11. Mixtures

the reference state

distributions of the molecules of a binary mixture

average properties in a binary mixture

MIXTURES:

The reference state —

Consider two states of a pure gas α and β. The difference in the Gibbs free energy of each state can be written as

$$G^{\alpha} - G^{\beta} = A^{\alpha} - A^{\beta} + P^{\alpha}V^{\alpha} - P^{\beta}V^{\beta} \qquad (1)$$

From $\left(\frac{\partial A}{\partial V}\right)_{T,n} = -P$ we can derive (2)

$$A^{\alpha} - A^{\beta} = -\int_{\beta}^{\alpha} P\,dV \qquad (3)$$

substituting this into the above eqn (1) and adding and subtracting $\int \frac{nRT}{V} dV$ from the right hand side gives:

$$G^{\alpha} - G^{\beta} = P^{\alpha}V^{\alpha} - P^{\beta}V^{\beta} - nRT\ln\left(\frac{V^{\alpha}}{V^{\beta}}\right) - \int_{\beta}^{\alpha}\left(P - \frac{nRT}{V}\right)dV \qquad (4)$$

now replace by

$$\rho^{\alpha} = \frac{n}{V^{\alpha}} \qquad \rho^{\beta} = \frac{n}{V^{\beta}} \qquad z = \frac{PV}{nRT} \qquad (5)$$

and $dV = \frac{-n}{\rho^2} d\rho$,

to get

$$\mu^{\alpha} - \mu^{\beta} = RT(z^{\alpha} - z^{\beta}) + RT\ln\left(\frac{\rho^{\alpha}}{\rho^{\beta}}\right) + \int_{\rho^{\beta}}^{\rho^{\alpha}} \frac{P - \rho RT}{\rho^2} d\rho \qquad (6)$$

Relating μ^β to a standard potential μ^0, defined as the chemical potential of the perfect gas at a standard density $\rho^0 = 1\,\mathring{A}^{-3}$ gives

$$\mu^\beta = \mu^0 + RT \ln \frac{\lambda^\beta}{\rho^0} \tag{7}$$

If we let $\rho^\beta \to 0$ then $z^\beta = 1$ and we can replace the activity λ^β by ρ^β and substitute the above eqn (7) into the preceding one (6) to give

$$\mu^\alpha - \mu^0 = RT(z^\alpha - 1) + RT \ln\left(\frac{\rho^\alpha}{\rho^0}\right) + \int_0^{\rho^\alpha} \left(\frac{P - \rho RT}{\rho^2}\right) d\rho \tag{8}$$

where $\mu^\alpha - \mu^0 = \mu$ the chemical potential we will be referring to, so that we can dispense with the superscript α:

For a pure gas at pressure P and density ρ we can therefore calculate the chemical potential μ using this reference state, if we have the equation of state for it:

$$\mu = RT(z-1) + RT \ln\left(\frac{\rho}{\rho^0}\right) + \int_0^{\rho} \left(\frac{P - \rho RT}{\rho^2}\right) d\rho \tag{9}$$

Now let us consider a binary mixture. Use a simple, not so accurate virial equation of state with two virial coefficients only:

$$P = RT(\rho + \rho^2 B) \tag{10}$$

which we can easily extend to a mixture.

For a binary mixture, the virial eqn of state is

$$P = RT\left(\rho + \rho_1^2 B_{11} + 2\rho_1\rho_2 B_{12} + \rho_2^2 B_{22}\right) \quad (11)$$

where B_{11} and B_{22} are the second virial coeffs of pure fluid 1 and pure fluid 2 respectively. B_{12} is a cross term, found experimentally for a particular binary mixture (that is, of fluid 1 and fluid 2). Assume all 3 virials are known as a function of temperature.

Subst (10) into (9):

$$\mu = 2RTB\rho + RT\ln(\rho/\rho^0) \quad (12)$$

for a pure gas

The Helmholtz free energy of a fluid mixture if the virial eqn of state containing only 2 virial coeffs is used, is:

$$A = \sum_i n_i \mu_i^0 + RT\sum_i n_i\left[\ln\left(\frac{n_i RT}{P^0 V}\right) - 1\right] + \frac{RT}{V}\sum_i\sum_j n_i n_j B_{ij} \quad (13)$$

For a binary mixture,

$$\mu_1 = (\partial A/\partial n_1)_{n_2} \quad \text{and} \quad \mu_2 = (\partial A/\partial n_2)_{n_1} \quad (14)$$

$$\mu_1 - \mu_1^0 = 2RT(\rho_1 B_{11} + \rho_2 B_{12}) + RT\ln\left(\frac{\rho_1}{\rho^0}\right) \quad (15)$$

$$\mu_2 - \mu_2^0 = 2RT(\rho_2 B_{22} + \rho_1 B_{12}) + RT\ln\left(\frac{\rho_2}{\rho^0}\right) \quad (16)$$

where again we will be using $\mu_1 - \mu_1^0$ itself and $\mu_2 - \mu_2^0$ itself as the chemical potentials in the simulations.

1. First step is to choose the equilibrium gas mixture (the bulk phase):

   specify T, P_1, P_2

   Calculate P_{tot} using eq. (11)

   calculate μ_1 using eq. (15)

   μ_2 using eq. (16)

   mole fraction in the bulk phase is

   $$y_1 = P_1 / (P_1 + P_2)$$

2. Now ready to begin the simulation.

   Parameters are : T, μ_1, μ_2, y_1

3. Markov chain is

   choose create/annih

   choose create/annih

   displace a random molecule

   a) choose to create or annihilate

   choose 1 or 2 according to y_1

   1 2

   choose 1 or 2 according to ~~x_1~~ y_1

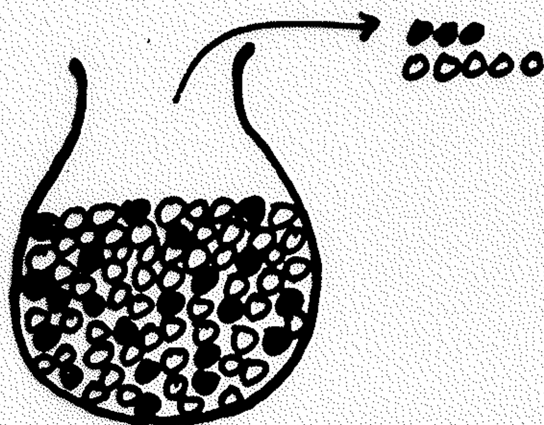
   1 2

• What is the probability of drawing K balls n of them black out of an urn with M balls of which N_0 are black?

$$\binom{M}{K} \text{ or } C_M^K = \frac{M!}{K!\,(M-K)!}$$

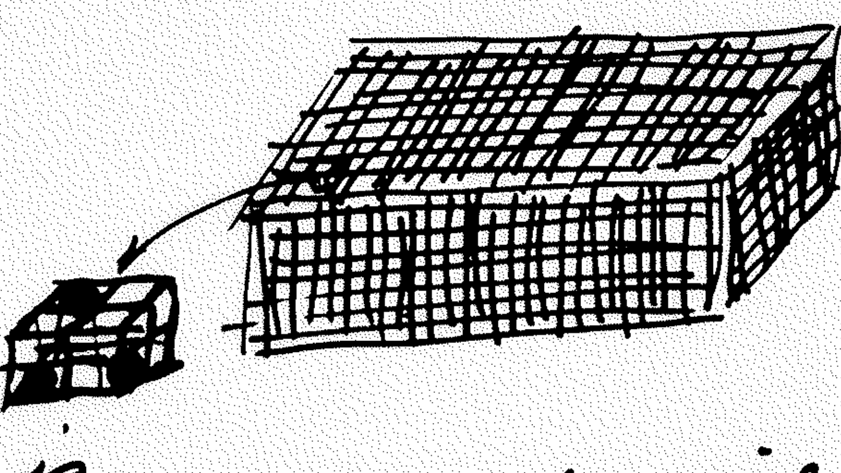
Answer:

$$P_n = \frac{\binom{N_0}{n}\binom{M-N_0}{K-n}}{\binom{M}{K}}$$



Exactly the same answer as the question: What is the probability of finding a cell with n particles when there are a total of N_0 particles distributed among M sites, given that a site can only be occupied by one particle and that each cell has exactly K sites?

$$P_n = \frac{\binom{N_0}{n}\binom{M-N_0}{K-n}}{\binom{M}{K}}$$



Correspondence is
each black ball represents an occupied site
each white ball represents an empty site

Let both $M \to$ very large and $N_0 \to$ very large

What becomes of P_n?

Let number of cells $= Z$ $\qquad M = KZ$

Let $\langle n \rangle$ be the average occupancy $\qquad N_0 = \langle n \rangle Z$

$$P_n(\langle n \rangle) = \frac{\binom{N_0}{n}\binom{M-N_0}{K-n}}{\binom{M}{K}} = \frac{\binom{\langle n \rangle Z}{n}\binom{(K-\langle n \rangle)Z}{K-n}}{\binom{KZ}{K}}$$

$$= \frac{\dfrac{(\langle n \rangle Z)!}{n!(\langle n \rangle Z - n)!} \quad \dfrac{[(K-\langle n \rangle)Z]!}{(K-n)!((K-\langle n \rangle)Z - K + n)!}}{\dfrac{(KZ)!}{K!(KZ-K)!}}$$

Approximation:

$$\frac{N!}{(N-n)!} = \frac{N(N-1)(N-2)(N-3)\cdots}{(N-n)(N-n-1)(N-n-2)\cdots} = \underbrace{N(N-1)\cdots(N-n+1)}_{n \text{ terms}}$$

$n \ll N$ so For very large N this is $\approx N^n$

$$\lim_{Z \to \infty} P_n(\langle n \rangle) = \frac{K!}{n!(K-n)!} \cdot \frac{(\langle n \rangle Z)^n [(K-\langle n \rangle)Z]^{K-n}}{(KZ)^K}$$

$$= \frac{K!}{n!(K-n)!} \frac{\langle n \rangle^n (K-\langle n \rangle)^{K-n}}{K^K} \cdot \frac{Z^n Z^{K-n}}{Z^K} \to 1$$

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What becomes of P_n ?

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$$= \frac{\dfrac{(\langle n \rangle Z)!}{n!\,(\langle n \rangle Z - n)!}\;\dfrac{[(K-\langle n \rangle)Z]!}{(K-n)!\,((K-\langle n \rangle)Z - K + n)!}}{\dfrac{(KZ)!}{K!\,(KZ-K)!}}$$

Approximation:

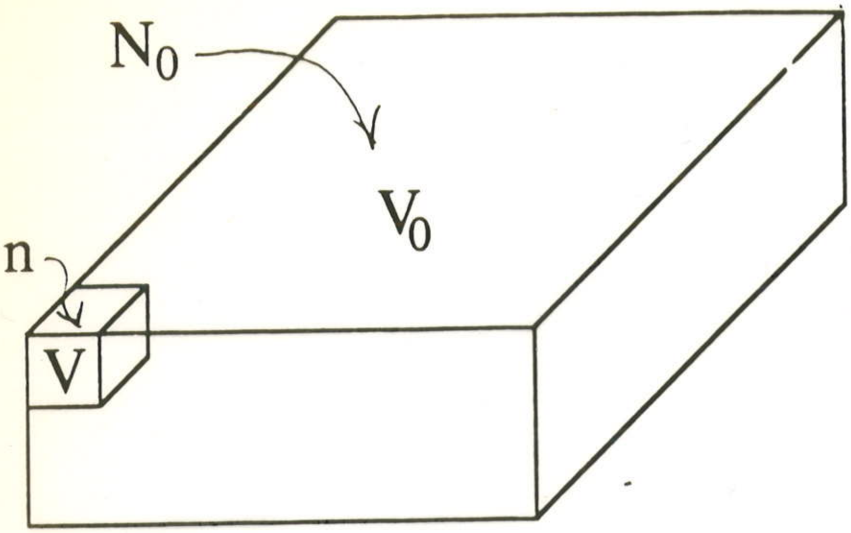
$$\frac{N!}{(N-n)!} = \frac{N(N-1)(N-2)(N-3)\cdots\cdots}{(N-n)(N-n-1)(N-n-2)\cdots\cdots} = \underbrace{N(N-1)\cdots(N-n+1)}_{n \text{ terms}}$$

$n \ll N$ so For very large N this is $\approx N^n$

$$\lim_{Z\to\infty} P_n(\langle n \rangle) = \frac{K!}{n!\,(K-n)!} \cdot \frac{(\langle n \rangle Z)^n\,[(K-\langle n \rangle)Z]^{K-n}}{(KZ)^K}$$

$$= \frac{K!}{n!\,(K-n)!}\;\frac{\langle n \rangle^n (K-\langle n \rangle)^{K-n}}{K^K} \cdot \frac{Z^n Z^{K-n}}{Z^K} \to 1$$

The Hypergeometric Distribution



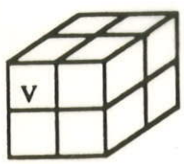
No. of zeolite cavities

$$Z = \frac{V_0}{V} \sim 10^{20}$$

Total no. of sites

$$M = \frac{V_0}{v}$$

No. of sites per cavity



$$K = \frac{V}{v} \sim 8$$

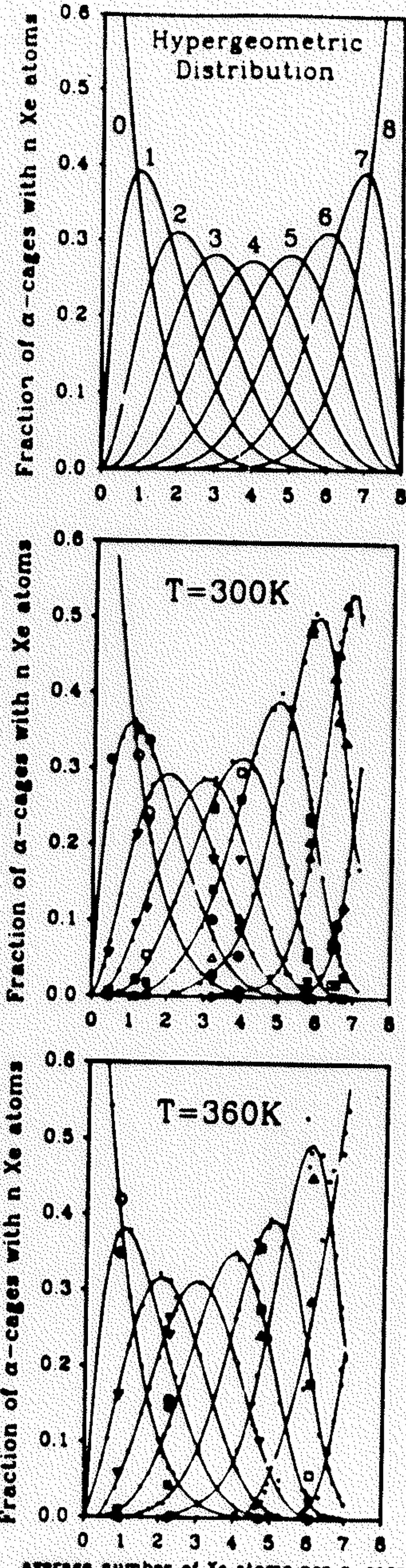
Average number atoms/cavity

$$\langle n\rangle = \frac{N_0}{(V_0/V)}$$

$$H_n(\langle n\rangle) = \frac{\dfrac{N_0!}{n!(N_0-n)!}\;\dfrac{(M-N_0)!}{(K-n)!(M-N_0-[K-n])!}}{\dfrac{M!}{K!(M-K)!}}$$

$$\lim_{Z\to\infty} H_n(\langle n\rangle) = \frac{\langle n\rangle^{n}(K-\langle n\rangle)^{(K-n)}}{K^{K}}\;\frac{K!}{n!(K-n)!}$$

How well does the hypergeometric distribution represent the actual distribution (EXPT) or distributions from "realistic" simulations?



The intrinsic probability of finding a blue particle in the mixture of blues and reds =

$$\frac{\langle i \rangle_{blue}}{\langle i \rangle_{blue} + \langle m \rangle_{red}}$$

The number of ways of arranging 4 blues and ~~3 reds~~ is $\frac{7!}{4!\,3!}$

$$f(\underset{\text{blue}}{4}, \underset{\text{red}}{3}) = \frac{\frac{7!}{4!3!} H(7) \left(\frac{\langle i \rangle}{\langle i \rangle + \langle m \rangle}\right)^4 \left(\frac{\langle m \rangle}{\langle i \rangle + \langle m \rangle}\right)^3}{\frac{7!}{0!7!}\left(\frac{\langle i \rangle}{\langle i \rangle + \langle m \rangle}\right)^0 \left(\frac{\langle m \rangle}{\langle i \rangle + \langle m \rangle}\right)^7 + \frac{7!}{1!6!}\left(\frac{\langle i \rangle}{\langle i \rangle + \langle m \rangle}\right)^1 \left(\frac{\langle m \rangle}{\langle i \rangle + \langle m \rangle}\right)^6 + \cdots + \frac{7!}{7!0!}\left(\frac{\langle i \rangle}{\langle i \rangle + \langle m \rangle}\right)^7 \left(\frac{\langle m \rangle}{\langle i \rangle + \langle m \rangle}\right)^0}$$

This simplifies to, in general, for $i + m = n$:

$$f(i, m) = H(n) \frac{\langle i \rangle^i}{i!} \frac{\langle m \rangle^m}{m!} \frac{1}{\sum_{k=0}^{n} \frac{\langle i \rangle^k}{k!} \frac{\langle m \rangle^{n-k}}{(n-k)!}}$$

The fraction of the cells that have exactly i blue particles and m red particles

where $H(n) = \frac{\langle n \rangle^n (8 - \langle n \rangle)^{8-n}}{8^8} \frac{8!}{n!\,(8-n)!}$

= fraction of the cells having exactly n particles regardless of the number of red or blue among the n

DISTRIBUTIONS OF the molecules of a binary mixture. A SIMPLE MODEL

Question:

What is the probability of finding a cell with i blue particles and m red particles ($i+m=n$) when there are a total of N_0 particles of which I_0 are blue and M_0 are red?

Model: Assume that the particles are distributed among M sites, given that a site can only be occupied by one particle and that each cell has exactly K sites.

- For a binary mixture, assume that red and blue particles compete equally for the K sites in each cell.

Cast in the form of average occupancies

Z cells altogether

$M = KZ$ sites altogether (let $K = 8$)

$\langle i \rangle = \frac{I_0}{Z}$ average number of blue particles per cell

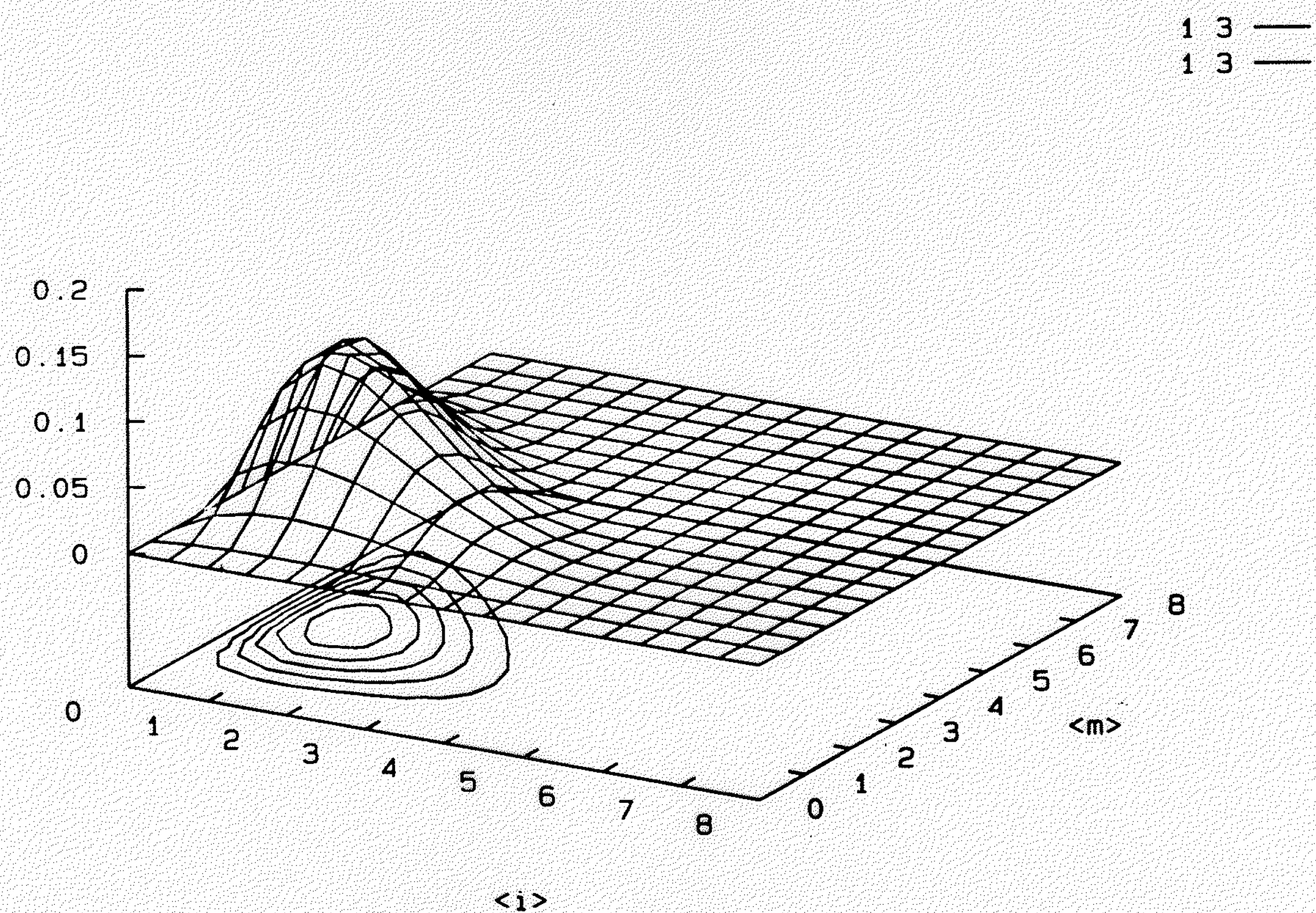
$\langle m \rangle = \frac{M_0}{Z}$ average number of red particles per cell

Distribution:

What is the fraction of cells that have exactly 4 blue and 3 red particles?

call this $f(\underset{\text{blue}}{4}, \underset{\text{red}}{3})$

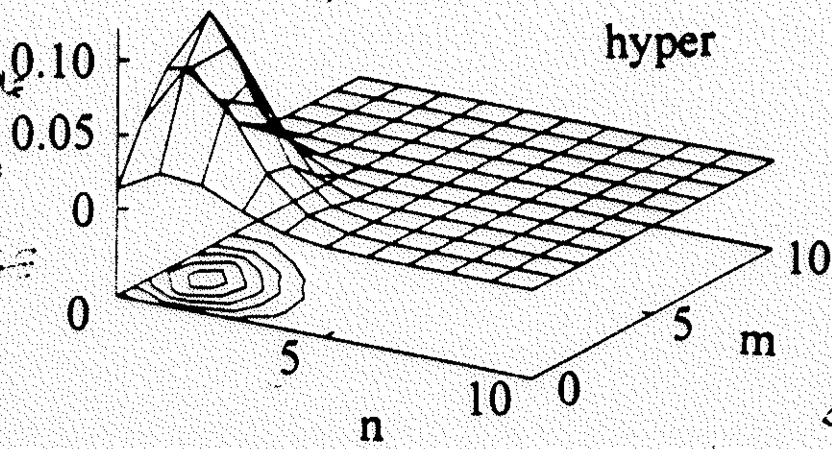
F (1, 3) IN ALPHA CAGES



COMPONENT ATOMS ARE DISTINGUISHABLE BUT EQUIVALENT IN COMPETITION FOR 8 LATTICE SITES PER CAGE UNDER MUTUAL EXCLUSION

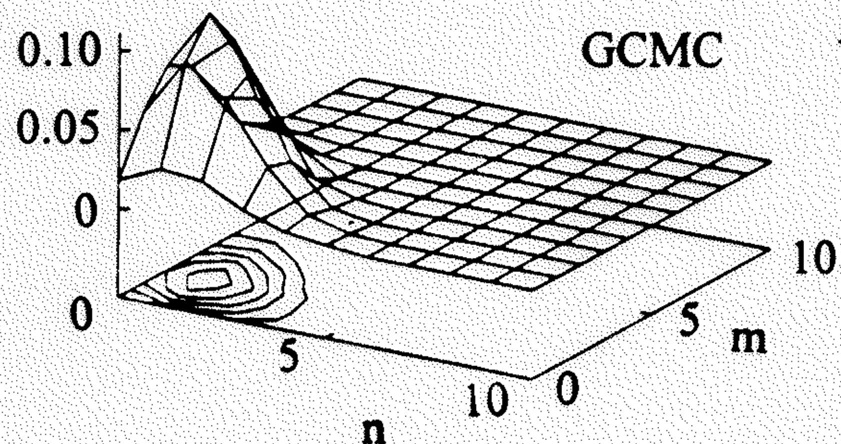
A SIMPLE MODEL for the DISTRIBUTION

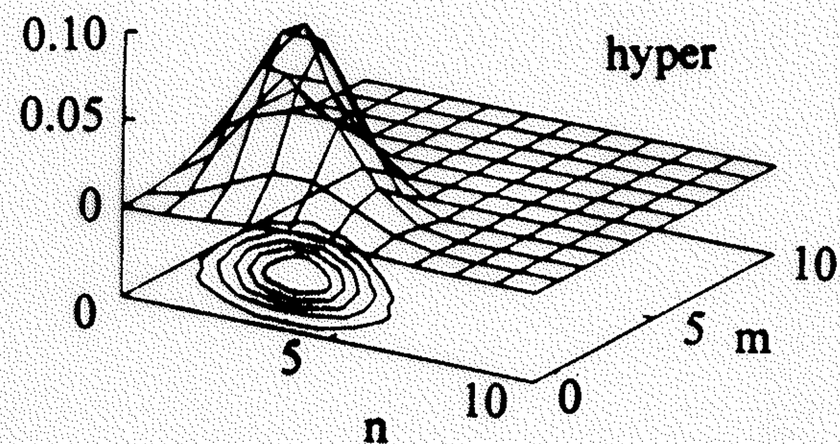
$f(Xe_n Ar_m)$



$\langle n \rangle_{Xe} =$ [illegible]

$\langle m \rangle_{Ar} = 2.083$





$\langle n \rangle_{Xe} = 2.429$

$\langle m \rangle_{Ar} = 3.140$

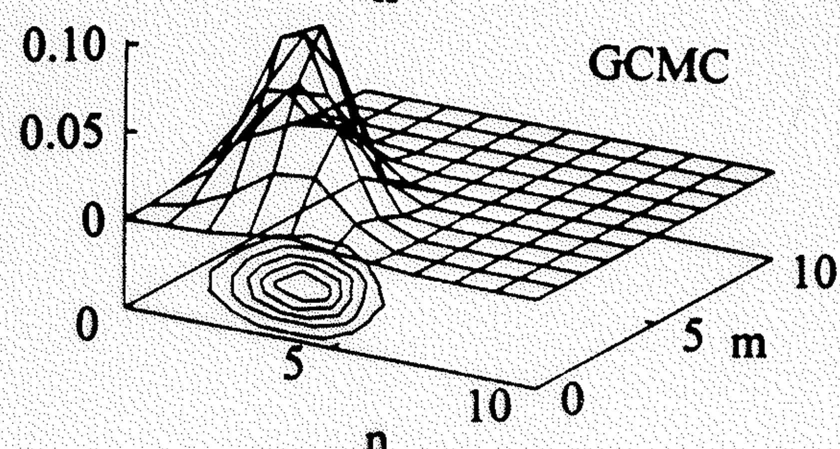
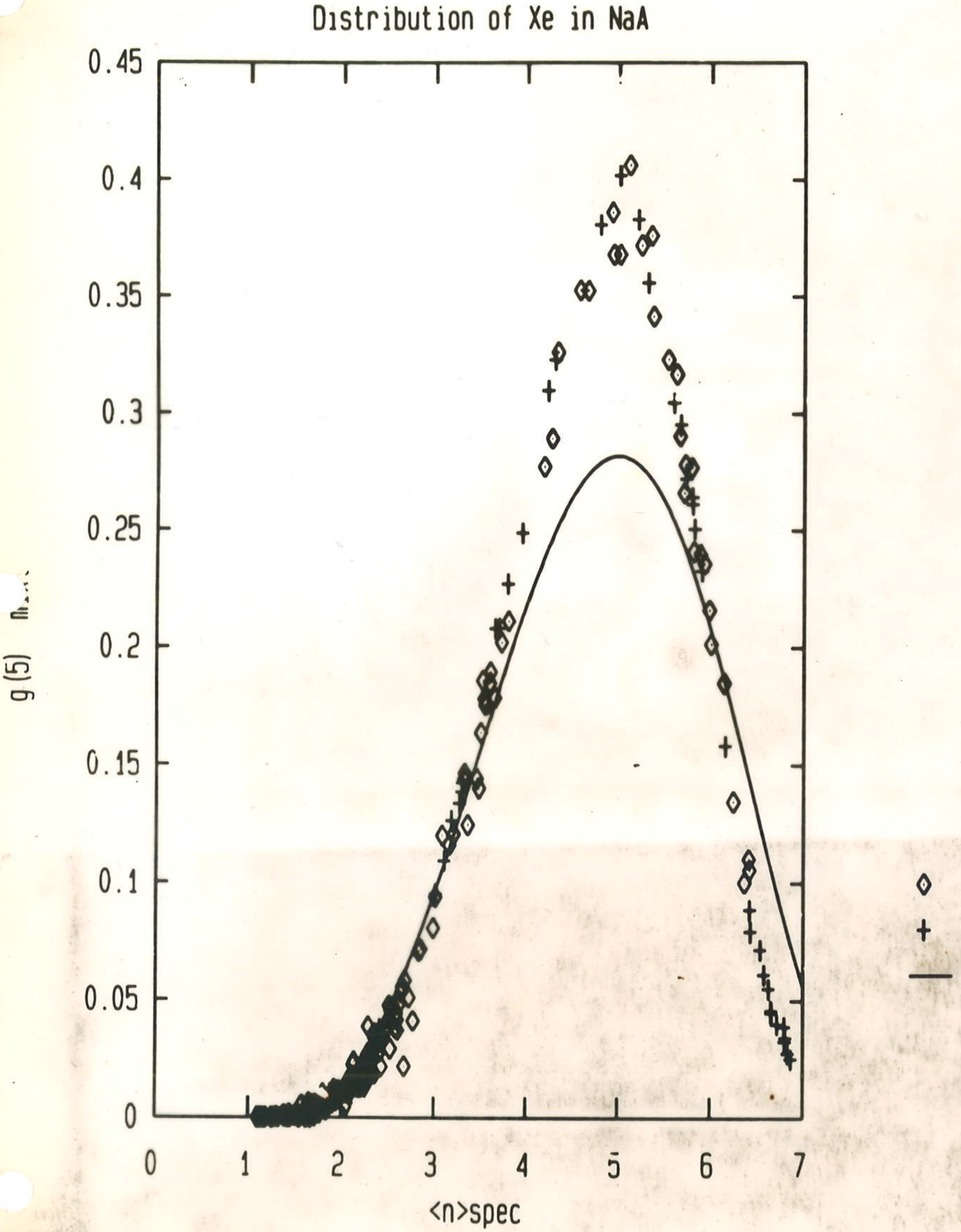


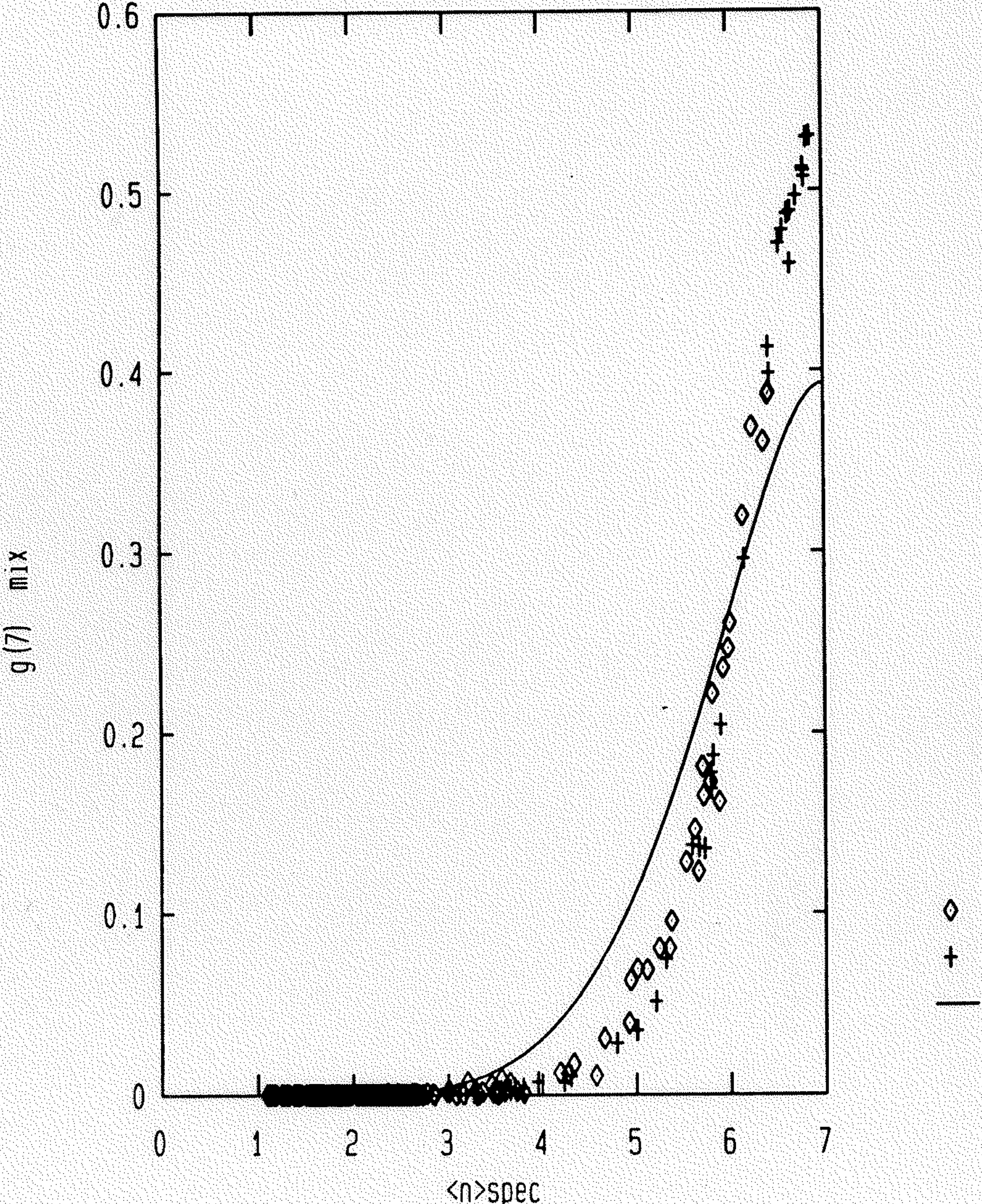
Table VI. Positive values of [$f(Xe_iAr_j)$-$f(Xe_jAr_i)$] for a Xe-Ar mixture in zeolite Na*A* $\langle n \rangle_X$ $\langle m \rangle_{Ar}$ = 3.65, obtained from GCMC simulations. Shown are the number of Xe and Ar aton cluster and the values of [$f(Xe_iAr_j)$-$f(Xe_jAr_i)$] > 0.

i+j									
1	1,0 none[a]	0,1 none							
2	2,0 none		0,2 none						
3	3,0 .00008	2,1 .00005	1,2	0,3					
4	4,0 .0006	3,1 .00114		1,3	0,4				
5	5,0 .0040	4,1 .0107	3,2 .0067	2,3	1,4	0,5			
6	6,0 .00567	5,1 .0225	4,2 .0338		2,4	1,5	0,6		
7	7,0 .00117	6,1 .00923	5,2 .0230	4,3 .0110	3,4	2,5	1,6	0,7	
8	8,0	7,1	6,2	5,3		3,5 .0142	2,6 .0194	1,7 .0038	0,8 .0001
9	9,0	8,1	7,2	6,3	5,4	4,5 .0170	3,6 .0220	2,7 .0153	1,8 .0022



Distribution of Xe in NaA
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
g(5)
0
1
2
3
4
5
6
7
<n>spec

Distribution of Xe in NaA



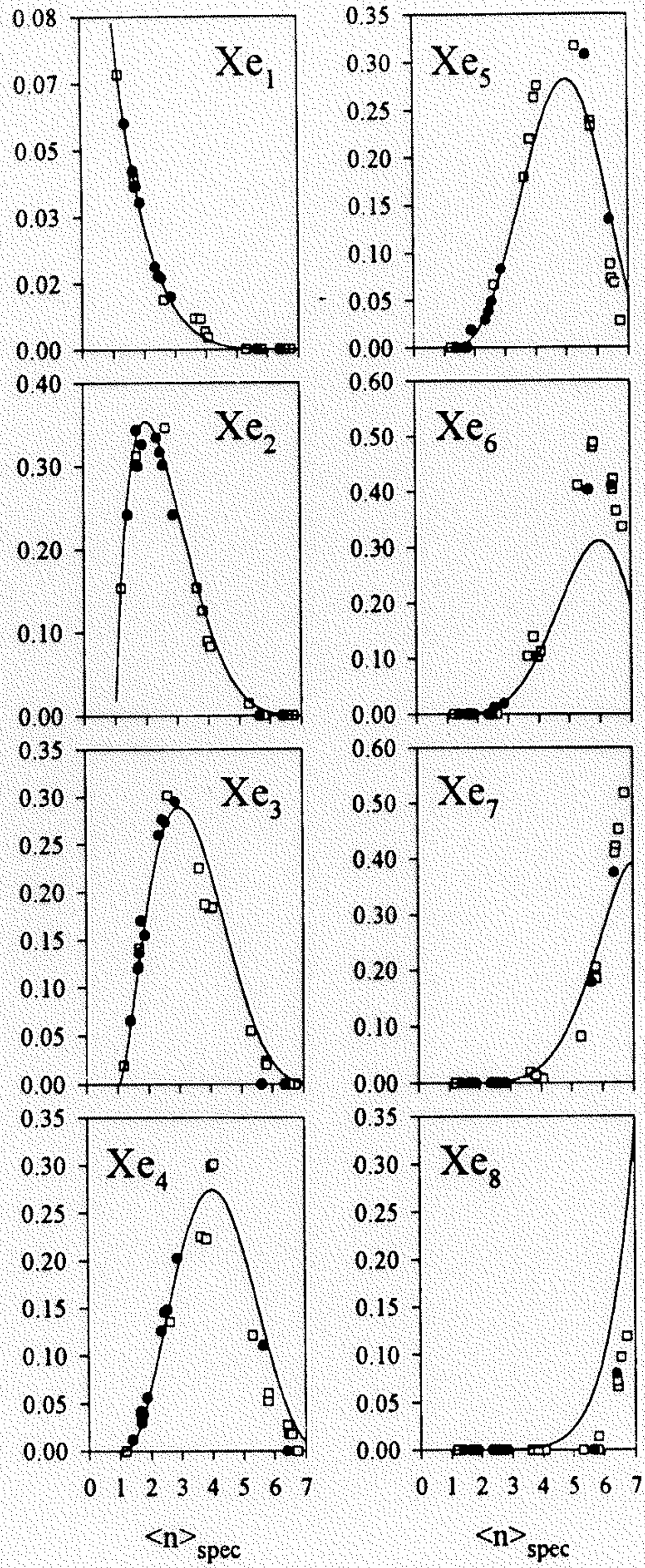


Fig. 14. Experimental equilibrium distribution of Xe atoms at 300 K *among those cages occupied by Xe atoms*. Shown are the fraction *g(n)* of cages containing Xe_n in samples of zeolite Na*A* containing: (❐) pure Xe and (●) a mixture of Xe and Ar. The fractions predicted by the hypergeometric distribution for 8 equivalent lattice sites is shown as the solid curve in each case.

We can use the fractions $f(i,m)$ to calculate averages such as: for a constant i

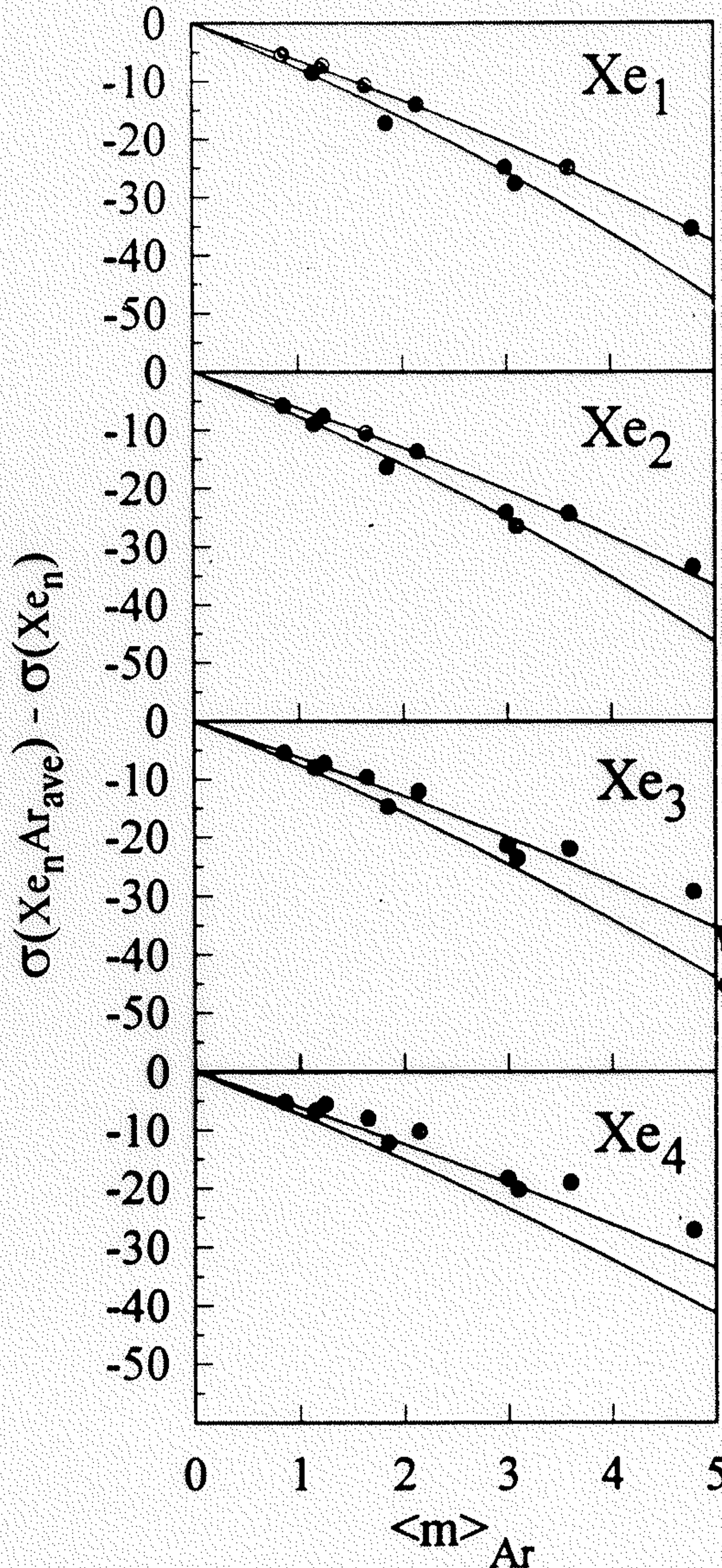
$$\langle \sigma(Xe_i\,A_{average}) \rangle = \frac{\sum_{m=0} \sigma(Xe_i\,A_m)\, i\, f(i,m)}{\sum_{m=0} i\, f(i,m)}$$

The fraction of cells containing i Xe atoms is $P_i = \sum_{m=0} f(i,m)$

Red and blue particles competing equally for the 8 sites in a cell means that

$$\underset{\text{blue}\ \ \text{red}}{f(n,m)} = \underset{\text{blue}\ \ \text{red}}{f(m,n)}$$ for all m and n combinations

That is, the particles are equivalent.



The points are EXPERIMENTAL DATA

$\langle n \rangle_{Xe} = 0.81 - 1.54$

$\langle n \rangle_{Xe} = 2.16 - 2.77$

The curves are based on simple model distribution for $\langle n \rangle_{Xe} = 1.00$ and $\langle n \rangle_{Xe} = 2.40$

using $\sigma(Xe_n Ar_m)$ mixed cluster