An Analysis of the Statistical Model Adsorption Isotherm

R. D. Kaminsky and P. A. Monson
Dept. of Chemical Engineering, University of Massachusetts, Amherst, MA 01003

The statistical model adsorption isotherm developed by Ruthven and coworkers and used in the prediction and correlation of adsorption in microporous materials especially zeolites is critically examined from the perspective of statistical mechanics. This is done by applying the method to a class of molecular models for which the statistical thermodynamics may be solved analytically without approximation. The models considered are finite length single component and binary one-dimensional systems in which the molecules interact via square well potentials. These are among the simplest realistic yet analytically solvable molecular models of adsorption in porous materials. Our analysis clarifies the theoretical status of the Ruthven approach as well as revealing some of the weaknesses in it.

Introduction

One of the most useful applications of ideas from statistical mechanics to the engineering thermodynamics of adsorption equilibrium is the statistical model isotherm (SMI) method developed by Ruthven and coworkers (Ruthven, 1971; Ruthven et al., 1973) for the prediction and correlation of the adsorption of gases in zeolites. The Ruthven statistical model isotherm (RSMI) addresses the problem of calculating the equilibrium between a bulk gas mixture and a mixture adsorbed in a porous material made up of identical independent cavities which can accommodate a limited number of molecules. The approach is thermodynamically consistent and can be derived by a series of approximations starting from the exact statistical mechanics in the grand canonical ensemble (Ruthven, 1984).

In the RSMI the calculation of the adsorption isotherm is made possible by an approximate decomposition of the configurational integrals which appear as coefficients in the expansion of the grand partition function in powers of the activity. The configurational integrals for a single pore are factorized into three terms: a term describing interactions of single adsorbate molecules with the cavity potential field, a free-volume contribution which describes effects associated with the finite size of the molecules, and a contribution describing the effects of attractive adsorbate-adsorbate interactions. The principal approximations in the RSMI may be summarized as follows:

- The adsorbate-adsorbent potential field is uniform throughout the pore.
- The adsorbate-adsorbate repulsive interactions can be modeled by the van der Waals excluded volume.
- The contribution from adsorbate-adsorbate attractive interactions can be modeled by a mean-field expression which is linear in the number of molecules in the pore.

The RSMI has proved fairly successful for the correlation of pure component and prediction of multicomponent adsorption, especially for light hydrocarbons in small zeolite pores (Ruthven and Loughlin, 1972; Ruthven et al., 1973; Rolniak and Kobayashi, 1980; Miller et al., 1987; Loughlin et al., 1990). For pure component isotherms the RSMI is not predictive but can often be used to correlate experimental data, using two adjustable parameters: the Henry's Law constant and the ratio of the molecular volume to the pore volume. The effects of adsorbate-adsorbate interactions are often neglected in practice (Ruthven, 1976). In the form most often used the RSMI can predict multicomponent adsorption from pure component parameters. Due to the approximations used in developing the approach, in many cases the parameters obtained from fitting the pure component isotherms are unphysical (Miller et al., 1987). In such cases it might be found that the Henry's constant or the number of molecules per cavity at saturation differ from those observed experimentally.

Perhaps the most striking failure of the RSMI occurs for systems which display large deviations from ideal adsorbed

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Correspondence concerning this article should be addressed to P. A. Monson.

solution behavior for binary and multicomponent systems. There are numerous instances where mixtures which behave ideally in the bulk show adsorption azeotropes and other signatures of nonideality when adsorbed in zeolites. Explanations for such behavior have most often been given in terms of energetic heterogeneity (Ruthven, 1984; Valenzuela et al., 1988). The idea being that one of the components sees a more nonuniform gas-solid intermolecular potential field than the others. This would occur, for example, in the case of the interaction between the charge distributions in the adsorbate molecules and the ion distribution in the zeolite.

The purpose of this article is to present a detailed investigation of the theoretical underpinnings of the RSMI with the goal of developing some insights which might form the basis for improved methods. In the context of traditional engineering thermodynamics the approach we take might be viewed as somewhat unconventional. Rather than focusing on further comparisons of the RSMI with experimental data we have chosen to apply the RSMI to some molecular models of adsorption in porous materials for which the statistical mechanics can be solved exactly without approximation. In this way we may view the RSMI as an approximation to the statistical mechanics of a particular molecular model of adsorption. We can then examine the approximate treatment of adsorption thermodynamics implicit in the RSMI independently of details of the intermolecular forces in the system.

The specific molecular models we consider are one-dimensional (1-D) systems of rods confined to a 1-D cavity with square-well potentials describing the interactions between the molecules and the cavity walls and between the molecules themselves. Figure 1 schematically depicts a binary bulk fluid in equilibrium with a 1-D cavity. Recently one of us (Monson, 1990) presented the exact solution for the properties of a 1-D binary mixture of particles interacting with nearest-neighbor square-well potentials and interacting with walls via square-well potentials. This is the model system upon which much of the work described in this article is based. It is perhaps the simplest exactly solvable molecular model for selective adsorption of a fluid mixture in a porous material, in which attractive interactions as well as molecular size differences between the adsorbed molecules are taken into account. Of course the issue of dimensionality is an important one and it is fair to argue that 1-D behavior is a rarity in nature. We do not wish to suggest that these models provide a complete picture of the molecular physics of adsorption in porous materials. Nonetheless, they can capture much of the qualitative behavior associated with realistic three-dimensional confined systems (Robledo and Rowlinson, 1986; Monson, 1990). Moreover the simplicity of the models provides an opportunity to examine with some clarity the relationship between the adsorption equilibria and details of the molecular level behavior. The physical effects observed in adsorption in real porous materials which are realistically captured by these molecular models include:

- The influence of confinement upon thermodynamic properties.
- Selective adsorption arising from differences in interactions with pore walls.
- Selective adsorption arising from molecular size differences.
- The influence of adsorbate-adsorbate interactions.
- Effects of energetic heterogeneity.

It is important to emphasize that in adsorption in porous materials molecular confinement is one of the principal influences upon the thermodynamics. The thermodynamics of these 1-D models exhibits a dependence upon confinement which is quite realistic (Robledo and Rowlinson, 1986). Indeed, studies of 1-D systems (Percus, 1976, 1982a,b) have provided the basis for important developments in the statistical mechanics of adsorption in porous materials (Kierlik and Rosinberg, 1990, 1991; Kierlik et al., 1992).

The article briefly reviews the SMI as implemented by Ruthven and coworkers. The 1-D models considered in this work are described as well as the exact solution of the statistical thermodynamics. The results obtained by applying the RSMI to a variety of pure component and binary 1-D systems are compared with the exact results, and the theoretical reasons underlying the differences between the RSMI predictions and the exact results are analyzed. We also address briefly the issue of energetic heterogeneity. Finally, our results are summarized, together with some suggestions for future work on improvements over the RSMI.

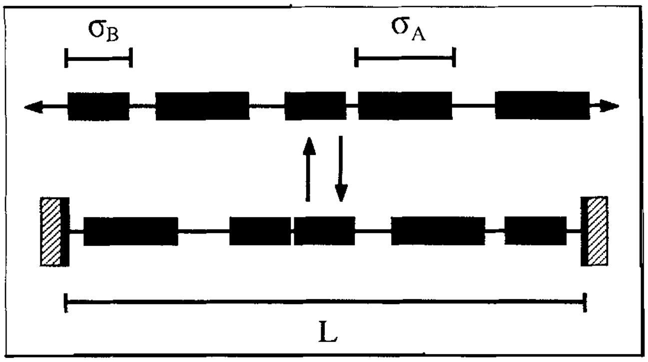


Figure 1. A schematic of a binary 1-D bulk mixture with particles of size σ_A and σ_B in equilibrium with mixture in a 1-D cavity of length L.

Statistical Model Isotherm

A derivation of the statistical model isotherm starts with the grand partition function expressed as a power series in the activity. We have:

$$\Xi = \sum_{N=0}^{\infty} \zeta^N Z_N \qquad (2.1)$$

where ζ is the activity multiplied by the molecular partition function (that is, $\zeta = q\, e^{\mu/kT}$) and Z_N is the configurational integral for N molecules in the system. The function Z_N involves an integral of the adsorbate-solid and adsorbate-adsorbate interaction Boltzmann factor over the coordinates of N adsorbate particles and is given by:

$$Z_N = \frac{1}{N!} \int_V \exp(-U(r_1, \ldots, r_N)/kT) dr_1 \ldots dr_N \qquad (2.2)$$

where r_i gives the coordinates of particle i, U the total potential energy, and V the system volume. Once the grand partition function is determined, all thermodynamic properties can be obtained by differentiation. For example the ensemble average number of molecules in the system is obtained by differentiating with respect to the activity.

$$\langle N\rangle=\zeta\left(\frac{\partial ln\Xi}{\partial\zeta}\right)=\frac{\zeta}{\Xi}\left(\frac{\partial\Xi}{\partial\zeta}\right)=\frac{\sum\limits_{N=1}^{\infty}N\zeta^{N}Z_{N}}{\sum\limits_{N=0}^{\infty}\zeta^{N}Z_{N}} \tag{2.3}$$

This is the general equation for the adsorption isotherm in the grand ensemble. For a system of finite volume only a finite number of molecules which can be accommodated, the partition function becomes a polynomial and the adsorption isotherm, Eq. 2.3, becomes a rational function. For the case where only the one molecule is adsorbed per cavity the approach immediately yields the Langmuir isotherm. Other more sophisticated isotherms may be developed by approximating the configurational partition functions for different numbers of molecules in the cavity.

Except for simple systems, the configurational integrals cannot be evaluated in closed form and approximations are necessary. Ruthven (1971) suggested that the configurational integrals may be decomposed into the product of three terms: a single molecule contribution, Z_1, raised to the Nth power, describing the interaction of the adsorbing molecules with the cavity walls; a free-volume contribution, $Z_{f.v.}$, due to the repulsive part of the adsorbate-adsorbate interactions; and a mean-field contribution, $Z_{m.f.}$, due to the attractive part of the adsorbate-adsorbate interactions. This leads to

$$Z_N=Z_1^N Z_{f.v.}Z_{m.f.} \tag{2.4}$$

where

$$Z_1=K \tag{2.5a}$$

$$\begin{aligned}Z_{f.v.}&=1 && N\leq 1\\ &=\frac{1}{N!}\left(1-\frac{Nb}{\nu}\right)^{N} && N\geq 2\\ &=0 && N\geq\frac{\nu}{b}\end{aligned} \tag{2.5b}$$

$$\begin{aligned}Z_{m.f.}&=1 && N\leq 1\\ &=\exp\left(\frac{Nb\epsilon}{\nu kT}\right) && N\geq 2\end{aligned} \tag{2.5c}$$

where K is the Henry's constant with respect to activity and particle number (not density), b is the excluded volume associated with the adsorbate particles, ν is the volume of the pore, and ϵ is a measure of the attractive adsorbate-adsorbate interaction.

These approximations are essentially the simplest sensible mathematical forms which could be used. The conditions on the free-volume term insure that the $Z_{N=1}$ is identically K and Z_N is identically zero for N greater than the maximum number of particles which can fit in the cavity. The conditions on the mean-field term insure that there are no adsorbate-adsorbate interaction contributions if only one particle is in the cavity. Equation 2.5a can be interpreted as implying a uniform potential field in the cavity affecting each particle identically since each particle contributes equally a factor of K to the configurational integral. Equation 2.5b is a simple van der Waals excluded volume approximation. Lastly, Eq. 2.5c is an approximation for the effect of attractive adsorbate-adsorbate interactions. It is not a mean field approximation in the strictest sense since the exponent is linear rather than quadratic in the number of molecules. Moreover, a full mean field treatment would couple the adsorbate-adsorbate interactions to the density inhomogeneity in the system. The linear dependence of the exponent upon particle number has the effect of eliminating contributions from unlike interactions in mixtures, but, as we shall see later, at the price of underestimating the importance of adsorbate-adsorbate interactions as a whole upon the adsorption equilibrium. Combining Eqs. 2.4 and 2.5 gives:

$$\begin{aligned}Z_N&=1 && N=0\\ Z_N&=K && N=1\\ Z_N&=\frac{1}{N!}\left[K\left(1-\frac{Nb}{\nu}\right)\exp\left(\frac{b\epsilon}{\nu kT}\right)\right]^{N} && 2\leq N\leq\nu/b\\ Z_N&=0 && N>\nu/b\end{aligned} \tag{2.6}$$

For the application of this method there are three parameters to be specified: K, b/ν, and ϵ/kT.

Extension of the treatment to multicomponent systems is straightforward (Ruthven 1973, 1984). For multicomponent systems each term decouples except for the free volume term to give:

$$\Xi=\sum_{\{N_i\}=0}^{\infty}\left[\prod_i \zeta_i^{N_i}\right]Z_N \tag{2.7}$$

where

$$Z_N=\left[\prod_i Z_{1i}^{N_i}\right][Z_{f.v.}]\left[\prod_i Z_{m.f._i}\right] \tag{2.8}$$

where

$$Z_{1_i}=K_i \tag{2.9a}$$

$$\begin{aligned}Z_{f.v.}&=1 && \sum_i N_i\leq 1\\ &=\frac{1}{\prod\limits_i N_i!}\left(1-\sum_i\frac{N_ib_i}{\nu}\right)^{N} && \sum_i\frac{N_ib_i}{\nu}<1 \text{ and } N\geq 2\\ &=0 && \sum_i\frac{N_ib_i}{\nu}\geq 1\end{aligned} \tag{2.9b}$$

$$\begin{aligned}Z_{m.f._i}&=1 && N_i\leq 1\\ &=\exp\left(\frac{N_ib_i\epsilon_i}{\nu kT}\right) && N_i\geq 2\end{aligned} \tag{2.9c}$$

The summation in Eq. 2.7 is over all combinations of the number of particles of each species. An especially useful feature of these expressions is the fact that the parameters in the multicomponent equations are the same as those for the individual pure component equations. Hence, multicomponent behavior can be predicted from parameters extracted from fits of the RSMI equations to pure component data.

One-Dimensional Square-Well System

The adsorption model we study in this article is that of a 1-D fluid confined to a 1-D pore (that is, a line segment). In particular, the 1-D fluid is a pure component or binary system consisting of particles interacting through square-well nearest-neighbor potentials. The walls of the pore interact with the fluid similarly through square-well nearest-neighbor potentials. The statistical thermodynamics of this model were solved analytically by Monson (1990).

The key to all the results is the analytic evaluation of the configuration integrals. Here we sketch the derivation only for a single component in a symmetric pore potential field. Since the pore potential acts only on the end particles, the configuration integral of N particles can be written in general as

$$Z(N,L,T)=\frac{1}{N!}\int_0^L\ldots\int_0^L e^{-\beta\phi(x_1)}e^{-\beta\phi(x_N)}\prod_{i<j}^{N}\times e^{-\beta u(|x_j-x_i|)}dx_1\ldots dx_N \quad (3.1)$$

where L is the length of the pore, T is the absolute temperature, β is $1/kT$ where k is the Boltzmann constant, $\phi(x)$ is the adsorbate-adsorbent (pore) potential field, and $u(x)$ is the adsorbate-adsorbate potential. Limiting the interaction potentials to nearest-neighbor square-wells allows for analytic evaluation of Eq. 3.1. In particular, the configuration integrals become convolutions which may be written

$$Z(N,L,T)=\int_0^{\Lambda}e^{-\beta\phi(x_N)}dy_N\int_0^{y_N}e^{-\beta\phi(x_N-x_{N-1})}dy_{N-1}\ldots\int_0^{y_3}e^{-\beta\phi(x_3-x_2)}dy_2\int_0^{y_2}e^{-\beta\phi(x_2-x_1)}e^{-\beta\phi(x_1)}dy_1 \quad (3.2)$$

where $\Lambda=L-N\sigma$ and $y_i=x_i-(i-1/2)\sigma$. The integrals in Eq. 3.2 decouple by applying the Laplace transform. Performing a binomial expansion the Laplace transform may be written

$$\tilde{Z}(N,s,T)=\frac{1}{s^{N+1}}\sum_{n=0}^{N-1}\binom{N-1}{n}e^{(N-1-n)\beta\epsilon}(1-e^{\beta\epsilon})^n \times[e^{2\beta\epsilon_w}e^{-sn\lambda}+2e^{\beta\epsilon_w}(1-e^{\beta\epsilon_w})e^{-s(n\lambda+\lambda_w}+(1-e^{\beta\epsilon_w})^2e^{-s(n\lambda+2\lambda_w)}] \quad (3.3)$$

Performing the inverse transform, which is standard, gives

$$Z(N,L,T)=\sum_{n=0}^{N-1}\binom{N-1}{n}e^{(N-1-n)\beta\epsilon}(1-e^{\beta\epsilon})^n \times[e^{2\beta\epsilon_w}(\Lambda-n\lambda)^N\theta(\Lambda-n\lambda)+2e^{\beta\epsilon_w}(1-e^{\beta\epsilon_w})(\Lambda-n\lambda-\lambda_w)^N\theta(\Lambda-n\lambda-\lambda_w)+(1-e^{\beta\epsilon_w})^2(\Lambda-n\lambda-2\lambda_w)^N\theta(\Lambda-n\lambda-2\lambda_w)] \quad (3.4)$$

where $\theta(x)$ is the Heaviside function. It is reasonably straightforward to extend this derivation to the more complex case of binary adsorption, which is explicitly treated by Monson (1990). With the configurational integral determined, it is a simple matter to calculate the grand partition function and apply Eq. 2.3 to obtain adsorption isotherm. It should be noted from an examination of Eq. 3.4 that a complete specification of the system requires five parameters: the cavity length to adsorbate particle size ratio, L/σ; the wall potential strength, ϵ_w; the wall potential range, λ_w; the adsorbate potential strength, ϵ; and the adsorbate potential range, λ.

We can apply the SMI to this model system as follows. First, the $Z_{m.f.}$ term is rederived, at the same level of approximation as Ruthven's, for a 1-D square-well potential. This produces the analogous form of Eq. 2.9c as

$$\begin{aligned} Z_{m.f.i}&=1 && N_i\leq 1\\ &=\exp\left(\frac{N_i\epsilon_i\lambda_i}{LkT}\right) && N_i\geq 2 \end{aligned} \quad (3.5)$$

where the cavity is of length L and the adsorbate-adsorbate square-well potential is of depth ϵ and of range λ. Second, we can slightly modify the free-volume and cavity terms to produce exact results under an important limiting condition. We start by noting that in 1-D the configurational integral may be written exactly and simply for a confined hard-rod fluid in a uniform potential field. Specifically for the pure component case with a uniform potential field of strength ϵ_c we have

$$\begin{aligned} Z_N&=\exp(N\epsilon_c/kT)\left[\frac{(L-N\sigma)^N}{N!}\right] && L>N\sigma\\ Z_N&=0 && L\leq N\sigma \end{aligned} \quad (3.6)$$

The quantity $L-N\sigma$ represents free-volume which is an exact concept in 1-D, unlike in higher dimensions. For $L>N\sigma$ Eq. 3.6 can be rearranged as follows

$$Z_N=\left[K\left(\frac{L}{L-\sigma}\right)\right]^N\left[\frac{1}{N!}\left(1-\frac{N\sigma}{L}\right)^N\right] \quad (3.7)$$

where

$$K=(L-\sigma)\exp(\epsilon_c/kT) \quad (3.8)$$

and K is the Henry's constant. Equation 3.8 follows from the standard statistical thermodynamic definition of Henry's constant (Steele, 1974)

$$K=Z_1=\int_V\exp\left(\frac{-\phi(r)}{kT}\right)dr \quad (3.9)$$

where $\phi(r)$ is the potential energy field describing the adsorbate-cavity wall interactions.

Noting the similarity between Eq. 3.7 and Eqs. 2.5a-b, for our work we use

$$Z_{1,i} = K_i\left(\frac{L}{L-\sigma_i}\right) \tag{3.10a}$$

$$Z_{f.v.} = \begin{cases} \left[\prod_i \frac{1}{N_i!}\right]\left(1-\sum_i \frac{N_i\sigma_i}{L}\right)^N & \sum_i \frac{N_i\sigma_i}{L} < 1 \\ =0 & \sum_i \frac{N_i\sigma_i}{L} \geq 1 \end{cases} \tag{3.10b}$$

The difference between this formulation and Ruthven's is slight but it does remove one minor and unnecessary level of approximation and produces exact results for the important case of hard particles in a uniform field and hence we apply it in our work. Furthermore for all our calculations, except where noted, we do not assume the bulk to be ideal and use the actual value of activity instead of P/kT as is typically done in other applications of the RSMI. In this way, we remove the error introduced by neglecting bulk nonidealities and thus can more readily assess the SMI approach. Hence the form of Ruthven's SMI we apply is

$$\langle N_i\rangle = \frac{K_i\zeta_i + \sum\limits_{\{N_j\}=0}^{\infty}{}' \left[N_i\left(\prod_j \frac{(K_j\zeta_jL)^{N_j}}{N_j!\,(L-\sigma_j)^{N_j}}\right)\left[\max\left(0,1-\sum_j \frac{N_j\sigma_j}{L}\right)\right]^N \exp\left(\frac{\sum_j N_j\epsilon_j\lambda_j}{LkT}\right)\right]}{1+\sum_j K_j\zeta_j + \sum\limits_{\{N_j\}=0}^{\infty}{}' \left[\left(\prod_j \frac{(K_j\zeta_jL)^{N_j}}{N_j!(L-\sigma_j)^{N_j}}\right)\left[\max\left(0,1-\sum_j \frac{N_j\sigma_j}{L}\right)\right]^N \exp\left(\frac{\sum_j N_j\epsilon_j\lambda_j}{LkT}\right)\right]} \tag{3.11}$$

where j is a component index and the summations over $\{N_j\}$ represent summations over all combinations of the number of each species with the $'$ indicating that only terms with $N \geq 2$ are included. The maximum (max) notation is an equivalent but more compact way of expressing the conditions in Eq. 3.10b.

Test of the RSMI for 1-D Systems

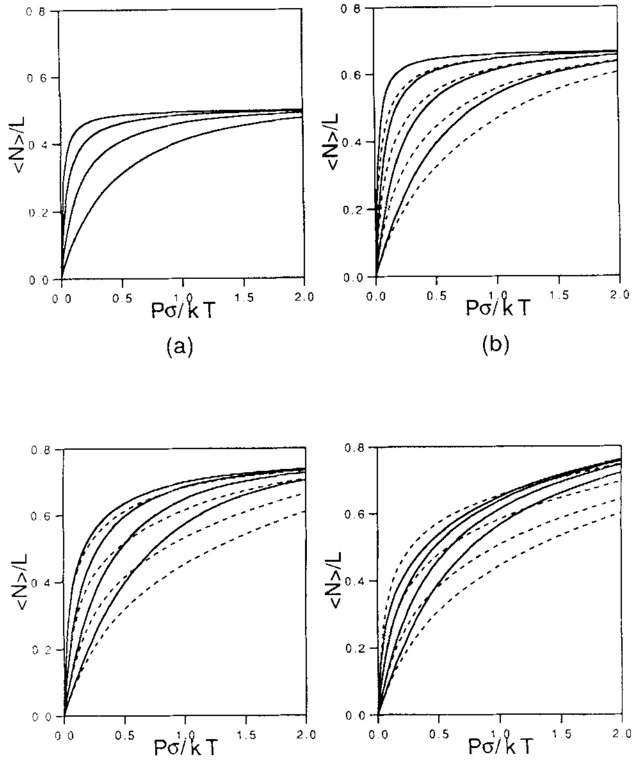
To test the RSMI approach, we have applied Eq. 3.11 to a variety of single component 1-D square-well systems. This section presents our results. Figure 2 shows a comparison of the calculated isotherms from the exact solution and the RSMI. It is important to note that in this test of the RSMI there are no adjustable parameters. The value of K is directly obtained from Eq. 3.9 which becomes for a 1-D cavity of length L with square-well wall potentials of depth ϵ_w and range λ_w

$$K = \int_0^L \exp\left(\frac{-\phi(x)}{kT}\right)dx = 2\lambda_w \exp\left(\frac{\epsilon_w}{kT}\right) + (L-2\lambda_w-\sigma) \tag{4.1}$$

The systems presented in Figure 2 represent a range of cavity length to particle size ratios: $L/\sigma = 2, 3, 4,$ and 6. Furthermore, several wall potential strengths are explored: $\epsilon_w/kT = 1, 2, 3,$ and 4. All the systems have $\epsilon/kT = 1$ and $\lambda = \lambda_w = 0.5\sigma$. We note that since the actual parameter values are used, the very low and very high activity (pressure) values for adsorption should be accurately predicted by the RSMI. The very low activity predictions are accurate since the correct Henry's constants are used. The very high activity predictions are accurate since the correct particle size to cavity length ratios are used which leads to the correct complete filling density. To assess the effect of assuming bulk-nonideality, the $L/\sigma = 6$ case was redone using the ideal gas approximation for activity, $\zeta = P/kT$. Figure 3 presents these results. We note that the quality of the agreement suffers somewhat due to the ideal gas estimate of activity which is too low in this case.

Ruthven (1984) has suggested that in practice the bulk value for ϵ should be used with b/ν (or σ/L) and K adjusted to give the best agreement between the experimental and theoretical isotherms. The bulk value of ϵ can be estimated from critical point data or obtained from second virial coefficient data. By adjusting the values for σ/L and K, much improvement in the agreement between the RSMI and the exact isotherms is achieved. Figure 4 shows a representative comparison for $L/\sigma = 6$. We note that although the agreement is good, it is not possible to fit the entire isotherm accurately in this way. The RSMI is not able to capture accurately both low-pressure adsorption and high-pressure adsorption. The parameters were fitted by minimizing the sum of the squares of the relative error between the RSMI prediction and exact values of adsorption at 60 pressures distributed evenly between $P\sigma/kT = 0$ and $P\sigma/kT = 1.5$. Table 1 lists parameters obtained by fitting the RSMI together with the exact values for several systems. It should be noted that the adjusted values of the parameters are somewhat sensitive to the method of fitting and choice of data points. Nevertheless, the overall quality of the agreement is only moderately sensitive to the details of the fitting procedure.

We now turn to the case of binary mixtures. The system we chose to study is that of a mixture of particles with ratios $\sigma_B/\sigma_A = \epsilon_B/\epsilon_A = 0.6$. All the potentials are conformal with adsorbate-adsorbate interactions of range $\lambda = 0.5\ \sigma_{ij}$ and adsorbate-wall interactions of range $\lambda_w = 0.5\ \sigma_i$. Parameters for the unlike interactions follow the Lorentz-Bethelot combining rules. As in the pure component study, we compared the exact solution against RSMI using both the actual values of σ_A/L,



(a) (b) (c) (d)

Figure 2. Comparison of exact (solid lines) and RSMI predicted (dashed lines) pure component adsorption isotherms for various length systems: (a) L = 2σ; (b) L = 3σ; (c) L = 4σ; (d) L = 6σ.

Each figure depicts isotherms for $\epsilon_w/kT = 1$ (lowest), 2, 3, and 4 (highest). All systems have $\epsilon/kT = 1$ and $\lambda = \sigma/2$. The actual values of K, σ/L, ϵ/kT, and ζ are used in the RSMI predictions.

σ_B/L, K_A, and K_B as well as values chosen to give the best fit for the pure component isotherms. Figure 5 shows the results where the RSMI is used without adjustable parameters for $P\sigma_A/kT = 2$ at several cavity lengths ($L/\sigma_A = 2$, 3, 4, and 6). Figure 5 also shows the effect of using different relative strengths for the wall potentials of the two components. Results for $\epsilon_{A_w}/\epsilon_{B_w} = 1$, 2, 3, and 4 (in all cases $\epsilon_{B_w}/kT = 1$). Figure 6 shows the results of repeating these calculations using parameters obtained by fitting the pure component isotherms as described above (several of the fitted values used are listed in Table 1). We see a noticeable improvement in the agreement.

Analysis of the Strengths and Weaknesses of the RSMI

From Figures 2 and 5 it is clear that without adjustable parameters the RSMI does not in general produce good agreement with the exact results for these model systems. On the other hand, the use of adjustable parameters produces very good agreement for single component systems and moderate agreement for binary systems. Nevertheless the agreement for binary systems though is by no means excellent—the locations of azeotropes especially are poorly predicted.

Of course the mathematical form of RSMI limits the type of behavior it can exhibit. For single component systems, RSMI requires only three parameters to be specified (K, b/ν and ϵ/kT) whereas the 1-D model (Eq. 3.4) indicates that five, not three, parameters are needed (L/σ, ϵ/kT, ϵ_w/kT, λ/σ, and λ_w/σ), although one could argue that the square well ranges are not significant parameters. More importantly, the approximations made for the single molecule and mean-field terms while simple in form and easy to use, do not reflect a significant portion of the adsorption physics. The quality of these approximations are of great importance since if they are inaccurate, the justification for using pure component parameters in multicomponent adsorption predictions is weakened.

The impact of the approximations employed in the RSMI approach can be further understood by comparing the predictions to the analytic 1-D solution in a somewhat different

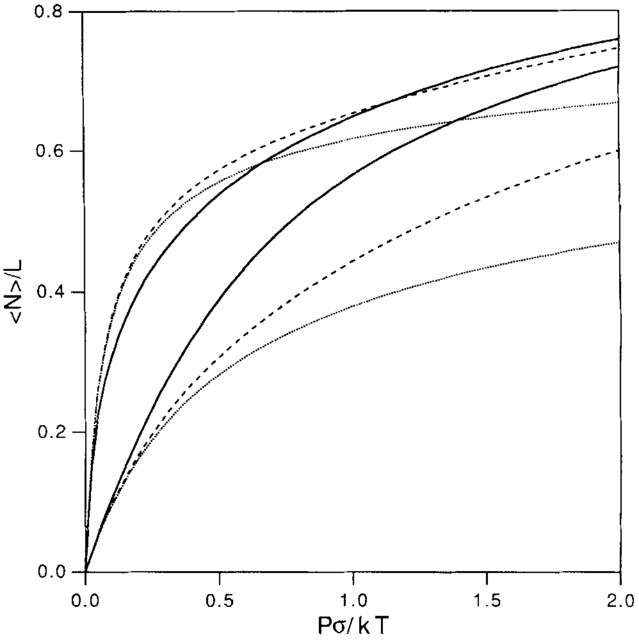


Figure 3. Comparison of pure component adsorption isotherms for a system of $L = 6\sigma$ using exact solution (solid lines), RSMI with nonideal bulk (dashed lines), and RSMI with ideal bulk (dotted lines).

The bulk is assumed to be ideal ($\zeta = P/kT$). The figure depicts isotherms for $\epsilon_w/kT = 1$ (lower) and 4 (higher). Each system has $\epsilon/kT = 1$ and $\lambda = \sigma/2$. The actual values of K, σ/L, and ϵ/kT are used in the RSMI predictions.

Table 1. Comparison of Exact and Fitted Parameters for RMSI for Selected Pure Component Systems

L	ϵ_w	σ_{exact}	σ_{fit}	K_{exact}	K_{fit}
2.0	1.0	0.6	0.547	2.431	2.554
3.0	1.0	0.6	0.494	3.431	3.477
3.0	2.0	1.0	0.897	8.389	10.66
3.0	4.0	1.0	0.977	55.60	99.99
4.0	1.0	0.6	0.488	4.431	4.513
4.0	1.0	1.0	0.746	4.718	4.941
4.0	3.0	1.0	0.873	22.09	22.76
6.0	1.0	0.6	0.483	6.431	6.607
6.0	1.0	1.0	0.738	6.718	7.179
6.0	2.0	1.0	0.794	11.39	11.69
6.0	4.0	1.0	0.974	58.60	39.97

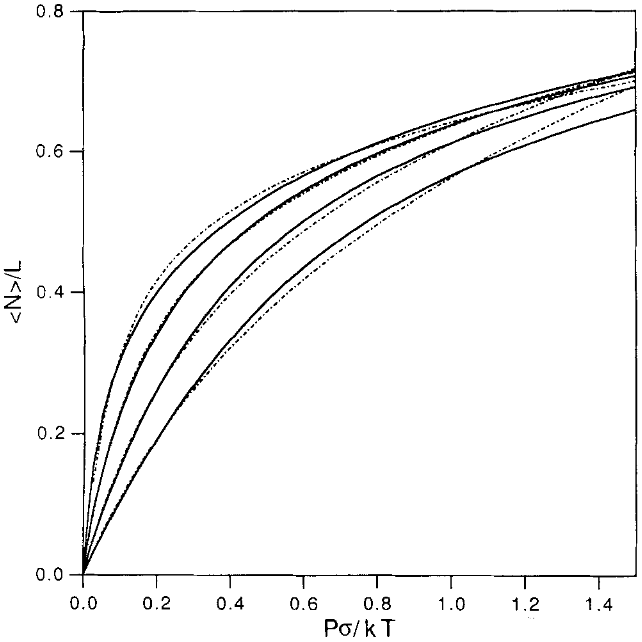


Figure 4. Comparison of exact (solid lines) and RSMI predicted (dashed lines) pure component adsorption isotherms for a systems of $L = 6\sigma$.

Fitted values for K and σ/L are used (see Table 1). The figure depicts isotherms for $\epsilon_w/kT = 1$ (lowest), 2, 3, and 4 (highest). Each system has $\epsilon/kT = 1$ and $\lambda = \sigma/2$. The actual values of ϵ/kT and ζ are used in the RSMI predictions.

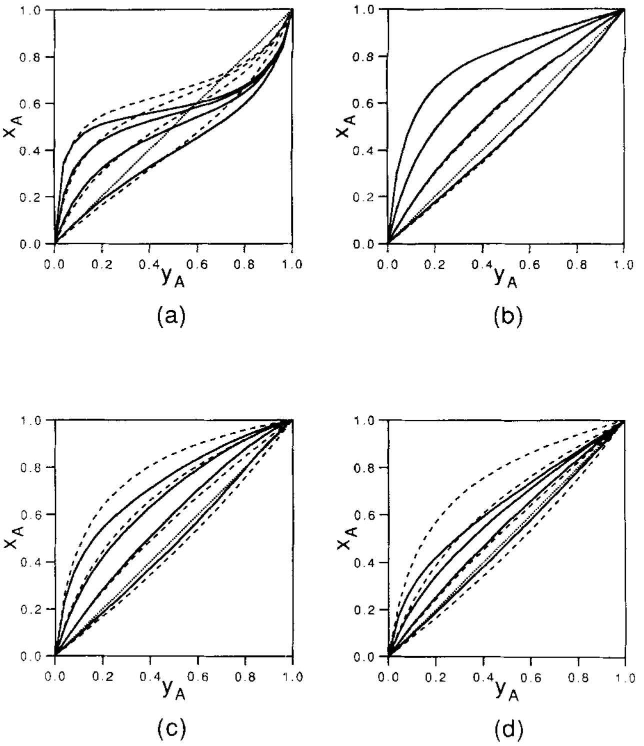


Figure 5. Comparison of exact (solid lines) and RSMI predicted (dashed lines) binary adsorption at $P\sigma_A/kT = 2$ for various length systems: (a) $L = 2\sigma_A$; (b) $L = 3\sigma_A$; (c) $L = 4\sigma_A$; (d) $L = 6\sigma_A$.

Each figure depicts isotherms for $\epsilon_{Aw}/kT = 1$ (lowest), 2, 3, and 4 (highest). All systems have $\sigma_B/\sigma_A = \epsilon_B/\epsilon_A = 0.6$, $\epsilon_{AA}/kT = \epsilon_{BB}/kT = \epsilon_{Bw}/kT = 1$, $\lambda_{iw} = \sigma_i/2$, and $\lambda_{ij} = \sigma_{ij}/2$. Lorentz-Berthelot combining rules are used. The actual values of K_i, σ_i/L, ϵ_i/kT, and ζ_i are used in the RSMI predictions.

way than that given in the previous section. The exact solution of the nearest-neighbor square-well model implies specifically how each of the three terms in Eq. 2.4 should behave if the true physics of the problem is to be captured. For example, as has already been noted, in 1-D using free-volume to calculate the configurational integrals is an exact concept for hard rods. This is readily apparent in Eq. 3.4 by the role of the $\Lambda = L - N\sigma$, which is indeed a free volume. In higher dimensions the concept of free-volume is not exact. Nevertheless, it is still a quite rational concept and produces fairly good estimates when an effective (fitted) co-volume is used. As a more precise investigation of each of the factors in the SMI configurational partition function, we have calculated each contribution via the exact pure component solution (Eq. 3.4).

The single molecule term (Eq. 2.9a) in the RSMI has some definite qualitative shortcomings. The RSMI single molecule term can be interpreted as approximating the effect of the adsorbate-cavity wall potential by a uniform field which yields the same Henry's constant. This implies that all adsorbate particles experience the same potential field, independently of the number of particles adsorbed. For the 1-D case this is clearly counterintuitive. In this case it is clear that only two particles, those nearest to the two cavity walls, would experience the wall potential strongly whereas the others would be influenced by the walls only weakly. Hence one would conclude that the approximation employed in RSMI leads to an overestimation of the effect of adsorbate-cavity interactions, especially when many particles are adsorbed. This effect should be present to some extent in higher dimensions also, although of course the higher the dimension the greater the number of particles which can be located near the walls. Nevertheless, this would indicate that it may be unwise to apply RSMI to cavities large enough to hold several layers of particles. To illustrate this point quantitatively, let us define a quantity Z'_N as

$$Z'_N = \frac{Z_{N_{SWW/HR}}}{Z_{N_{HW/HR}}} \tag{5.1}$$

where $Z_{N_{SWW/HR}}$ is the configurational partition function for a square-well wall/hard rod (SWW/HR) system and $Z_{N_{HW/HR}}$ is that for the identical system except with hard walls (that is, no attractive wall-particle potential). By this definition, in Z'_N the adsorbate-adsorbate contribution is absent and the free volume contribution is divided out leaving a contribution arising from the interaction of the molecules with the cavity walls. Hence Z'_N is essentially what is approximated by Z_1^N in the RSMI. By examining the ratio Z'_N/Z'_{N-1} we obtain a measure of the effective contribution made by each molecule added to the system. This is shown in Table 2. It is clear that two particles interact strongly with the walls whereas the remaining particles interact comparatively weakly. We note that the approximation employed in RSMI (Eq. 3.10a) using the actual value of K would indicate a constant value for $Z'_N/Z'_{N-1} = K/(L - \sigma)$, which is the first value in each column of Table 2. Hence it is obvious that the simple approximation in RSMI can significantly

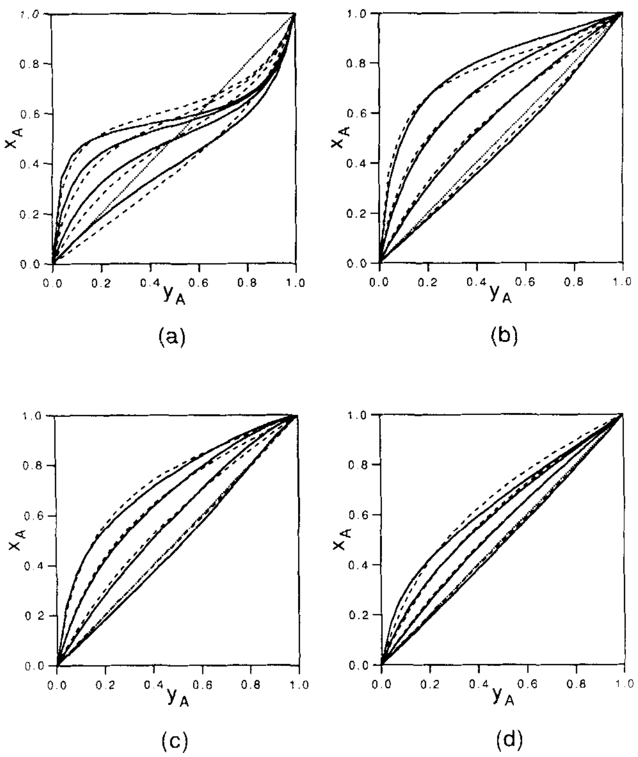


Figure 6. Comparison of exact (solid lines) and RSMI predicted (dashed lines) binary adsorption at $P\sigma_A/kT=2$ for various length systems: (a) $L=2\sigma_A$; (b) $L=3\sigma_A$; (c) $L=4\sigma_A$; (d) $L=6\sigma_A$.

The values for K_i and σ_i/L are fitted from pure component behavior (see Table 1). Each figure depicts isotherms for $\epsilon_{Aw}/kT=1$ (lowest), 2, 3, and 4 (highest). All systems have $\sigma_B/\sigma_A=\epsilon_B/\epsilon_A=0.6$, $\epsilon_{AA}/kT=\epsilon_{BB}/kT=\epsilon_{Bw}/kT=1$, $\lambda_{iw}=\sigma_i/2$, and $\lambda_{ij}=\sigma_{ij}/2$. Lorentz-Berthelot combining rules are used. The actual values of ϵ_i/kT, and ζ_i are used in the RSMI predictions.

overestimate the contribution to the partition function from the adsorbate-cavity wall interactions.

Table 2. A Measure of the Single Particle Contribution to the Configurational Integral Z_N.

System Parameters: $\sigma=1.0$; $\epsilon_w/kT=4.0$; $\lambda_w=0.5$

	-------Z'_N/Z'_{N-1}-------		
N	$L=4.0$	$L=6.0$	$L=10.0$
1	18.866	11.720	6.955
2	21.572	9.889	5.237
3	5.526	3.841	2.856
4		2.940	2.249
5		2.138	1.993
6			1.856
7			1.751
8			1.586
9			1.234

Note: RSMI predicts constant values for Z'_N/Z'_{N-1} equal to the first value in each column.

Table 3. A Measure of the Adsorbate-Adsorbate Interaction Contribution to the Configurational Integral Z_N

System Parameters: $\sigma=1.0$; $\epsilon/kT=1.0$; $\lambda=0.5$

	-----Z''_N/Z''_{N-1}-----		
N	$L=4.0$	$L=6.0$	$L=10.0$
1	1.00 (1.00)	1.00 (1.00)	1.00 (1.00)
2	1.75 (1.28)	1.40 (1.18)	1.21 (1.10)
3	3.55 (1.13)	2.03 (1.09)	1.46 (1.05)
4		3.33 (1.09)	1.80 (1.05)
5		5.28 (1.09)	2.31 (1.05)
6			3.10 (1.05)
7			4.47 (1.05)
8			6.31 (1.05)
9			4.56 (1.05)

Note: Results from the RSMI are shown in parentheses.

There are also several qualitative shortcomings in the mean-field term employed in RSMI. First, a more advanced treatment shows that there should be a quadratic rather than linear dependence on the number of particles (Hansen and McDonald, 1986). Moreover for the multicomponent systems, the mean-field term in RSMI has no cross-interactions. Second, it is quite unlikely that the adsorbed material in a small cavity will behave similarly to a bulk fluid. The overall density in the pore can be quite high leading significant pair correlations which are neglected by the mean-field approximation used in RSMI. Furthermore, the cavity introduces a significant spatial inhomogeneity into the density profile (Monson, 1990). The assumption of uniform density in general leads to an underestimation of adsorbate-adsorbate interactions. Taking these effects together, it is clear that the mean-field term in RSMI significantly underestimates the effect of the adsorbate-adsorbate interactions. Indeed, Ruthven has noted that dropping the mean-field term altogether does not greatly effect the accuracy of the method (Ruthven, 1976). We can look at this more quantitatively by defining a quantity Z''_N via

$$Z''_N=\frac{Z_{N_{HW/SWR}}}{Z_{N_{HW/HR}}} \tag{5.2}$$

where $Z_{N_{HW/SWR}}$ is the configurational integral for a hard wall/square-well rod (HW/SWR) system and $Z_{N_{HW/HR}}$ is that for the identical system except with hard walls. By this definition, Z''_N is essentially what is approximated by $Z_{m.f.}$ in the RSMI. Table 3 shows values of Z''_N/Z''_{N-1}. We note from the approximate linear increase in Z''_N/Z''_{N-1} vs. N, that Z''_N, and hence the mean-field term, must have about a second-order dependence on N. Comparing the exact values to the values from the RSMI we clearly see that the approximation used in RSMI can severely underestimate the adsorbate-adsorbate contribution to the configurational integral.

Lastly, it should be noted that the entire concept behind the SMI approach, namely decomposing the configurational integrals into a single molecule contribution, a free volume contribution, and an adsorbate-adsorbate contribution, is not rigorous even in 1-D. The exact solution of the 1-D square-well system does not allow for any such decomposition in general. All three effects are coupled. (It is of interest to note, however, that if there are no adsorbate-adsorbate interactions, the single molecule contribution can be separated from the free volume contribution for the 1-D square-well system.) Table 4 shows a measure of the error introduced by the assumption that the configurational integrals may be factorized as in Eq. 2.4. Specifically we tabulate Z'''_N/Z_N where

$$Z'''_N=[Z'_N][Z_{N_{HW/HR}}][Z''_N] \tag{5.3}$$

Table 4. A Measure of the Error Associated with the Decomposition Approximation in the RSMI

System Parameters: $\sigma=1.0$; $\epsilon/kT=1.0$; $\lambda=0.5$; $\epsilon_w/kT=4.0$; $\lambda_w=0.5$

		Z'''_N/Z_N	
N	$L=4.0$	$L=6.0$	$L=10.0$
1	1.000	1.000	1.000
2	1.655	1.332	1.156
3	1.065	1.629	1.338
4		1.609	1.507
5		1.006	1.637
6			1.676
7			1.521
8			1.106
9			1.000

Z'''_N is the estimate of Z_N via a decoupled evaluation of the cavity potential contribution, free-volume contribution, and adsorbate-adsorbate interaction contribution. The ratio of Z''_N to the exact value of Z_N reflects the error introduced by the decomposition assumption. From Table 4 it is clear that as much as a 65% overestimation of Z_N can result due to the decomposition for these systems.

The behavior exhibited by RSMI in Figure 2 can be explained in terms of the above observations. The exact agreement for $L/\sigma=2$ (Figure 2a) is explained by the fact that at most one particle fits (with a nonzero free volume) in the cavity and the adsorbate-cavity wall potential is uniform across the cavity. Hence adsorbate-adsorbate interactions are absent and the single molecule term is exact. Since the free volume term is also exact, the grand partition function is estimated without error. It should be also noted that for the case of a maximum of one particle in a cavity, RSMI reduces to the Langmuir isotherm. The underestimation of adsorption in the larger length cavities (Figures 2b–d) is primarily due to the mean-field term as discussed above. In the $L/\sigma=6$ case (Figure 2d) some overestimation of adsorption is apparent and is due to the single molecule term as discussed above. It should again be noted that since the actual values of σ/L and K are used in Figure 2, the very low and very high activity (pressure) values for adsorption will be accurate. The errors in the predicted isotherms increase if an ideal bulk is assumed and the actual values of σ/L and K are used (see Figure 3). This is simply a reflection of the underestimation of activity from the ideal bulk assumption ($\zeta=P/kT$).

Although there are several shortcomings in the approximations employed in RSMI, there is some cancellation of errors to be expected. The RSMI treatment of the single molecule term should tend to overestimate adsorption at moderate to high activities. On the other hand, the treatment of the adsorbate-adsorbate interactions will lead to an underestimation of the adsorption under the same conditions. Some partial cancellation between these effects improves the accuracy of the RSMI as a whole.

Of course these pure component effects influence the prediction of the binary systems. The selectivity behavior exhibited in Figures 5 and 6 are a direct result of the competing effects of the smaller size of component B vs. the stronger potential interactions of component A. It is this competition that is especially acute for small cavities and accounts for the azeotropy exhibited in Figure 5a. The deviations from the exact values which RSMI exhibits is due primarily to the underestimation of the adsorbate-adsorbate interactions. This underestimation means that within the model the selectivity is dominated by the competition between the effects of size differences and the relative strengths of the adsorbate-cavity wall interactions. Hence, RSMI tends to overpredict the selectivity of component B for $\epsilon_{Aw}/\epsilon_{Bw}=1$ but underpredict the selectivity of component B for $\epsilon_{Aw}/\epsilon_{Bw}=2$, 3, and 4. The discrepancies become even worse as the cavity size increases. Then the influence of the relative strengths of the adsorbate-cavity wall interactions is overestimated which favors adsorption of the component which interacts more strongly with the cavity walls. The near exact agreement for the $L/\sigma_A=3$ case in Figure 5b is simply due to a fortuitous cancellation of errors since the RSMI predictions of the corresponding pure component isotherms shown in Figure 2 have significant errors.

The results obtained using parameters adjusted to give the best agreement for the pure component adsorption are more difficult to interpret since compensating errors are introduced by adjusting both σ/L and K. From Figure 4 it is clearly seen that although using fitted parameters in RSMI allows for very good estimation of the isotherm, the method does not fit the entire isotherm equally well. In fact, RSMI basically allows for fitting of the low activity region well or the high activity region well, but not both in general. If an accurate value of K is used, the low activity region is accurately predicted since Henry's Law is correctly incorporated. If an accurate value of σ/L is used the high activity region is accurately predicted since the pore fills completely at the correct density. Depending on the method of fit and data points used, one region or the other of the isotherm is favored, forcing most of the discrepancy to occur in the other region. In Figure 4 we note that the lower portion of the isotherms are in excellent agreement but the higher portion is not (except for $\epsilon_w/kT=4$). This is a direct result of the significant difference between σ_{fit} and σ as seen in Table 1. Although in fitting the pure component parameters some of their physical significance is lost, the use of these adjusted parameters produces moderately good agreement for binary mixtures as seen in Figure 6. The improved agreement obtained using adjusted pure component parameters (Figure 6) over those obtained without adjustable parameters (Figure 5) is primarily due to σ_{fit} being less that the correct value (see Table 1). This has the effect of increasing the contribution from the free-volume term and compensating for the underestimation of the effect of adsorbate-adsorbate interactions.

Energetic Heterogeneity

Up to this point we have focused principally upon models which are most relevant to systems where the adsorbate molecules are nonpolar and where the strength of the cavity potential field depends principally on the molecular weight of the adsorbate, as would be the case if only van der Waals forces are involved. The molecular models considered here can also be adapted quite simply to the treatment of energetic heterogeneity similar to that which is thought to occur in adsorption in zeolites when the molecular charge distribution in one of the components undergoes classical electrostatic interactions with the charge distribution in the adsorbent cavity. To begin with suppose that instead of just a square well interaction acting only at the ends we add a further uniform potential field with potential energy $-\epsilon_{c,i}$ experienced by component *i* and acting at any point on the line. This is equivalent to multiplying Eq. 3.4 by $\exp(\beta N\epsilon_{c,i})$ for pure component *i* or, in the case of a mixture, multiplying the configurational partition function by $\exp(\beta N\epsilon_{c,i})$ for each component. If we then remove the square well interaction of one component with the end walls and replace it with a hard wall, we then have a molecular model of adsorption in which the molecules of one component experience a uniform potential field inside the pore but the molecules of the other component experience a nonuniform potential field. This is the type of energetic heterogeneity which is often cited as the cause of adsorbed phase nonidealities (Ruthven, 1984; Valenzuela et al., 1988). It is instructive to apply the RSMI to such a model.

We again consider a binary mixture with $\sigma_B/\sigma_A=\epsilon_B/\epsilon_A=0.6$ and we examine adsorption in two types of pore with parameters: $\epsilon_{AW}=0$, $\epsilon_{c,A}=3$, $\epsilon_{BW}=0$, and $\epsilon_{c,B}=1$; $\epsilon_{AW}=0$, $\epsilon_{c,A}=3$, $\epsilon_{BW}=4$, and $\epsilon_{c,B}=1$. In the second of these cases component *B* experiences a nonuniform field (energetic heterogeneity) inside the pore. In each case we took the system length as $L=4\sigma_A$. Figure 7 shows results for selective adsorption from the binary mixture in the two types of pore for $P\sigma_A/kT=0.25$. For the case of cavity which generates a uniform potential field for both components we see that component *A* is selectively adsorbed since it has the stronger interactions with the cavity. Also the RSMI gives good agreement with the exact results. In this case the molecular model conforms closely with the assumptions of the RSMI, the only source of error being the mean field treatment of the adsorbate-adsorbate interactions. For the case of the cavity where component *A* experiences a uniform field and component *B* experiences energetic heterogeneity, we see that the adsorbed phase composition undergoes a change in curvature as the bulk phase composition is changed and an azeotrope occurs. This is a strong indication of adsorbed phase nonideality and is not reproduced by the RSMI which predicts a slight selectivity for component *B* at all concentrations. In the RSMI the energetic heterogeneity appears only in the calculation of *K* and is averaged over. This is another manifestation of the way in which the RSMI treats the single particle contribution to the configurational partition function.

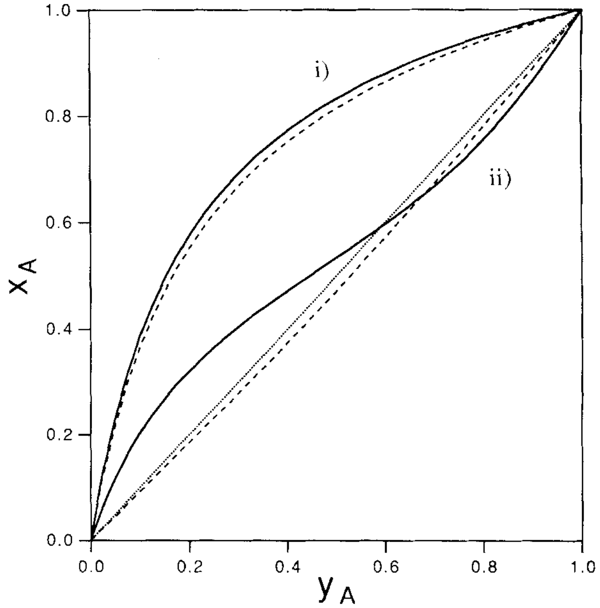


Figure 7. Comparison of exact (solid lines) and RSMI (dashed lines) for selective adsorption in model systems illustrating the effects of energetic heterogeneity.

In each case we are considering a mixture with $\sigma_B/\sigma_A=\epsilon_B/\epsilon_A=0.6$ adsorbed in cavities with $L=4\sigma_A$ at pressure $P\sigma_A/kT=0.25$. The two sets of curves are for: i) $\epsilon_{AW}=0$, $\epsilon_{c,A}=3$, $\epsilon_{BW}=0$, and $\epsilon_{c,B}=1$; $\epsilon_{AW}=0$, $\epsilon_{c,A}=3$, $\epsilon_{BW}=3$, and $\epsilon_{c,B}=1$. In the case ii) component *B* experiences a nonuniform field (energetic heterogeneity) inside the pore.

Summary and Conclusions

Overall the RSMI approach for modelling and predicting adsorption in microporous materials is an appealing one. It is easy to use yet includes significant parts of the underlying physics. Since the method directly approximates the grand partition function, thermodynamic consistency is guaranteed. It also provides a rational basis for predicting multicomponent adsorption equilibria from pure component data. Although the basic approach is sensible, the implementation is subject to several compromises between simplicity and accuracy. RSMI employs very simple approximations for the configurational partition functions. As a result some important functionality is lost and, in general, both the low-and high-pressure adsorption cannot be accurately predicted simultaneously. Nevertheless, compensating errors partially make up for some of this, especially when multicomponent selectivity is considered.

The idea of decoupling the contributions to the configurational integrals into a single particle contribution, a free-volume contribution, and an adsorbate-adsorbate contribution is a sound first approximation but is not rigorously correct. From our analysis it appears that the mean-field approximation for the adsorbate-adsorbate contribution used in RSMI is a also particularly significant source of error. The functionality is quite simplistic predicting a linear dependence on cavity particle density. This linear dependence precludes any cross-interactions for multicomponent systems. The study of the exact solution to 1-D systems indicates that the dependence is closer to quadratic. Furthermore, the influence of pair correlations between adsorbate molecules and the spatial density inhomogeneity upon the effect of attractive forces are not considered. Hence, the actual contribution of the adsorbate-adsorbate interactions can be considerably greater than is predicted by RSMI. The approximation for the single molecule contribution is good for small pores but gets progressively worse as the pore size and adsorbate density increases. A significant shortcoming of the approximation is that it treats all particles in the pore equivalently and hence does not recognize that particles excluded from being near the pore walls feel the influence adsorbate-cavity wall potential much less than those near the walls. This can lead to a considerable overestimation of the adsorption for large pores and high cavity particle densities. It is of course true that the restriction to one dimension does have a tendency to exaggerate this effect which should be smaller for a three dimensional cavities of small size.

Energetic heterogeneity is often quoted as a reason for the failure of the RSMI in practical applications (Ruthven, 1984), especially in the prediction of azeotropes in selective adsorption. What is meant by this is the occurrence of large spatial variations in the adsorbate-cavity wall potential. When these variations are very different for each component they can cause adsorbed phase nonideality. Such effects are clearly not accounted for within the RSMI. We have shown how such effects can be incorporated into the molecular models considered in this work and that they do indeed lead to nonidealities which cannot be reproduced by the RSMI. The failure of RSMI for such systems is related to the error in the single particle contribution to the configurational partition function. There is in our view more work to be done in distinguishing clearly between effects of this kind of energetic heterogeneity from those effects associated with density inhomogeneities produced simply by confinement and in understanding the way in which these effects couple with the adsorbate-adsorbate and adsorbate-cavity wall interactions.

The results of the study presented here suggest several possibilities for future research. Our immediate focus is on two areas. First, it will be interesting to extend our investigation to three-dimensional systems. This can be done by comparing to experimental data for very well defined systems and by comparing with computer simulations. Some data already exists in the literature on configurational integrals in 3-D cavities which was obtained via Monte Carlo integration (Woods et al.,1988). Second, we believe that the approximations employed in RSMI apparently can be modified to reflect the underlying statistical mechanics more accurately without adding excessive complexity. We are currently investigating possible improvements and their implications for both pure and multicomponent cases.

Acknowledgment

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Notation

b = excluded co-volume
k = Boltzmann factor
K = Henry's constant with respect to activity and particle number
L = 1-D cavity length
N = number of particles
P = pressure
q = molecular partition function
r_i = coordinates of particle i
T = absolute temperature
u = adsorbate-adsorbate potential
V = volume
x_A = pore composition of species A
y_A = bulk composition of species A
Z_1 = single molecule configurational partition function
$Z_{f.v.}$ = contribution to Z_N due to free volume associated with the repulsive part of the adsorbate-adsorbate interactions
$Z_{m.f.}$ = contribution to Z_N due to attractive adsorbate-adsorbate interactions evaluated in a mean field approximation
Z_N = configurational integral for N particles
Z_N' = measure of single molecule contribution to Z_N as defined by Eq. 5.1
Z_N'' = measure of adsorbate-adsorbate contribution to Z_N as defined by Eq. 5.2
Z_N''' = decomposition approximation for Z_N as defined by Eq. 5.3

Greek letters

β = $1/kT$
ϵ = well depth of adsorbate-adsorbate potential
ϵ_w = cavity wall square-well potential depth
ϵ_c = strength of uniform potential inside cavity
ζ = activity
Θ = Heaviside function
κ = parameter defined by Eq. 6.1
λ = adsorbate-adsorbate square-well potential range
λ_w = cavity wall square-well potential range
Λ = 1-D free volume ($L-N\sigma$) used in Eq. 3.2
μ = chemical potential
ν = cavity volume
Ξ = grand partition function
σ = adsorbate particle size
ϕ = potential field in cavity

Literature Cited

Hansen, J. P., and I. R. McDonald, *Theory of Simple Liquids*, 2nd edition, Academic Press (1986).

Kierlik, E., and M. Rosinberg, "Free-Energy Density Functional for the Inhomogeneous Hard-Sphere Fluid: Application to Interfacial Adsorption," *Phys. Rev. A*, **42**, 3382 (1990).

Kierlik, E., and M. Rosinberg, "Density Functional Theory for Inhomogeneous Fluids. II. Adsorption of Binary Mixtures," *Phys. Rev. A*, **44**, 5025 (1991).

Kierlik, E., M. Rosinberg, J. E. Finn, and P. A. Monson, "Binary Vapor Mixtures Adsorbed on Graphite Surface: A Comparison of Mean Field Density Functional Theory with Results from Monte Carlo Simulations," *Mol. Phys.*, **75**, 1435 (1992).

Loughlin, K. F., M. A. Hasanain, and H. B. Abdul-Rehman, "Quaternary, Ternary, Binary, and Pure Component Sorption on Zeolites. 2. Light Alkanes on Linde 5A and 13X Zeolites at Moderate to High Pressures," *Ind. Eng. Chem. Res.*, **29**, 1535 (1990).

Miller, G. W., K. S. Knaebel, and K. G. Ikels, "Equilibria of Nitrogen, Oxygen, Argon, and Air in Molecular Sieve 5A," *AIChE J.*, **33**, 194 (1987).

Monson, P. A., "The Properties of Inhomogeneous Square Well Mixtures in One Dimension," *Mol. Phys.*, **70**, 401 (1990).

Percus, J. K., "Equilibrium State of a Classical Fluid of Hard Rods in an External Field," *J. Stat. Phys.*, **15**, 505 (1976).

Percus, J. K., "One-Dimensional Classical Fluid with Nearest-Neighbor Interaction in Arbitrary External Field," *J. Stat. Phys.*, **28**, 67 (1982a).

Percus, J. K., *Liquid State of Matter*, E. W. Montroll and J. L. Lebowitz, eds., North-Holland, 31 (1982b).

Robledo, A., and J. S. Rowlinson, "The Distribution of Hard Rods on a Line of Finite Length," *Mol. Phys.*, **4**, 711 (1986).

Rolniak, P. D., and R. Kobayashi, "Adsorption of Methane and Several Mixtures of Methane and Carbon Dioxide at Elevated Pressures and Near Ambient Temperatures on 5A and 13X Molecular Sieves by Tracer Pertubation Chromatography," *AIChE J.*, **26**, 616 (1980).

Ruthven, D. M., "Simple Theoretical Adsorption Isotherm for Zeolites," *Nature Phys. Sci.*, **232**, 70 (1971).

Ruthven, D. M., and K. F. Loughlin, "Sorption of Light Paraffins in Type-A Zeolites," *J. Chem. Soc. Faraday Trans. I.*, **68**, 696 (1972).

Ruthven, D. M., K. F. Loughlin, and K. A. Holborow, "Multicomponent Sorption Equilibria in Molecular Sieve Zeolites," *Chem. Eng. Sci.*, **28**, 701 (1973).

Ruthven, D. M., "Sorption of Oxygen, Nitrogen, Carbon Monoxide, Methane, and Binary Mixtures of these Gases in 5A Molecular Sieve," *AIChE J.*, **22**, 753 (1976).

Ruthven, D. M., *Principles of Adsorption and Adsorption Processes*, Wiley (1984).

Ruthven, D. M., "Generalized Statistical Model for the Prediction of Binary Adsorption Equilibria in Zeolites," *Ind. Eng. Chem. Fund.*, **24**, 27 (1985).

Steele, W. A., *The Interaction of Gases with Solid Surfaces*, Pergamon Press (1974).

Valenzuela, D. P., A. L. Myers, O. Talu, and I. Zwiebel, "Adsorption of Gas Mixtures: Effect of Energetic Heterogeneity," *AIChE J.*, **34**, 397 (1988).

Woods, G. B., A. Z. Panagiotopoulos, and J. S. Rowlinson, "Adsorption of Fluids in Model Zeolite Cavities," *Mol. Phys.*, **63**, 49 (1988).

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