

Ordering behavior of albite using the modified sequential construction method

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ABSTRACT

In order to use a local unit larger than that suggested by Andersen and Mazo (1979), a new method—the modified sequential construction method or “MSCM”—has been developed for the calculation of order parameters and configurational entropies in albite. This method has several advantages over the older methods, such as being readily usable for any size of local structural unit. The number of distributions of atoms among sites is first reduced to noninteracting units, and the resulting combinatorial factor is then corrected by an approximated correction factor. In comparison with Monte Carlo results, this new approximation gives a better order parameter for the 2-D model of albite of Andersen and Mazo than the quasi-chemical and the sequential construction methods. The maximum numerical deviation of the calculated order parameter (for Andersen and Mazo’s 2-D model of albite) from the Monte Carlo results is about 6% for the quasi-chemical method, 2% for the sequential construction method, and only about 1% for the modified sequential construction method. It is also shown that if the size of the local unit becomes larger, the entropy curve becomes steeper at temperatures in which the high albite–low albite transition occurs.

INTRODUCTION

The extent of Al-Si ordering in feldspar minerals depends directly on a number of variables, such as temperature, time, rate of cooling, and pressure. Temperature is probably the most influential variable, and the ordering behavior of feldspars has recently been under intensive study.

The structure of feldspar minerals is well known, and readers are referred to reviews by MacKenzie and Zussman (1974) and Smith (1974). In the feldspar framework, there are four different types of sites that are occupied by Al and Si atoms. Crystallographically, these sites are denoted by $T_1(O)$, $T_1(m)$, $T_2(O)$, and $T_2(m)$. It seems that, unlike most ordering phenomena, the site energies in these minerals have a more important role than the interaction energies in the ordering behavior of the lattice. Al has a tendency to occupy the $T_1(O)$ site, especially at lower temperatures, and in “low” albite, almost all the Al atoms are located on this site. As temperature increases, Al atoms migrate to other sites, and the lattice becomes more disordered. At sufficiently high temperatures, but still below the melting point of albite, each site is statistically occupied by Al and Si atoms, i.e., with probability $\frac{1}{4}$ and $\frac{3}{4}$, respectively. The distribution of Al and Si atoms on T sites is such that no two Al atoms sit next to each other, however. This phenomenon, known as the Al-avoidance principle, is based on experimental observations (Smith, 1974).

The ordering behavior of albite has been modeled using various approximation methods, such as the quasi-chemical method (Mazo, 1977) and the Kikuchi method (Rajabali, 1981). In these models, site preference energies

and the Al-avoidance principle were included in the calculations. Andersen and Mazo (1979) then pointed out that local charge neutrality, as well as the global charge balance, have to be imposed on the distributions; only those distributions that allow local charge neutrality are accepted. After this suggestion, new calculations that included local charge neutrality were carried out by the sequential construction method (Rajabali, 1986) and the independent pairs-and-sites method (Rajabali, 1987). In all these calculations, the smallest possible size for the neutral local units has been considered, and the idea of Andersen and Mazo is simply that the ratio of aluminums to silicons in a unit must be equal to that for the whole lattice. This is referred to as local charge neutrality.

Obviously, the effect of local charge balance is to reduce the number of distributions of atoms among T sites, therefore reducing the configurational entropy. Recent work (Rajabali, 1987), however, shows that the size of the local unit may have some important effects on the ordering behavior of the model lattice. A crucial question, therefore, relates to how big the local unit must be. There is no theoretical way of choosing an acceptable local unit size, and one may even expect that it changes with temperature.

In the first calculations (with no local charge neutrality), the whole lattice was chosen as a unit. In the later calculations (those with local charge neutrality) the smallest possible size was chosen as a unit. Thus only the largest and the smallest possible unit sizes have been considered, in order to simplify the mathematics. To use local unit sizes that are temperature dependent complicates the problem, and, as in the previous calculations, local units



Fig. 1. Local units: (a) with two squares, (b) with three squares. In each square the a site is shown by a circle and the other corners of the squares are b sites. The X at the center of each square represents the position of an atom of Na. The sides of squares are smaller than the distance between the squares ($l_1 < l_2$).

are used that are independent of temperature. For intermediate local unit sizes, it seems that it is not possible to use the previous approximations in straightforward calculations. The main purpose of this paper is to use a new model with local units that are larger and more realistic than the local unit used by Andersen and Mazo and to introduce a new method of calculation, the modified sequential construction method (MSCM).

In the framework of albite, each Na atom is surrounded by 12 Al and Si atoms. For this reason, a unit that is three times as big as the one proposed previously seems to be reasonable. In the following, units that are 1, 2, and 3 times larger than the unit of Andersen and Mazo will be used.

MODEL AND UNIT

The two-dimensional model of Andersen and Mazo is a plane that is constructed of squares of tetrahedral sites. Unlike the $T_1(O)$ site, the other T sites do not show any preference for occupation by Al and so are treated as being equivalent in this model. These sites will be denoted by b and the special site, $T_1(O)$, by a . One-half of the squares have one Na atom at their centers, and each of these squares is surrounded by four squares with no Na atoms at their centers. Any square with Na at its center is considered to be a unit, containing one a and three b sites. In order to obey the principle of local charge neutrality, only those distributions of Al and Si on T sites in which each unit has one Al (A) and three Si (B) atoms are allowed.

To obtain units twice as large as those of Andersen and Mazo, two parallel and identical planes are selected, each of which is the same as the plane of the previous model. However, the distance between the planes is greater than the size of the squares in order to still have four nearest T sites around any T site. Two parallel squares (one from each plane) with Na at their centers can be chosen as a unit. Of course, in this model, distributions obeying local charge balance in each unit have only two A and six B atoms located on their T sites. Such a unit is shown in Figure 1a. Similarly, in order to have units with 3, 4, . . .

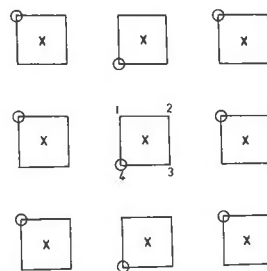


Fig. 2. A sublattice with nine units. The square at the middle is considered to be a nonsolid unit, and the rest are solid units. The a sites are shown by circles, and the positions of Na atoms are shown by X 's.

squares, the model will be constructed by 3, 4, . . . parallel identical planes, respectively, in which each plane is the same as in Andersen and Mazo's model. A unit with three squares is shown in Figure 1b. It should be noted that there is no energetic interaction between the layers. They are coupled only by the local charge balance condition.

MODIFIED SEQUENTIAL CONSTRUCTION METHOD

For the calculation of the order parameter p , which is the probability of an a site being occupied by an A atom, and the configurational entropy, the sequential-construction-method (SCM) approximation is used. In this method, units are divided arbitrarily into two imaginary groups, called solid and nonsolid units, in such a way that each solid unit is surrounded only by nonsolid units and vice versa. There are, therefore, no solid-solid and nonsolid-nonsolid interactions (only the nearest-neighbor interactions among atoms on T sites are considered). This method will first be applied to Andersen and Mazo's model, in order to make a comparison with the previous results.

Suppose that one-half of the A atoms are distributed on the solid units in such a way that each solid unit has one A , either on an a site or on a b site. The probability that an a site of a solid unit has been occupied by an A atom is p . It can easily be shown that the probability of occupation of a b site of the solid unit by an A atom (P_b^s) is given by $P_b^s = (1 - p)/3$. The sublattice shown in Figure 2 reveals the following probabilities for the availability of T sites of a nonsolid unit for occupation by A : probability for site 1 = $1 - [p + (1 - p)/3] = 2/3(1 - p)$; probability for site 2 = $1 - [p + (1 - p)/3] = 2/3(1 - p)$; probability for site 3 = $1 - [(1 - p)/3 + (1 - p)/3] = (1 + 2p)/3$; probability for site 4 = $1 - [(1 - p)/3 + (1 - p)/3] = (1 + 2p)/3$. (Note that any site of a nonsolid unit will be unavailable by probability p for any a site of a solid unit that is next to it and by probability $(1 - p)/3$ for any b site of a solid unit that is in its neighborhood.)

The probability of availability of the one a and three b sites of any nonsolid unit is therefore given by $(1 + 2p)/3$ and $(1 + 2p)/3 + 2/3(1 - p) + 2/3(1 - p) = (5 - 2p)/3$, respectively.

The total number of available a sites (for A occupation) is $[(1 + 2p)/3]N/2 + N/2 = N[(p + 2)/3]$, where the first

TABLE 1. Probabilities, P_n , and the multiplicities, λ_n , of different units

$n = 1$		$n = 2$		$n = 3$	
λ_i	P_i	λ_i	P_i	λ_i	P_i
$\lambda_1 = 1$	P_1	$\lambda_2 = 1$	P_2	$\lambda_3 = 1$	P_3
$\lambda_0 = 3$	P_0	$\lambda_1 = 8$	P_1	$\lambda_2 = 15$	P_2
		$\lambda_0 = 11$	P_0	$\lambda_1 = 51$	P_1
				$\lambda_0 = 45$	P_0

Note: The value of n represents the number of squares in a unit or the number of planes in the model. The subscript i on P_i and λ_i denotes the number of A atoms on a sites of the unit.

term belongs to the nonsolid units and the second term to the solid units. N is the total number of units. Now, the number of distributions of A atoms on available a sites is needed. Since each a site is occupied with probability p , there are pN of A atoms that have to be distributed among $N[(p + 2)/3]$ available a sites. The number of such distributions, $\omega(a)$, is given by

$$\omega(a) = \frac{\{N[(p + 2)/3]\!}{(pN)! \{[2/3(1 - p)N]\!}}$$

Similarly, there are

$$\{(5 - 2p)/3\}(N/2) + 3(N/2) = N[(7 - p)/3]$$

available b sites for A occupation. The remaining A atoms, whose number is $3[(1 - p)/3]$, have to be distributed on the available b sites. The number of such distributions, $\omega(b)$, is

$$\omega(b) = \frac{\{N[(7 - p)/3]\!}{\{(1 - p)N\}! \{[(4 + 2p)/3]N\}!}}$$

In the above calculations of both $\omega(a)$ and $\omega(b)$, the Al-avoidance principle was taken into account. If this restriction was not included in the calculation, the number of distributions on a and b sites would have been $W(a)$ and $W(b)$, respectively, such that,

$$W(a) = \frac{N!}{(Np)! [N(1 - p)]!}$$

and

$$W(b) = \frac{(3N)!}{\{(1 - p)N\}! \{(2 + p)N\}!}}$$

In the calculation of $W(a)$ and $W(b)$, all a and b sites are considered to be available. Note that local charge neutrality was not included in the calculation of either the ω or the W values. In the calculation of ω values, the principle of Al avoidance was included, however, so that the difference between ω and W values is due only to the principle of Al avoidance.

In the following calculations, it is assumed that the units are all noninteracting, and with this unrealistic as-

 TABLE 2. Order parameter, p , and configuration entropy (per mole Na), S/R , of model albite with different sizes of local unit

U	$n = 1$		$n = 2$		$n = 3$	
	p	S/R	p	S/R	p	S/R
$1/3$	0.332	1.032	0.324	1.145	0.366	1.202
0.4	0.351	1.026	0.331	1.140	0.394	1.185
0.5	0.380	1.012	0.366	1.128	0.444	1.148
$2/3$	0.431	0.983	0.411	1.102	0.537	1.056
1	0.540	0.891	0.506	1.023	0.794	0.628
2	0.829	0.467	0.780	0.617		
4	0.990	0.047	0.983	0.076		

Note: The value of n denotes the number of squares in a unit.

sumption, the total number of distributions is calculated. The incorrect combinatorial factor is then corrected by multiplying it by a correction factor f , where $f = [\omega(a)/W(a)][\omega(b)/W(b)]$. The value of f is assumed to be independent of the size of the unit, although it seems that as the number of parallel planes in the model increases, f actually decreases. As a result of increasing the number of planes, the number of units on the sides of planes increases so that, on average, interaction between units decreases and a smaller correction factor becomes necessary. In the present model the lattice is so large that this side effect does not play an important role, however.

For the model with one plane, Table 1 gives all allowed distributions and their probabilities for a unit that are consistent with both the local charge neutrality and Al-avoidance principle. To impose local charge balance, only one A atom has to be allocated to each unit. In this case there are no A - A nearest neighbors in any units. In Table 1, the subscript n of probability P_n and multiplicity, λ_n , represents the number of A atoms on a sites of a unit.

If the interactions among units are not taken into account, the total number of distributions would be W , where

$$W = \frac{N!}{(P_1N)! [(P_0N)!]^3}$$

Because of the local charge balance and the normalization condition, P_1 and P_0 are not independent variables. Since the a site of each unit is occupied by A with probability p , $P_1 = p$, and the normalization condition gives $P_1 + 3P_0 = 1$. Hence, W in terms of p is given by

$$W = \frac{N!}{(pN)! \left\{ \left[\left(\frac{1-p}{3} \right) N \right]! \right\}^3}$$

In order to impose the principle of Al avoidance among units, W has to be multiplied by the correction factor, and the approximated true combinatorial factor g is given by

$$g = \frac{N!}{(pN)! \left\{ \left[\left(\frac{1-p}{3} \right) N \right]! \right\}^3} \times f$$

TABLE 3. Calculated order parameters for the 2-D model of albite of Andersen and Mazo (1979) using different approximations

U	P_{GC}	P_{SCM}	P_{MSCM}	P_{MC}	$P_{MC} - P_{SCM}$	$P_{MC} - P_{MSCM}$	$P_{MC} - P_{GC}$
					$\times 100$	$\times 100$	$\times 100$
1/3	0.346	0.328	0.332	0.334	1.8	0.6	-5.4
0.4	?	0.347	0.351	0.355	2.3	1.1	?
0.5	0.398	0.377	0.380	0.385	2.1	1.3	-5.9
2/3	0.451	0.431	0.431	0.435	0.9	0.9	-6.3
1	0.552	0.548	0.540	0.543	-0.9	0.6	-3.8
2	0.776	0.837	0.829	0.824	-1.6	-0.6	4.9

Note: P_{GC} , P_{SCM} , P_{MSCM} , and P_{MC} have been calculated by the quasi-chemical, sequential-construction, modified-sequential-construction, and Monte Carlo approximation methods, respectively.

To find the configurational entropy, we use the Boltzmann equation, $s = k \ln g$. The resulting entropy is $-S/Nk = p \ln p + 2[(1-p)/3] \ln[(1-p)/3] - 2/3(p+2) \ln(p+2) - [(7-p)/3] \ln[(7-p)/3] + 2/3(p+2) \ln 3 + 2 \ln 2$.

We take $\epsilon_A^a < 0$ for the energy of an A atom on one a site, in such a way that all other site energies and interaction energies become zero, except for the interaction energy between two nearest-neighbor A atoms, to which an infinite energy has already been devoted (Al avoidance). (No A - A nearest-neighbor distributions have been allowed in g .) The lattice energy E and the free energy of the lattice A are $E = pN\epsilon_A^a$ and $A = E - TS = pN\epsilon_A^a - TS$. $\phi = A/NkT = -pU - S/Nk$, where U is defined as $-\epsilon_A^a/kT$.

To find the equilibrium state, ϕ has to be minimized with respect to p , $\partial\phi/\partial p = 0$, giving $U = \ln p - 2/3 \ln[(1-p)/3] - 2/3 \ln(p+2) + 1/3 \ln[(7-p)/3] + 2/3 \ln 3$. The numerical results are given in Table 2.

CALCULATION FOR UNITS CONSISTING OF TWO SQUARES

In this case the approximated combinatorial factor is given by

$$g = \frac{(N/2)!}{[(N/2)P_2]! \{[(N/2)P_1]!\}^8 \{[(N/2)P_0]!\}^{11}} \times f,$$

where the correction factor f is the same as before and the probabilities and multiplicities for the different configurations of the unit with two squares are included in Table 1. Probabilities P_0 , P_1 , and P_2 are not independent variables. On the one hand, there are $(N/2)P_2$ units with two A atoms on their a sites and $8(N/2)P_1$ units with one A atom on their a sites. The total number of A atoms on a sites is then $2 \times (N/2)P_2 + 1 \times 8(N/2)P_1$. On the other hand, there are Np A atoms on a sites and, therefore $pN = 2(N/2)P_2 + 8(N/2)P_1$ or $P_2 + 4P_1 = p$. The normalization also gives $P_2 + 8P_1 + 11P_0 = 1$. If the above equations are solved for P_2 and P_0 , one obtains $P_2 = p - 4P_1$ and $P_0 = (1-p-4P_1)/11$.

If P_2 , P_0 , and f are substituted in the combinatorial factor g and the Boltzmann equation is used, the following expression is obtained for the entropy:

$$\begin{aligned} -S/Nk = & 1/2\{(p-4P_1)\ln(p-4P_1) + 8P_1\ln P_1 \\ & + (1-p-4P_1)\ln[(1-p-4P_1)/11]\} \\ & - 2/3(p+2)\ln(p+2) - [(1-p)/3] \times \\ & \ln[(1-p)/3] - [(7-p)/3]\ln[(7-p)/3] \\ & + 2/3(p+2)\ln 3 + 2 \ln 2, \end{aligned}$$

where k is the Boltzmann constant.

Again, the function ϕ can be defined as $\phi = A/NkT = -pU - S/Nk$, and to find the equilibrium state, ϕ has to be minimized with respect to p and P_1 . The results are

$$P_1 = [2 - \sqrt{4 - 5p(1-p)}]/5$$

and

$$\begin{aligned} U = & 1/2\{\ln(p-4P_1) - \ln[(1-p-4P_1)/11]\} \\ & - 2/3 \ln(p+2) + 1/3 \ln[(1-p)/3] \\ & + 1/3 \ln[(7-p)/3] + 2/3 \ln 3. \end{aligned}$$

The results for the order parameter, p , and the configurational entropy per mole Na, S/R , are given in Table 2.

CALCULATION FOR UNITS WITH THREE SQUARES

In this case there are 220 ways to distribute three A and nine B atoms on T sites of a unit. However, in order to impose the principle of Al avoidance, only 112 of these configurations are acceptable. The probabilities and multiplicities for different acceptable distributions are given in Table 1. Like the previous cases, the variables p , P_0 , P_1 , P_2 , and P_3 are not all independent, and with similar arguments, the following relationships can be obtained: $P_3 + 15P_2 + 51P_1 + 45P_0 = 1$ and $3p = 3(P_3) + 2(15P_2) + 51P_1$ or $P_3 = p - 10P_2 - 17P_1$ and $P_0 = (1-p-5P_2-34P_1)/45$.

By using MSCM and the equation $S = k \ln g$, the approximated configurational entropy is given by $-S/Nk = 1/3\{(p-10P_2-17P_1)\ln(p-10P_2-17P_1) + 51P_1\ln P_1 + 15P_2\ln P_2 + (1-p-5P_2-34P_1)\ln[(1-p-5P_2-34P_1)/45]\} - 2/3(p+2)\ln(p+2) - [(1-p)/3] \cdot \ln[(1-p)/3] - [(7-p)/3]\ln[(7-p)/3] + 2/3(p+2)\ln 3 + 2 \ln 2$, where k is the Boltzmann constant.

To find the state of equilibrium, the function ϕ is again defined as $\phi = -pU - S/Nk$. This is then minimized

with respect to all the independent variables, p , P_1 , and P_2 . The following equations have been obtained:

$$U = \frac{1}{3} \ln(p - 10P_2 - 17P_1) - \frac{1}{3} \ln[(1 - p - 5P_2 - 34P_1)/45] - \frac{2}{3} \ln(2 + p) + \frac{1}{3} \ln[(1 - p)/3] + \frac{1}{3} \ln[(7 - p)/3] + \frac{2}{3} \ln 3$$

and

$$2025P_1^3 / [(p - 10P_2 - 17P_1)(1 - p - 5P_2 - 34P_1)^2] = 1.$$

Also,

$$45P_2^3 / [(p - 10P_2 - 17P_1)^2(1 - p - 5P_2 - 34P_1)] = 1.$$

Although it seems to be difficult to solve the three equations above simultaneously, the problem is simplified if a new variable α is introduced: $\alpha = P_1/P_2$. At the high-temperature limit (in which P_1 and P_2 become equal), $\alpha = 1$; at very low temperatures, $\alpha = 0$. The results of the calculation are tabulated for p and S/R in Table 2.

DISCUSSION

The approximation in the sequential construction method (SCM) comes from the discrimination in the order of distributing atoms among equivalent units. In the modified sequential construction method (MSCM), the same discrimination is used as a starting point. By adding all the available sites of each type and distributing atoms on them, however, an average of the equal available sites is devoted to each class, solid and nonsolid, and the degree of discrimination is reduced. MSCM should therefore give a better approximation than SCM. To clarify this point, let us suppose that our lattice has four sites on a line and we wish to distribute two A atoms such that no A - A nearest-neighbor pair is permitted. There is a total of three ways of doing this (true combinatorial factor). If we divide sites into two classes a and b , such that no a - a nearest-neighbor pair of sites exists, the distribution of one A on a sites can be carried out in two ways and the distribution of another A on b sites, on average, in $1/2$ way. SCM predicts a total of one way ($2 \times 1/2$), instead of three ways, of distributing two A atoms. Following the MSCM approach, there is a total of $2 + 0.5 = 2.5$ available sites (a and b) for occupation by two A atoms, i.e., the two A atoms have to be distributed on 2.5 available sites. This gives a combinatorial factor equal to $2.5 \times 1.5/2! = 1.9$, where 2.5 and 1.5 are the number of available sites for the first and the second A atom, respectively, and $2!$ in the denominator is due to the indistinguishability of the two A atoms. This result is better than that of SCM (compare 1.9 of MSCM and 1.0 of SCM with 3.0 of true combinatorial factor).

For testing the MSCM in a more realistic model, calculated values of the order parameter of the quasi-chemical (QC) approach of Andersen and Mazo (1979), SCM of Rajabali (1986), and MSCM are tabulated in Table 3 along with the Monte Carlo results of Rajabali (1981) for Andersen and Mazo's 2-D model of albite. The Monte Carlo method gives estimates of the configurational en-

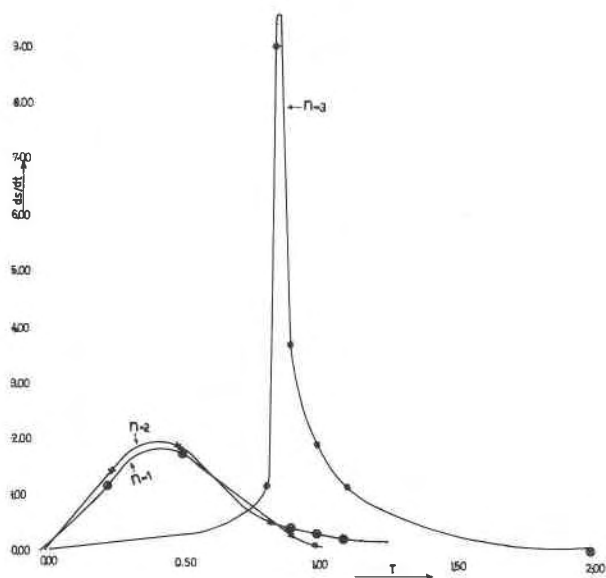


Fig. 3. The slope of entropy against T , dS/dT , for three different local units. Each value of n represents the number of squares of a unit or the number of parallel planes of the model lattice.

ergy that are accurate to 1% or better—except in the immediate neighborhood of the phase transition—within a reasonable amount of computing time (Fosdick, 1959). The data in Table 3 show that the MSCM approximation gives a better order parameter than SCM and that both of these approximations work better than quasi-chemical estimates. Numerically speaking, the maximum difference of the calculated order parameter from that of the Monte Carlo calculations is about 6% for quasi-chemical, 2% for SCM, and only about 1% for MSCM.

To see the effect of the size of the local unit on the thermodynamic behavior of the model lattice, the slope of the entropy curve, dS/dT , is plotted against T in Figure 3. This figure shows two points. First, in the model lattice with three squares, which may be more realistic than the others, the low albite-high albite transition occurs at higher temperatures. The second point, which may be more important, is that as the size of the local unit increases, the plot of dS/dT versus T becomes sharper around the transition temperatures, especially for $n = 3$. Although none of these models predicts a first-order transition (no discontinuity is observed), the $n = 3$ case gives a peak that is very much sharper than for $n = 1$ and $n = 2$ and is very much closer to first-order transition behavior.

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