separation of solute particles an effective solvent-mediated hydrophobic attraction arises which is superimposed on and may even dominate the direct interaction between solute particles.

This interplay between favorable energy and unfavorable entropy has been illustrated in an idealized lattice model where each solvent particle is allowed to be in one of \( q \) discrete states (orientations) \[3\]. There is a nearest neighbor interaction between solvent particles with energy \( w \) if both particles are in one particular state and \( u \) (with \( u > w \)) otherwise. A solute particle may be accommodated in the interstitial site between solvent particles, provided both solvent particles are in that special state, which is energetically favorable by the amount \( u - w \). Calculation of the solvent-mediated part of the potential of mean force between solute particles and of the solubility (done exactly in one dimension \[3\] and numerically in two and three dimensions \[4\]) has revealed in all space dimensions an inverse relationship between the magnitude of the attractive force and its range. Furthermore, the solubility of the hydrophobe decreases with increasing temperature. In one dimension the decay of the potential of mean force with distance is monotonic, while in two and three dimensions there is an oscillatory modulation.

Here we first review and extend this basic model to continuous state variables, thus being somewhat more realistic with regard to the interpretation of the molecular states as orientations (Sec. II) and show that both the original discrete model and the continuous model are equivalent to the ferromagnetic Ising model with a magnetic field with a temperature-dependent strength (Sec. III). Since this mapping retains the local structure of the interactions, all the known results about the Ising model can be translated directly into properties of the hydrophobic model. Finally, we model symmetries of the solvent particles in a simple fashion by allowing for the accommodation of solute particles between solvent molecules that are in any \( n \) rather than just
one energetically favorable pair of special states (Sec. IV). The resulting $(n + 1)$-state model is not equivalent to an Ising model, but may still be solved exactly in one dimension. These exact results are discussed in the concluding Sec. V.

2 Model of the hydrophobic attraction with discrete and continuous state variables

In the model of Refs. [3, 4] each solvent molecule is placed on a $d$-dimensional lattice and can be found in $q$ different states. These states may be thought of representing orientations with respect to some arbitrarily chosen reference axis. There is a nearest neighbor interaction which favors pairs of molecules which are both in one particular state. We shall refer to this state as the special state, or state 1. Thus the interaction energy between molecules in states $i, j$ has the form

$$w_{ij} = \begin{cases} w, & \text{when } i = j = 1 \\ u, & \text{otherwise} \end{cases}$$  \hspace{1cm} (1)

with

$$u > w.$$  \hspace{1cm} (2)

Without loss of generality we shall set the global reference energy $u = 0$ and therefore consider the case $w < 0$. The energy of interaction of an interstitial solute molecule with its neighbors is taken to be $v$. This quantity, however, does not enter the expression for the solvent-mediated part of the potential of mean force; only the solubility depends on $v$.

We calculate the potential of mean force $W(r)$ on the basis of the potential-distribution theorem [6]. We define $P_{11}$ as the probability of finding a given neighboring pair of molecules in the special state 1 and $P(r)$ as the probability of finding two such pairs at a distance $r$, measured in lattice units. Following [6] one then finds

$$W(r) = -kT \ln \left[ P(r) / P_{11}^2 \right]$$  \hspace{1cm} (3)

at temperature $T$.

As solubility we define the dimensionless ratio

$$\Sigma = \rho_{\text{soln}} / \rho_{\text{gas}}$$  \hspace{1cm} (4)
where \( \rho_{\text{soln}} \) is the number density of the solute in the solution and \( \rho_{\text{gas}} \) is its number density in an ideal gaseous phase in osmotic equilibrium with the solution. For small solubility (such that the saturated solution is very dilute) this quantity is the Ostwald absorption coefficient. Within the lattice model one finds [3]

\[
\Sigma = P_{11} e^{-v/kT}.
\]

The equilibrium properties of the model are encoded in the partition function

\[
Z_L = \sum_C e^{-\beta E(C)}
\]

where \( L \) is the number of lattice sites, \( \beta = 1/(kT) \), and the sum is over all configurations \( C \) the system may be found in. The nearest neighbor sum

\[
E(C) = w \sum_{i<j} \delta_{s_i,1} \delta_{s_j,1}
\]

is the total energy of a configuration \( C \) of state variables \( s_i = 1, \ldots, q \).

For the actual computation of the quantities \( P_{11} \) and \( P(r) \) one uses the standard transfer matrix formulation of statistical mechanics models; see e.g. [7]. In one dimension the transfer matrix is the \( q \times q \) matrix

\[
V = \begin{pmatrix}
    b & 1 & \ldots & 1 \\
    1 & 1 & \ldots & 1 \\
    \vdots & \vdots & \ddots & \vdots \\
    1 & 1 & \ldots & 1
\end{pmatrix}
\]

which has

\[
b = e^{-w/kT} > 1
\]

at the (1,1) position and 1 everywhere else. The partition function becomes

\[
Z_L = \text{trace } V^L.
\]

In order to calculate thermal averages we also introduce the projectors \( S(k) = |k\rangle\langle k| \) on states \( k \). These are the diagonal matrices with 1 at the diagonal element \( k \) and 0 elsewhere. This yields the formal expressions

\[
P_{11} = \frac{1}{Z_L} \text{trace } [S(1)V S(1)V^{L-1}] = \frac{b}{Z_L} \langle 1|V^{L-1}|1 \rangle
\]

\[
P(r) = \frac{1}{Z_L} \text{trace } [S(1)V S(1)V^{r-1}] S(1)V S(1)V^{L-r-1}]
\]

\[
= \frac{b^2}{Z_L} \langle 1|V^{r-1}|1 \rangle \langle 1|V^{L-r-1}|1 \rangle
\]
In the thermodynamic limit $L \to \infty$ the leading contribution to the partition function comes from the largest eigenvalue $\lambda$ of the transfer matrix. Anticipating the finite gap in the spectrum of $V$ we may therefore write

$$P_{11} = \frac{b}{\lambda} \rho_1$$  \hspace{1cm} (13)
$$P(r) = \frac{b^2}{\lambda^2} Q_{11}(r)$$  \hspace{1cm} (14)

where $\rho_1$ is the probability of finding a molecule in state 1 and the correlation function

$$Q_{11}(r) = \lim_{L \to \infty} \frac{1}{Z_L} \text{trace} \left[ S(1)V^{r-1}S(1)V_{L-r+1} \right]$$  \hspace{1cm} (15)

is the probability of finding molecules at both sites $(i, i + r - 1)$ in state 1, irrespective of the configuration of other molecules.

In higher dimensions the transfer matrix is constructed analogously. On a hypercubic lattice in $d$-dimensions the transfer matrix can be written as a product of two non-commuting matrices $V = V^{(2)}V^{(1)}$. The diagonal matrix

$$V^{(1)} = e^{-\beta E}$$  \hspace{1cm} (16)

gives the Boltzmann weight of a configuration in a $(d - 1)$-dimensional hyperplane with

$$E = w \sum_{<i,j>} \langle S_i(1)S_j(1) \rangle.$$  \hspace{1cm} (17)

The projectors $S_i$ act as unit matrices on all sites except $i$. The prime on the sum marks the restriction of the summation to the hyperplane of states on which the transfer matrix acts. The non-diagonal part

$$V^{(2)} = \prod_i V_i$$  \hspace{1cm} (18)

is the tensor product of the one-dimensional transfer matrix over all sites of the hyperplane. Thermal averages are calculated by inserting projectors $S_i(k)$ at the appropriate positions in $V$ and in the trace over $V^L$.

In the previous discussion the states that the molecule may be found in were chosen to belong to a discrete set. Since the model is not designed to be realistic for any particular solvent such an artificial representation of the orientation of a molecule is not really a cause for concern. Nevertheless, for a proper interpretation of these states as orientations it is useful to extend the
model to continuous state variables by the following limit procedure. One imagines there to be \( n \) distinct states \( 1, \ldots, n \) which have mutual interaction energy \( w \). Thus there are \( n^2 \) pairs of states with energy \( w \) and \( q^2 - n^2 \) pairs which have interaction energy \( u = 0 \). Hence we shall refer to this model as the \( n^2 \)-model. These \( n \) states may be interpreted as labeling infinitesimal solid angle segments on a sphere surrounding the solvent molecule (see Fig. 1 for a two-dimensional representation). Not all of these segments have to be in close proximity on the sphere; they may belong to distinct blocks which define those areas on the surface of the molecule between which a solute particle may be accommodated. Taking the limit \( n, q \to \infty \) with the ratio \( \tilde{q} = q/n \) fixed, one obtains a continuous version of the model where the range of states \([0, 4\pi/\tilde{q}]\) represents the total amount of solid angle on the surfaces of each of the two neighboring solvent molecules between which solute molecules may be found. Parts of that interval may then refer to distinct areas on the surface of the solvent particle.

For fixed \( n \) and \( q \) the one-dimensional transfer matrix has a block form similar to (8), but where instead of the matrix element \( b \) one has an \( n \times n \) matrix with all elements equal to \( b \). All other matrix elements are equal to 1. As will be shown in the next section, the \( n^2 \)-model and the original \( 1^2 \)-model are equivalent, thus proving that the earlier restriction to discrete states did not constitute an additional oversimplification. In the interpretation of the \( 1^2 \)-model as a model with a continuous degree of freedom the special state 1 simply represents a fraction \( 4\pi/q \) of solid angle (oriented in some direction) rather than a discrete single direction. Notice, however, that the analogue of the quantity \( P_{11} \) is the double sum

\[
P_{11} \to \sum_{i,j=1}^{n} P_{i,j} \tag{19}
\]

which turns into an integral in the limit \( n, q \to \infty \). The pair correlation function \( P(r) \) has to be redefined accordingly. With the proper redefinitions all results of the \( 1^2 \)-model may be interpreted in terms of the continuum limit of the \( n^2 \)-model, i.e., with the integer \( q \) being replaced by \( \tilde{q} = q/n \), and \( 1 < \tilde{q} < \infty \) considered a real number.
3 Equivalence to the Ising model

In the $n^2$-model all special states are indistinguishable, as are the non-special states. Hence it is important to know only to which group of states the state of a molecule belongs, but not to which particular state within each group. Any joint probability involving some state $k$ depends only on whether $k$ belongs to the group of special states ($k \in \{1, \ldots, n\}$) or not ($k \in \{n + 1, \ldots, q\}$). Hence the $n^2$-model is equivalent to a 2-state model, i.e., to an Ising model. We may identify the special states with an Ising spin $s_i = +1$ whereas the other states may be collectively identified with $s_i = -1$.

In order to work out the equivalence in detail we note that the partition function (6) of the original $1^2$-model may be cast in the form of a double sum

$$
\sum_C e^{-\beta E(C)} = \sum_{C_1} \sum_{C'(C_1)} e^{-\beta E(C)}.
$$

(20)

The first sum runs over all fixed configurations $C_1$ of $N_1$ molecules in state 1; the second sum then includes all other configurations $C'$ with the configuration $C_1$ specified by the first sum. Since the energy $E(C) = E(C_1)$ depends only on the positions of molecules in state 1, i.e., on $C_1$, the second sum can be evaluated trivially to give

$$
\sum_{C'(C_1)} = (q - 1)^{L-N_1}.
$$

(21)

This originates in the degeneracy of states with a fixed number $N_1$ of molecules in state 1 in the configuration $C_1$, and we obtain

$$
Z_L = \sum_{C_1} e^{-\beta E(C_1)} (q - 1)^{L-N_1} = \sum_{C_1} e^{-\beta \tilde{E}(C_1)}
$$

(22)

with a new energy function

$$
\tilde{E} = E + kT \ln (q - 1) \sum_i (1 - \delta_{s_i,1}).
$$

(23)

In those terms the partition function (22) of the model for hydrophobic attraction turns into the partition of a ferromagnetic Ising model in a magnetic field with energy

$$
\tilde{E} = -J \sum_{\langle i,j \rangle} s_i s_j - h \sum_i s_i - \text{const.}
$$

(24)
The Ising interaction parameters are given by the relations

\begin{align}
J &= -\frac{w}{4}, \\
h &= -\frac{cw}{4} - \frac{1}{2}kT \ln (q - 1),
\end{align}

with \( c \) the coordination number of the lattice. This enters since part of the contribution of the magnetic field strength is contained in the nearest neighbor sum \( (\text{6}) \). If some lattice sites have a coordination number different from \( c \) (e.g. at the boundary in case of non-periodic boundary conditions), additional local magnetic fields would contribute to the Ising energy. The temperature dependence of the entropic contribution \( kT \ln (q - 1)/2 \) to the field arises since the number of unfavorable states does not depend on temperature and hence the factor \( kT \) must cancel in the partition function. The constant term in \( (\text{24}) \) does not affect the thermodynamical properties of the system and may be dropped. Notice that \( q \) is a discrete variable and therefore within this formulation of the model \( h \) changes discontinuously as a function of \( q \).

A similar resummation may be performed for the partition function of the \( n^2 \)-model by first fixing a configuration of favorable states with \( N_f \) molecules (which yields a factor \( (q - n)^{L-N_f} \) from the summation over the remaining degenerate configurations) and then counting the degeneracy of all such favorable states. For each given \( N_1 = N_f \) this yields another factor \( n^{N_1} \). Thus we are left with an Ising partition function with a magnetic field

\[ h' = -\frac{cw}{4} - \frac{1}{2}kT \ln (q/n - 1). \]

The continuum limit of the state variable may now be taken and yields an Ising partition function identical to that derived from the original \( 1^2 \)-model but where now \( q \) is is replaced by \( \tilde{q} = q/n \) and treated as a continuous variable in the range \( 1 < \tilde{q} < \infty \). Hence the \( n^2 \)-models are all equivalent to each other and to the Ising model in a magnetic field given by \( (\text{27}) \), i.e., by the replacement \( q \to q/n \). Without loss of generality one may therefore discuss only the \( 1^2 \)-model.

On the level of the transfer matrix description the equivalence may be shown by a similarity transformation \( \tilde{V} = YY^{-1} \). Because of the cyclic property of the trace the partition function is invariant under any such transformation. For the \( 1^2 \)-model we define

\[ \omega = e^{2\pi i/(q-1)} \]
The matrix
\[
Y = \frac{1}{\sqrt{q-1}} \begin{pmatrix}
\sqrt{q-1} & 0 & 0 & 0 & \ldots & 0 \\
0 & 1 & 1 & 1 & \ldots & 1 \\
0 & 1 & \omega^{-1} & \omega^{-2} & \ldots & \omega^{-(q-2)} \\
0 & 1 & \omega^{-2} & \omega^{-4} & \ldots & \omega^{-2(q-2)} \\
\vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\
0 & 1 & \omega^{-(q-2)} & \omega^{-2(q-2)} & \ldots & \omega^{-(q-2)^2}
\end{pmatrix}
\] (29)

has as its inverse the transposed matrix, \(Y^{-1} = Y^T\). The transformation leaves the projector \(S(1)\) invariant and brings \(V\) into a block diagonal form with the \(2 \times 2\) matrix

\[
W = \begin{pmatrix}
\frac{b}{\sqrt{q-1}} & \sqrt{q-1} \\
\sqrt{q-1} & q-1
\end{pmatrix}
\] (30)

in the upper left diagonal and 0 everywhere else. Therefore the trace reduces to a trace over the two-dimensional subspace on which \(\tilde{V}\) acts in a nontrivial way, i.e., \(\text{trace } V^L = \text{trace } \tilde{V}^L = \text{trace } W^L\). In \(W\) one recognizes the transfer matrix of the Ising model and hence the equivalence is recovered. In higher dimensions the transformation \(Y\) is applied to each lattice site, thus reducing the full model to a two-state Ising model with parameters as defined above.

Varying the temperature \(T\) corresponds to moving along a curve in the field-temperature plane of the Ising model which starts at \(T = 0, h = -cw/4 > 0\) (all molecules are in the favorable state) and crosses the line \(h = 0\) at a point defined by the condition

\[-w = \frac{2}{c} kT \ln (q - 1)\] (31)

or, equivalently, \(b^{c/2} = q - 1\) (Fig 2). In two and three dimensions the Ising model has a phase transition of second order at finite temperature along this zero-field line. Above the critical point the probability of finding a molecule in the favorable state is 1/2, below the critical point one has spontaneous symmetry breaking between a “favorable” and an “unfavorable” phase. On a \(d\)-dimensional square lattice \((c = 2d)\) some values of \(q\) at the critical point are given by \[8\]

\[
q_c = 1 + e^{-d w/kT_c} = \begin{cases} 
\infty & d = 1 \text{ (exact)} \\
18 + 12 \sqrt{2} & d = 2 \text{ (exact)} \\
\approx 27 & d = 3 \text{ (numerical)} \\
1 + e^2 & d = \infty \text{ (mean field)}
\end{cases}
\] (32)
At the critical point the range of the potential of mean force would diverge if the model were applicable at such low values of $q$. At large distances the decay would be algebraic and proportional to the decay of the magnetization correlation function.

For larger values of $q$ (which seem more realistic) the zero-field condition corresponds to subcritical temperatures. Hence, following the curve defined by varying the temperature of the hydrophobic model one expects a jump discontinuity in the probability of finding a favorable state from a value greater than 1/2 to a value less than 1/2 at $h = 0$. The strength of the discontinuity increases with increasing $q$. The regime which appears to be relevant for the hydrophobic effect [3, 4] corresponds to $h < 0$. For all coordination numbers ($c = 2$ being the smallest possible) this is consistent with the requirement that the change of free energy $\Delta F = w + kT \ln (q - 1)$ arising from the accommodation of a solute particle be positive.

## 4 Symmetry effects

Implicit in the construction of the $1^2$-model is the view that the surface structure of the solvent molecule is made up of certain regions between which a solute molecule may be accommodated. No provision is made for more structured solvent molecules which have chemically different surface regions. One could imagine $n$ non-identical regions on each solvent molecule such that each identical pair of regions allows for the accommodation of a solute particle between two solvent molecules, but the accommodation between distinct pairs would be energetically so unfavorable that it may be considered forbidden. In this section we extend the model to allow for $n$ pairs of orientations between which a solute particle may be accommodated (Fig. 1). We denote these special states by 1, ..., $n$, with $1 \leq n \leq q$ and assign non-positive interaction energies

$$w_{ij} = \begin{cases} w, & \text{when } 1 \leq i = j \leq n \\ 0, & \text{otherwise} \end{cases} \quad (33)$$

We shall refer to this model as the $n$-model. With regard to solubility a solvent molecule of type $n$ described by these interactions would have a higher symmetry than a molecule described by the original 1-model with the same value of $q$, since there are more, but mutually exclusive pairs of favorable orientations. The limiting case $n = q$ corresponds to the zero-field, $q$-state Potts model [8]. We stress that we define this model in the spirit of Refs.
3. i.e., not with the intention of describing a particular real solvent, but with the aim of exhibiting what may be found to emerge as generic behavior resulting from an increase in symmetry. Since some of the important features of the 1-model were already seen in the simple one-dimensional model, we restrict our analysis of the n-model also to the one-dimensional case. This can be solved exactly by diagonalizing the transfer matrix. A reader not interested in the details of the diagonalization may skip the following more technical subsection.

4.1 Exact solution of the one-dimensional model

The $q \times q$ transfer matrix $V$ of the n-model has $b$ for its first $n$ diagonal elements and 1 everywhere else. By a transformation similar to (29) – with the 1 at the (1,1)-position replaced by an $n \times n$ unit matrix and the quantity $q - 1$ in the normalization factor and in $\omega$ replaced by $(q - n)$ – the transfer matrix becomes block diagonal with

$$W = \begin{pmatrix}
    b & 1 & \ldots & 1 & \sqrt{q - n} \\
    1 & b & \ldots & 1 & \sqrt{q - n} \\
    \vdots & \vdots & \ddots & \vdots & \vdots \\
    1 & \sqrt{q - n} & \sqrt{q - n} & \ldots & \sqrt{q - n} \\
    \sqrt{q - n} & \sqrt{q - n} & \ldots & \sqrt{q - n} & q - n
\end{pmatrix} \tag{34}$$

in the upper left corner and 0 elsewhere. Hence the model is equivalent to an $(n + 1)$-state model, which is, however, not equivalent to some Ising or Potts model. Nevertheless the degree of degeneracy is high and therefore it is not difficult to guess the eigenvectors of $W$ and hence of $V$ by a second transformation, again analogous to $Y$, but with the first two columns replaced by matrix elements of the form $Y_{11} = y_+/z_+$, $Y_{k1} = 1/z_+$ and $Y_{12} = y_-/z_+$, $Y_{k2} = 1/z_-$ for all $2 \leq k \leq n + 1$, and with the quantity $q - 1$ replaced by $n$. Since the columns of the transformation matrix are eigenvectors of $W$ the variables

$$y_\pm = \frac{1}{2\sqrt{q - n}} \left( q + 1 - 2n - b \pm \sqrt{(b - q - 1)^2 + 4n(b - 1)} \right) \tag{35}$$

are determined by the two solutions of a quadratic equation. The constants

$$z^2_{\pm} = n + y^2_{\pm} \tag{36}$$
are normalization factors for the eigenvectors.

The full transformation which diagonalizes $V$ may then be constructed and all quantities of interest may be calculated. One finds four distinct eigenvalues which take the values $b - 1$ (which is $(n - 1)$-fold degenerate), 0 ($(q - n - 1)$-fold degenerate), and

$$\lambda_{\pm} = \frac{1}{2} \left( b + q - 1 \pm \sqrt{(b - q - 1)^2 + 4n(b - 1)} \right).$$

(37)

The largest eigenvalue is $\lambda_+$. Before proceeding further we give the asymptotic expansion up to first order in $1/q$ which is necessary for the study of the hydrophobic regime of large values of $q \gg b$. One finds:

$$\lambda_+ = q + (b - 1)n/q$$

(38)

$$\lambda_- = (b - 1)(1 - n/q)$$

(39)

$$z_+^2 = q - 2(b - 1)(1 - n/q)$$

(40)

$$z_-^2 = [q + 2(b - 1)n/q]/(q - n).$$

(41)

The exact components $\lambda^{(k)}$ of the eigenvectors $|\lambda\rangle$ belonging to the eigenvalues $\lambda$ are given as follows:

$\lambda = \lambda_+$:

$$\lambda^{(k)} = 1/z_\pm \quad (1 \leq k \leq n)$$

(42)

$$\lambda^{(k)} = y_\pm/(z_\pm\sqrt{q - n}) \quad (n + 1 \leq k \leq q)$$

(43)

$\lambda = b - 1$: ($p = 1, \ldots, n - 1; \omega_1 = e^{2\pi i/n}$)

$$\lambda^{(k)}_p = \omega_1^{p(k-1)}/\sqrt{n} \quad (1 \leq k \leq n)$$

(44)

$$\lambda^{(k)}_p = 0 \quad (n + 1 \leq k \leq q)$$

(45)

$\lambda = 0$: ($p = 1, \ldots, q - n - 1; \omega_2 = e^{2\pi i/(q-n)}$)

$$\lambda^{(k)}_p = 0 \quad (1 \leq k \leq n)$$

(46)

$$\lambda^{(k)}_p = \omega_2^{p(k-n-1)}/\sqrt{q - n} \quad (n + 1 \leq k \leq q)$$

(47)
The matrix elements needed for the calculation of average values presented below are then given by
\[
\langle k | V^n | k' \rangle = \begin{cases} 
\lambda^n_n + \frac{(b - 1)^n}{z^n_2} \left( \delta_{k,k'} - \frac{1}{n} \right) + \frac{\lambda^n_n}{z^n_-} & (1 \leq k, k' \leq n) \\
\lambda^n_n \frac{y^n_+}{z^n_+ \sqrt{n}} + \frac{\lambda^n_n}{z^n_- \sqrt{n}} & (1 \leq k \leq n; n + 1 \leq k' \leq q) \\
\lambda^n_n \frac{y^n_+^2}{z^n_+ (q - n)} + \frac{\lambda^n_n}{z^n_- (q - n)} & (n + 1 \leq k, k' \leq q)
\end{cases}
\]  \hspace{1cm} (48)

These expressions are obtained by inserting a complete set of eigenstates of the transfer matrix,
\[
\langle k | V^n | k' \rangle = \sum_\lambda \langle k | \lambda \rangle \langle \lambda | V^n | k' \rangle,
\]  \hspace{1cm} (49)

and using the components \( \lambda^{(k)} = \langle k | \lambda \rangle \) and their complex conjugates \( \lambda^{(k)*} = \langle \lambda | k \rangle \) given above.

4.2 Potential of mean force and solubility

To study the properties of the model we consider first
\[
P(k) = \lim_{L \to \infty} \frac{\text{trace } (S(k)V^L)/Z_L}{\lim_{L \to \infty} \langle k | V^L | k \rangle/Z_L}
\]  \hspace{1cm} (50)

which is the probability of finding a molecule in state \( k \). Using the matrix elements calculated in the above one finds
\[
P(k) = \begin{cases} 
1/z^n_+^2 & 1 \leq k \leq n \text{ (special states)} \\
y_+/(z^n_2 (q - n)) & n + 1 \leq k \leq q
\end{cases}
\]  \hspace{1cm} (51)

At the temperature defined by
\[
-w = kT \ln (q - 2n + 1)
\]  \hspace{1cm} (52)

the probability
\[
P_s = \sum_{k=1}^n P(k) = n/z^n_+
\]  \hspace{1cm} (53)

of finding a molecule in any one of the special states equals 1/2. This is the analogue of the zero field condition (31) in the 1-model in one dimension and suggests that the condition \( q - 2n + 1 > b \) limits the parameter range of the \( n \)-model relevant for modeling the hydrophobic effect.
The quantity entering the solubility is the nearest-neighbor correlation function

\[ P_{11} = \lim_{L \to \infty} \sum_{k=1}^{n} \text{trace} \left( S(k) V S(k) V^{L-1} \right) / Z_L = \frac{b}{\lambda_+} P_s. \]  

(54)

For the computation of the potential of mean force we also need

\[ P_r = \lim_{L \to \infty} \sum_{k=1}^{n} \sum_{l=1}^{n} \text{trace} \left[ S(k) V S(k) V^{r-1} S(l) V S(l) V^{L-r-1} \right] / Z_L \]

\[ = \frac{b^2}{\lambda_+^2} \lim_{L \to \infty} \sum_{k=1}^{n} \sum_{l=1}^{n} \text{trace} \left[ P(k) V^{r-1} P(l) V^{L-r-1} \right] / Z_{L-2} \]

\[ = \frac{b^2 n^2}{\lambda_+^2 z_+^2} \left[ 1 + \frac{z_+^2}{z_-^2} \left( \frac{\lambda_+}{\lambda_-} \right)^{r-1} \right]. \]  

(55)

The potential of mean force therefore takes the form

\[ W(r) = -kT \ln \left[ 1 + A e^{-(r-1)/\xi} \right] \]  

(56)

with the amplitude

\[ A = \frac{z_+^2}{z_-^2} \]  

(57)

and the localization length

\[ \xi = \left( \ln \frac{\lambda_+}{\lambda_-} \right)^{-1}. \]  

(58)

We remark that the expression of the potential of mean force does not involve the eigenvalue and eigenvectors of the the \((n-1)\)-fold degenerate eigenvalue \(b - 1\) characteristic for the \(n\)-model. The eigenvalues \(\lambda_\pm\) and the quantities \(z_\pm\), however, do depend on \(n\).

The amplitude \(A\) is a monotonically increasing function of temperature, with \(A \sim (q/n - 1)n^2/b^2\) as \(T \to 0\) and \(A = q/n - 1\) at infinite temperature. The localization length vanishes in both these limiting cases and has a maximum at \(b = q + 1\), independently of \(n\). For this temperature we find in terms of the ratio \(\nu = n/q\)

\[ A = \frac{1 - \sqrt{\nu}}{1 + \sqrt{\nu}} \]  

(59)
\[ \xi = \left[ \ln \frac{1 + \sqrt{\nu}}{1 - \sqrt{\nu}} \right]^{-1} \approx 1/\sqrt{4\nu} \quad (60) \]

\[ \Sigma = \frac{1}{2} \nu b e^{-\nu/(kT)}. \quad (61) \]

For large \( q \) the maximal localization length grows proportionally to the square root of \( q \), but decreases with increasing \( n \). As a function of \( n \) the amplitude of the potential of mean force also decreases. The solubility is enhanced by a factor of \( n \).

In analogy to the original 1-model one expects the regime most relevant to the hydrophobic effect to correspond to \( q \gg b \). Using again \( \nu = n/q \) and expanding the relevant quantities \( \lambda_{\pm}, z_{\pm}^2 \) up to first order in \( 1/q \), (38) - (41) yield

\[ A = \frac{1 - \nu}{\nu} \quad (62) \]

\[ \xi = \left[ \ln \frac{q}{(b - 1)(1 - \nu)} \right]^{-1} \quad (63) \]

\[ \Sigma = \frac{b\nu}{q} e^{-\nu/(kT)}. \quad (64) \]

The inverse localization length may be written as a sum of two terms,

\[ \xi^{-1} = \ln \frac{b}{q - 1} + \ln \frac{1}{1 - \nu}, \quad (65) \]

the second of which is positive and describes the reduction of \( \xi \) as a function of \( n \). As in the previous special case the amplitude decreases with increasing \( n \), while the solubility increases by a factor of \( n \).

At sufficiently large distance the potential of mean force decays exponentially

\[ W(r) \sim -kT A e^{-(r-1)/\xi} \quad (66) \]

For small \( n \) and large \( q \) the localization length \( \xi \) depends on \( n \) only very weakly. The amplitude is reduced by a factor of \( n \) while the solubility is increased by the same factor. Hence one finds for two different systems the relations

\[ \frac{W(r)}{W'(r)} = \frac{\nu'}{\nu} \quad \text{for } \xi = \xi' \quad (67) \]

\[ \frac{\Sigma}{\Sigma'} = \frac{\nu q'}{\nu' q} \quad \text{for } T(v' + w') = T'(v + w) \quad (68) \]
\[ \frac{1}{\xi} - \frac{1}{\xi'} = \ln \left( \frac{q}{q'} \right) \quad \text{for} \ T'w' = T'w. \quad (69) \]

One can analyze in a similar fashion the effect of symmetry within the \(1^2\) model where higher symmetry corresponds to a larger solid angle of accommodation and hence to a decrease in \(q\). This corresponds to setting \(\nu = 1/q\) in Eqs. (67) - (69).

5 Concluding remarks

The equivalence of the hydrophobic interaction model to the Ising model in a magnetic field with temperature-dependent strength allows for the interpretation of the solubility, the potential of mean force and other quantities of interest in terms of the well-known properties of the Ising model. For realistic values for water in the hydrophobic model, the strength of the magnetic field in the corresponding Ising model is significant, and consequently the model is far away from the Ising critical point. We can however not rule out that some real system is appropriately described by an Ising model, in which case a solvation effect associated with the corresponding short range interaction would change dramatically at the critical point. Indeed, the interpretation of \(q\) as a fraction of the surface area between which solute particles may be accommodated suggests lower realistic values of \(q\) than previously assumed and hence the zero-field condition for criticality might be satisfied if such a system exists. A more tangible consequence of a lower value of \(q\) (but not as low as required for the second order phase transition) would be to bring the minimum of the solubility as a function of temperature to larger and more realistic values, thus indicating that the mechanism by which this minimum occurs in a real system is similar to that described by the model.

The most striking features of the original hydrophobic interaction model, the inverse relationship between amplitude and range of the potential of mean force and the decrease of solubility with increasing temperature in reasonable temperature ranges, are present also in the more symmetric \(n\)-model. However, the amplitude of the potential decreases with increasing degree of symmetry. This is in agreement with the notion that the origin of the hydrophobic effect is entropic. With increasing degree of degeneracy (and hence symmetry) the entropy decrease associated with the requirement to orient molecules in a particular direction is less and hence also the balance in the free energy difference is reduced. For solvents differing in their degree of symmetry the \(n\)-model predicts an inverse relationship (67) also between
the ratios of the potential of mean force (at sufficiently large distance and temperatures at which the localization length are equal) and the ratios of solubilities (at temperatures such that the exponential prefactors are equal).

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Figure 1: Accommodation of solute particles (black disks) on the interstitial sites between solvent particles (circles) on a square lattice. Depending on the model the figure has different interpretations. (i) In the $n^2$-model with $q$ discrete orientations (states) the whole circle consists of $4q$ discrete points which consist of quadruples related to each other by a 90 degree rotation. Each quadruple defines one orientation and there is always one quadruple of points which is located on the lattice axis. The special states $1, \ldots, n$ correspond to quadruples of points on the dark sections of the circumference of the circles. A solute particle may be accommodated whenever special points of two neighboring molecules are located on the lattice axis. (In the $1^2$-model of Ref. [3] there would be only one such quadruple of points.) (ii) In the continuum limit the interpretation of the open circles in the figure is that if dark segments of the circumference of neighboring circles intersect with the lattice axis then a solute particle may be accommodated. (iii) In the $n$-model defined below one distinguishes between $n$ different special states. Accommodation of solute particles is possible only between neighboring solvent molecules which are in the same special state corresponding to one particular of $n$ special quadruples of points. In the continuum version of the $n$-model this corresponds to distinguishing between different surface areas on the solvent molecule. E.g. for $n = 2$ one would say that a solute particle could be accommodated if on both neighboring molecules either the long or the short dark segment intersect with the lattice axis, but not if for one molecule the long segments intersects and for the other molecule the short segment. (This scenario would allow for accommodation of a solute particle in the continuum version of the $n^2$-model.)
Figure 2: Curve in the $h - T$ plane of the Ising model which corresponds to varying $T$ in the hydrophobic model (dashed line). Larger $q$ leads to a steeper (more negative) slope. The bold line at $h = 0$ marks the region of spontaneous symmetry breaking, ending in the critical point at $T_c$. In the regime $h < 0$ relevant for the hydrophobic effect the probability $P_s$ of finding a solvent molecule in the special state is less than 1/2.