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# THE MOLECULAR BASIS FOR LOCAL COMPOSITIONS IN LIQUID MIXTURE MODELS

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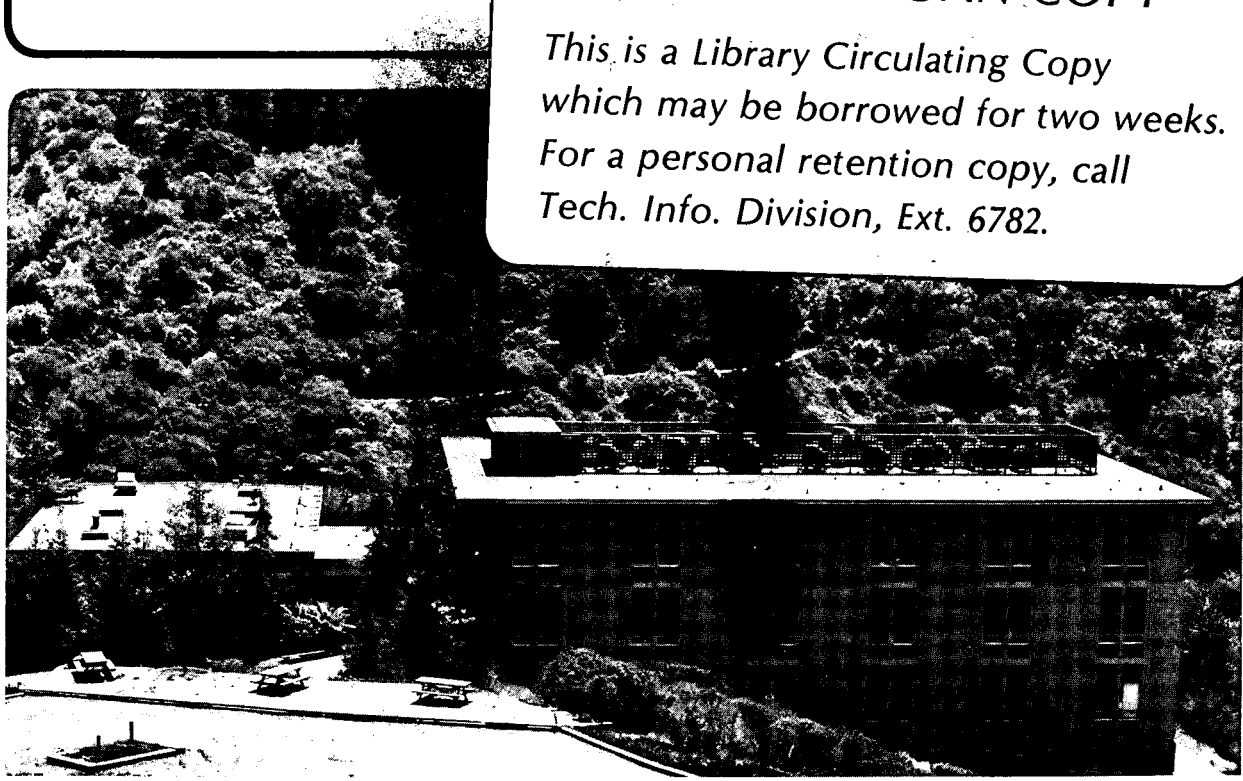

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# THE MOLECULAR BASIS FOR LOCAL COMPOSITIONS IN LIQUID MIXTURE MODELS

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## ABSTRACT

The local-composition concept is examined critically. When a general local-composition model is subjected to different constraints, we obtain different forms, corresponding to those presented earlier by Wilson[3] or Renon[4] or Abrams[5] or Guggenheim.[1,2]

For a simple mixture, a physically meaningful constraint gives a one-parameter model whose properties are obtained from the Lennard-Jones potential. For this model, the calculated excess Gibbs energy and calculated local compositions are in good agreement with results from Monte Carlo data and with results from perturbation theory, recently reported by Nakanishi et al. [8,9]

These studies indicate that local-composition models, when developed with care, can have physical significance as well as engineering utility.

## INTRODUCTION

The local-composition concept can be traced back to the quasi-chemical theory of liquid mixtures developed by Guggenheim[1,2] in 1935. Thirty years later, Wilson,[3] Renon,[4] Abrams[5] and others used Guggenheim's ideas toward development of various practical local-composition models for VLE and LLE calculations at moderate pressures. Recently, Whiting[6] and Mollerup[7] used the local-composition concept to develop density-dependent mixing rules in the equation of state for mixtures; these rules suggest possible advantages for high-pressure VLE calculations.

To obtain a more fundamental understanding of local compositions in fluid mixtures, Nakanishi and co-workers[8,9] published a series of papers applying molecular dynamics and Monte Carlo calculations to mixtures of

Lennard-Jones molecules. Their calculations show the physical significance of local compositions which are different from the overall mole fractions in nonideal mixtures. Calculated excess Helmholtz energies for several systems are in good agreement with results from perturabation theory. Nakanishi's results serve as a useful reference to test any local-composition model.

Several authors have compared local-composition-model predictions with results from molecular dynamics and Monte Carlo calculations. Different conclusions have been drawn from these comparisons; Fischer[10] found that UNIQUAC predictions are worse than those from Guggenheim's theory and concluded that the physical basis of all equations based on local-composition concept seem to be doubtful. However, Lee, Chung, Starling,[11] considering the energy parameters as the potential of mean force, obtained good results using Wilson's equation.

It is useful to compare molecular dynamics and Monte Carlo results with predictions from local-composition models because such comparison can offer physical understanding and possibly valuable suggestions toward improvement of the model. However, care must be taken in these comparisons.

In this work, we discuss those basic requirements which a local-composition model must have to compare favorably with results from molecular dynamics and from Monte Carlo calculations.

## DERIVATION OF A GENERAL LOCAL-COMPOSITION MODEL

To derive a local-composition model for the Gibbs energy of a real fluid mixture, we use and extend the work of Pierotti[12,13] based on scaled-particle theory.[14]

We form a real fluid mixture as indicated in Fig. 1. We start with $k$ components in the standard state (1 bar, ideal gas) at temperature $T$ (a). The pure components are mixed and compressed to volume $V_m$ (occupied by the real mixture) to form an ideal gas mixture (b) of composition $x_i$. The corresponding Gibbs energy change is

$$\Delta G_{(a)\to(b)} = \sum_{i=1}^{k} x_i RT \ln \frac{x_i RT}{V_m} \tag{1}$$

In the next step, each molecule (a point) is inflated into a hard sphere of diameter $\sigma_i$ to form a hard-sphere mixture (c). For this step, $\Delta G$ is given by

$$\Delta G_{(b)\to(c)} = - \sum_{i=1}^{k} x_i W_{ci} \tag{2}$$

where $W_{ci}$ is the work of creating 1 mole of impenetrable cavities of component i in the hard-sphere mixture. Finally, (d), the hard spheres are charged an appropriate potential with $\Delta G$ given by

$$\Delta G_{(c)\rightarrow(d)} = -\sum_{i=1}^{k} x_i W_{Ii} \tag{3}$$

where $W_{Ii}$ is the work of charging the hard spheres to form 1 mole of real mixture. The total change in Gibbs energy is then given by

$$\Delta G_m = \Delta G_{(a)\rightarrow(d)} = \sum_{i=1}^{k} x_i (RT\ln \frac{x_i RT}{V_m} - W_{ci} - W_{Ii}) \tag{4}$$

For an ideal solution, the corresponding Gibbs energy change is

$$\Delta G_{m,id} = \sum_{i=1}^{k} x_i RT\ln (f_i^o x_i) \tag{5}$$

where $f_i^o$ is the fugacity of pure component i at the temperature and pressure of the real mixture.

From Eqs. (4) and (5), the excess Gibbs energy is:

$$G_m^E = \Delta G_m - \Delta G_{m,id} = \sum_{i=1}^{k} x_i (-W_{ci} - W_{Ii} - RT\ln f_i^o) + RT\ln\frac{RT}{V_m} \tag{6}$$

For pure component i , it follows from Eq. (6) that

$$RT\ln f_i^o = -W_{ci}^o - W_{Ii}^o + RT\ln\frac{RT}{V_{mi}} \tag{7}$$

where for pure component i at the temperature and pressure of the mixture, $W_{Ci}^o$ is the work of creating cavities and $W_{Ii}^o$ is the work of charging them.

From Eqs. (6) and (7),

$$G_m^E = \sum_{i=1}^{k} x_i (-W_{ci} + W_{ci}^o - W_{Ii} + W_{Ii}^o + RT\ln V_{mi}) - RT\ln V_m \tag{8}$$

To evaluate $W_{Ci}$, we use the results of the scaled-particle theory for mixtures developed by Lebowitz et al.[15]:

$$W_{ci} = RT\left\{\ln(1-\xi_3) - \frac{6\xi_2}{(1-\xi_3)}\frac{\sigma_i}{2} - \left(\frac{12\xi_1}{(1-\xi_3)} + \frac{18\xi_2^2}{(1-\xi_3)^2}\right)\left(\frac{\sigma_i}{2}\right)^2 - \frac{4}{3}\frac{\pi}{kT}P\left(\frac{\sigma_i}{2}\right)^3\right\} \quad (9)$$

where

$$\xi_n = \frac{1}{6}\pi \sum_{i=1}^{k} \frac{x_i N}{V_m}\sigma_i^n \quad (10)$$

and $N$ is Avogadro's number.

Due to the different types of molecular interactions, the charging process is accompanied by changes in local composition in the surroundings of the molecule being charged. The work of charging hard spheres can be expressed by

$$\sum_{i=1}^{k} x_i W_{Ii} = -\Delta G_I = -\Delta A_I - \Delta PV = -\Delta U_I + T\Delta S_I - \Delta PV \quad (11)$$

For a binary mixture, and assuming pairwise additivity, $\Delta U_I$ is given by[17]

$$\Delta U_I = \frac{1}{2}N\left\{x_1\left[\int_{\sigma_1}^{\infty}\rho_1\varepsilon_{11}(r)g_{11}(r)4\pi r^2dr + \int_{\sigma_1}^{\infty}\rho_2\varepsilon_{21}(r)g_{21}(r)4\pi r^2dr\right]\right.$$
$$\left. + x_2\left[\int_{\sigma_2}^{\infty}\rho_1\varepsilon_{12}(r)g_{12}(r)4\pi r^2dr + \int_{\sigma_2}^{\infty}\rho_2\varepsilon_{22}(r)g_{22}(r)4\pi r^2dr\right]\right\} \quad (12)$$

where $g_{ij}(r)$ is the radial distribution function, $\varepsilon_{ij}$ is the interaction energy of the $i$-$j$ pair, and $\rho$ is the number density.

Since little is known about $g_{ij}$ in a real mixture, we use an approximate model based on the assumption of short-range order and long-range randomness.[16] The environment surrounding molecule $i$ is approximated by a first coordination shell with a local composition $x_{ji}$. The radius $\bar{r}$ of the shell is calculated, e.g., from a face-centered lattice. In the region beyond the first coordination shell, molecules are randomly distributed as indicated in Fig. 2; these molecules beyond the first shell, also contribute to the

total energy of the system. Fig. 3 compares our approximate radial distribution function, $g(r)$, and potential energy, $\varepsilon(r)$, with the corresponding real functions.

With these assumptions, Eq. (12) can be rewritten

$$\Delta U_I = \Delta U_{I,SR} + \Delta U_{I,LR} \tag{13}$$

$$\Delta U_{I,SR} = \frac{1}{2}N\left\{x_1 z_1\left[x_{11}\varepsilon_{11}(\bar{r})+x_{21}\varepsilon_{21}(\bar{r})\right] + x_2 z_2\left[x_{12}\varepsilon_{12}(\bar{r})+x_{22}\varepsilon_{22}(\bar{r})\right]\right\} \tag{14}$$

$$\Delta U_{I,LR} = \frac{1}{2} N \sum_{i=1}^{2} x_i \sum_{j=1}^{2} \int_{\sqrt{2}\,\bar{r}}^{\infty} \rho_j \varepsilon_{ji}(r) 4\pi r^2 dr \tag{15}$$

where subscripts "SR" and "LR" stand for short-range and long-range respectively, and $z_1$ and $z_2$ are the coordination numbers. The radius of the first coordination shell, $\bar{r}$, is estimated from a relation corresponding to a face-centered lattice:

$$\bar{r} = (V_m \sqrt{2}/N)^{1/3} \tag{16}$$

The lower limit of integration in Eq. (15) is $\sqrt{2}\bar{r}$, the distance of the second coordination shell.

As a result of the charging process, there are composition changes in the first coordination shell. The resulting change in entropy is

$$\Delta S_I = \frac{1}{2}Nk\left\{x_1 z_1\left[x_{11}\ln\frac{x_1}{x_{11}} + x_{21}\ln\frac{x_2}{x_{21}}\right] + x_2 z_2\left[x_{12}\ln\frac{x_1}{x_{12}} + x_{22}\ln\frac{x_2}{x_{22}}\right]\right\} \tag{17}$$

For a stable configuration, the composition changes during the constant volume charging process must satisfy the minimum Helmholtz energy criterion,

$$d(\Delta A_I) = 0 \tag{18}$$

We now show that the relation between local composition and bulk composition depend on what constraints are applied to Eq. (18).

Case 1:

If we adopt a one-fluid model for a real mixture, the following constraints[21,22] must be satisfied:

$$x_{11} + x_{21} = x_{12} + x_{22} = 1 \tag{19}$$

$$z_1 x_1 x_{21} = z_2 x_2 x_{12} \tag{20}$$

Eq. (19) is a consequence of normalization. Eq. (20) implies that the number of 1-2 pairs calculated for component 1 must be the same as those calculated for component 2 . With these constraints, there is only one independent variable. Equation (18) can be rewritten

$$\left(\frac{\partial \Delta A_I}{\partial x_{21}}\right)_{T,V,x_1} = 0 \tag{21}$$

Substituting Eqs. (11, 13, 14, 15, 17) with $\varepsilon_{21}(r) = \varepsilon_{12}(r)$ into Eq. (21), we obtain

$$x_{21} = \frac{\left(z_1x_1+z_2x_2\right) - \sqrt{\left(z_1x_1+z_2x_2\right)^2 - 4z_1z_2x_1x_2K}}{2z_1x_1K} \tag{22}$$

where

$$K = 1 - \exp\left[\left(2\varepsilon_{12}-\varepsilon_{11}-\varepsilon_{22}\right)/kT\right] \tag{23}$$

Eq. (22) with $z_1 = z_2 = z$ is the result obtained from Guggenheim's quasichemical theory.[12] This form of local composition has been recently extended to the local surface area fraction by Panayietou and Vera.[18,19]

Case 2:

If we adopt a hypothetical two-liquid model, we need to keep only Eq. (19). In this case, as discussed by Maurer[23] and by Kemeny and Rasmussen,[20] the two hypothetical fluids 1 and 2 are independent. There are two independent variables, $x_{21}$ and $x_{12}$ which are not related through Eq. (20).

Eq. (18) can then be rewritten,

$$\left(\frac{\partial \Delta A_I}{\partial x_{21}}\right)_{T,V,x_1,x_{12}} = 0 \tag{24}$$

$$\left(\frac{\partial \Delta A_I}{\partial x_{12}}\right)_{T,V,x_1,x_{21}} = 0 \tag{25}$$

Substitution of Eqs. (11, 13, 14, 15, 17) into the last two equations gives

$$x_{21} = \frac{x_2 \exp\left[-\left(\varepsilon_{21}-\varepsilon_{11}\right)/kT\right]}{x_1 + x_2 \exp\left[-\left(\varepsilon_{21}-\varepsilon_{11}\right)/kT\right]} \tag{26}$$

$$x_{12} \quad \frac{x_1 \exp\left[-\left(\varepsilon_{12}-\varepsilon_{22}\right)/kT\right]}{x_2 + x_1 \exp\left[-\left(\varepsilon_{12}-\varepsilon_{22}\right)/kT\right]} \tag{27}$$

These equations are the local-composition expressions developed by Wilson,[3] Renon[4] and Abrams,[5] although with some modifications.

This form of local composition has been questioned by Flemr[21] and McDermott and Ashton,[22] because they do not satisfy to Eq. (20).

As discussed here, the local-composition expressions are density-dependent, since radius $\bar{r}$ in $\varepsilon(\bar{r})$ is closely related to the volume. The thermodynamic consistency of our basic assumptions is discussed in the Appendix.

## A Local-Composition Model for Lennard-Jones Mixture

To compare predictions from case 1 and case 2 with Nakanishi's calculations for Lennard-Jones mixtures, we use:

$$\varepsilon_{ij}(r) = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right] \tag{28}$$

$$\sigma_{11} = \sigma_{12} = \sigma_{22} = 3.405 \text{ Å} \tag{29}$$

$$(\epsilon_{11}\,\epsilon_{22})^{1/2}/k = 119.8 \text{ K} \tag{30}$$

$$C = \epsilon_{12}/\epsilon_{11} \quad , \qquad D = \epsilon_{22}/\epsilon_{11} \tag{31}$$

Using for $\varepsilon_{12}$ ,

$$\epsilon_{12} = \sqrt{\epsilon_{11}\,\epsilon_{22}} \times (1 - k_{12}) \tag{32}$$

we obtain

$$k_{12} = 1 - C/\sqrt{D} \tag{33}$$

Table 1 shows various combinations of C and D used in our calculations. The nomenclature, the value of $\rho\sigma^3$ (0.75) and the temperature (120 K) , are the same as those used by Nakanishi et al.

In all calculations z was arbitrarily set equal to 10 , and in case 1 we adopt Guggenheim's approximation, i.e., $z_1 = z_2 = z$ . Figures 4 and 5 compare molar excess Gibbs energies for mixtures A-2 , LB-2 , S-2 , LB-3 , LB-4 (as defined in Table 1) calculated for case 1 and for case 2 with Nakanishi's results. Figure 6 shows the local-composition values for Lennard-Jones mixtures for mixture D = 2 , at equimolar concentration, as a function of parameter C , which is a measure of the strength of unlike interaction.

These figures show that case 2 gives poor prediction for $G_m^E$ and local composition. This is a consequence of the pseudonature of local compositions of case 2, since it is a two fluid model. Its energy and size parameters are not necessarily the same as the true Lennard-Jones parameters.

Predictions from case 1 with Guggenheim's approximation are closer to the machine data but are still unsatisfactory.

However, the results of Fig. 6 showing that "experimental" local composition values lie between results of case 1 (with Guggenheim's approximation) and case 2, lead us to introduce an empirical correction to our model.

If we modify the constraints of case 2, namely that its local-composition expressions must satisfy Eq. (20), i.e., $z_1x_1x_{21} = z_1x_2x_{12}$ , (as in case 1), coordination numbers $z_1$ and $z_2$ must be given by

$$z_1 = z\,[x_1 \exp(-\varepsilon_{11}/kT) + x_2 \exp(-\varepsilon_{21}/kT)] \tag{34}$$

$$z_2 = z\,[x_1 \exp(-\varepsilon_{12}/kT) + x_2 \exp(-\varepsilon_{22}/kT)] \tag{35}$$

where $z$ is the coordination number before charging.

Now we suggest the introduction of an empirical factor $\alpha$ which lies somewhere between zero and unity:

$$z_1 = z\,[x_1 \exp(-\alpha\varepsilon_{11}/kT) + x_2 \exp(-\alpha\varepsilon_{21}/kT)] \tag{36}$$

$$z_2 = z\,[x_1 \exp(-\alpha\varepsilon_{12}/kT) + x_2 \exp(-\alpha\varepsilon_{22}/kT)] \tag{37}$$

When $\alpha = 0$ and $z_1 = z_2 = z$ , we obtain case 1 with Guggenheim's approximation. When $\alpha = 1$ , we have local compositions, just like in case 2 although the physical picture is as in case 1 because Eq. (20) is still valid. Fig. 7 shows the effect of $\alpha$ on local composition. Figure 8 shows the marked influence of parameter $\alpha$ on excess Gibbs energy for the LB-2 mixture. In Eqs. (36) and (37) $z$ was not set equal to 10 (as is usually assumed for liquids) but instead we considered $z$ to be slightly dependent on $\alpha$ , according to

$$z = 10\exp(-\alpha) \tag{38}$$

We found that when $\alpha = 0.05$ , Nakanishi's Monte Carlo data can be fitted well, as shown in Figs. 4 and 5.

Table 2 compares the excess Gibbs energy (with $\alpha = 0.1$ and $\alpha = 0.05$) for all ten equimolar mixtures with perturbation theory and with Monte Carlo predictions. When $\alpha = 0.1$ , the predictions of the proposed model are almost coincident with those of perturbation theory.

Figures 6 and 7 show that when $\alpha$ is in the range between 0.05 and 0.1 , the local-composition predictions are close to Monte Carlo data. However, we must point out that the local composition defined by Nakanishi is not exactly the same as that used here. In Nakanishi's work, local composition calculations are truncated after $r = 1.35\sigma$ . In our model, contributions of all molecules are added to those from the first coordination shell.

Fig. 9 shows the temperature dependence of local composition for the LB-2 mixture. Again, the trend is close to that from Monte Carlo results.

## Conclusion

We conclude that the predictions of the proposed model for Lennard-Jones fluids are in good agreement with the available Monte Carlo and perturbation theory data. Our model has a universal constant, $\alpha$ and one adjustable parameter, C or $k_{12}$ . The wide range of mixtures tested ( $\varepsilon_{22}/\varepsilon_{11}$ from 2 to 4 , $k_{12}$ from 0.293 to -0.414) indicate that this model gives a good description of both macroscopic thermodynamic properties, such as excess Gibbs energy, and microscopic structure, as expressed by local compositions for Lennard-Jones mixtures.

It is likely that for systems exhibiting molecular interactions other than those of the Lennard-Jones type, the proposed model is not adequate, but may serve as a first basis for the construction of a more general model.

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## Appendix

Since $\Delta U_I$ and $\Delta S_I$ in the derivation presented are defined independently, the thermodynamic consistency can be put in doubt, e.g., whether the Gibbs-Helmholtz equation is satisfied.

Let us take case 1 for example. Substitution of Eqs. (11, 13, 14, 15, 17) into the Gibbs-Helmholtz equation,

$$\Delta U_I = \frac{\partial(\Delta A_I/T)}{\partial(1/T)} \tag{A-1}$$

gives

$$\Delta U_{I,calc} = \Delta U_I + \frac{1}{2}N[x_1 z_1(\varepsilon_{21}-\varepsilon_{11}) + x_2 z_2(\varepsilon_{12}-\varepsilon_{22})x_1 z_1/x_2 z_2 - kT \times (x_1 z_1(\ln\frac{x_2}{x_{21}} - 1 - \ln\frac{x_1}{x_{11}} + 1) + x_2 z_2(\ln\frac{x_1}{x_{12}} - 1 - \ln\frac{x_2}{x_{22}} + 1)x_1 z_1/x_2 z_2)](\frac{\partial x_{21}}{\partial 1/T}) \tag{A-2}$$

From Eqs. (21) we obtain

$$\left(\frac{\partial \Delta A_I}{\partial x_{21}}\right)_{T,V,x_1} = 0 \tag{A-3}$$

The bracketed term in Eq. (A-2) is precisely $\left(\frac{\partial \Delta A_I}{\partial x_{21}}\right)_{T,V,x_1}$. Consequently,

$$\Delta U_{I,calc} = \Delta U_I \tag{A-4}$$

However, we must point out that this is true only if the energy and size parameters of the energy function $\varepsilon(r)$ and the coordination numbers $z_1$ and $z_2$ are temperature independent or only slightly temperature dependent. Should these parameters be temperature dependent, this model has to be considered as a Gibbs energy model, not an internal energy and entropy model.

## References


1. Guggenheim, E.A., Proc. Roy. Soc. A148, 304 (1935).
2. Guggenheim, E.A., "Mixtures", Oxford Unversity Press, 1952.
3. Wilson, G.M., J. Am. Chem. Soc., 86, 127 (1964).
4. Renon, H., Prausnitz, J.M., AIChE J., 14, 135 (1968).
5. Abrams, D.S., Prausnitz, J.M., AIChE J., 21, 116 (1975).
6. Whiting, W.B., Prausnitz, J.M., Fluid Phase Equilibria, 9, 119 (1982).
7. Mollerup, J., Fluid Phase Equilibria, 7, 121 (1981).
8. Nakanishi, K., Toukubo, K., J. Chem. Phys., 70, 5848 (1979).
9. Nakanishi, K., Okazaki, S., Ikari, K., Higuchi, T., Tanaka, H., J. Chem. Phys., 76, 629 (1982).
10. Fischer, J., Fluid Phase Equilibria, to be published.
11. Lee, L.L., Chung, T.H., Starling, K.E., to be published.
12. Pierotti, R.A., J. Phys. Chem., 67, 1840 (1963).
13. Pierotti, R.A., Chem. Rev., 76, 717 (1976).
14. Reiss, H., Frisch, H.L., Lebowitz, J.L., J. Chem. Phys., 31, 369 (1959).
15. Lebowitz, J.L., Helfand, E., Praestagard, E., J. Chem. Phys., 43, 774 (1965)
16. Moelwyn-Hughes, E.A., "Physical Chemistry", 2nd Ed., Pergamon Press 1961.
17. Reed, T.M., Gubbins, K.E., "Applied Statistical Mechanics" McGraw-Hill Book Co., 1973.
18. Panayiotou, C., Vera, J.H., Fluid Phase Equilibria, 5, 55 (1980).
19. Panayiotou, C., Vera, J.H., Can. J. Chem. Eng., 59, 501 (1981).
20. Kemeny, S., Rasmussen, P., Fluid Phase Equilibria, 7, 197 (1981).
21 Flemr, V., Coll. Czech. Chem. Commun., 41, 3347 (1976).
22. McDermott, C., Ashton, N., Fluid Phase Equilibria, 1, 33 (1977).
23. Maurer, G., Prausnitz, J.M., Fluid Phase Equilibria, 2, 91 (1978).


## Figure Captions

Figure 1 Formation of a real mixture

Figure 2 Short-range order and long-range randomness in a real mixture

Figure 3 Approximate and real radial distribution function and potential energy function

Figure 4 Comparison of excess Gibbs energies for mixtures A-2, LB-2 and S-2 at $T = 120K$ and $\rho\sigma^3 = 0.75$

Figure 5 Comparison of excess Gibbs energies for mixtures LB-3 and LB-4 at $T = 120K$ and $\rho\sigma^3 = 0.75$

Figure 6 Comparison of local composition ($x = 0.5$) of Lennard-Jones mixtures with $D=2$

Figure 7 Variation of local composition with $\alpha$

Figure 8 Excess Gibbs energy of LB-2 mixtures for $\alpha = 0$, 0.1 and 1.0

Figure 9 Temperature dependence of local composition for LB-2 mixture at $\rho\sigma^3 = 0.75$

Table 1

Types of Mixtures and Their Parameters

| Mixture | D | C | $k_{12}$ |
|---|---|---|---|
| A-2 | 2 | 1 | 0.293 |
| 0.85LB-2 | 2 | $0.85\sqrt{2}$ | 0.15 |
| 0.9LB-2 | 2 | $0.9\sqrt{2}$ | 0.1 |
| 0.95LB-2 | 2 | $0.45\sqrt{2}$ | 0.05 |
| LB-2 | 2 | $\sqrt{2}$ | 0 |
| 1.2LB-2 | 2 | $1.2\sqrt{2}$ | -0.2 |
| S-2 | 2 | 2 | -0.414 |
| LB-3 | 3 | $\sqrt{3}$ | 0 |
| 0.9LB-4 | 4 | 1.8 | 0.1 |
| LB-4 | 4 | 2 | 0 |

Table 2

Comparison of Excess Gibbs Energy Calculated from the Proposed Model with those from Monte Carlo (MC) and Perturbation Theory (PT) at 120K, $\rho\sigma^3 = 0.75$ and $x = 0.5$

| $G_m^E/kJ\ mol^{-1}$ | MC | PT | This work $\alpha = 0.05$ | This work $\alpha = 0.1$ |
|---|---|---|---|---|
| A-2 | 0.894 | 0.925 | 0.897 | 0.928 |
| 0.85LB-2 | - | 0.568 | 0.552 | 0.576 |
| 0.9LB-2 | - | 0.441 | 0.427 | 0.448 |
| 0.95LB-2 | - | 0.314 | 0.299 | 0.317 |
| LB-2 | 0.174 | 0.187 | 0.171 | 0.186 |
| 1.2LB-2 | - | -0.328 | -0.369 | -0.369 |
| S-2 | -0.944 | -0.884 | -0.988 | -1.007 |
| LB-3 | 0.438 | 0.476 | 0.432 | 0.474 |
| 0.9LB-4 | - | 1.023 | 0.937 | 1.019 |
| LB-4 | 0.767 | 0.769 | 0.694 | 0.768 |

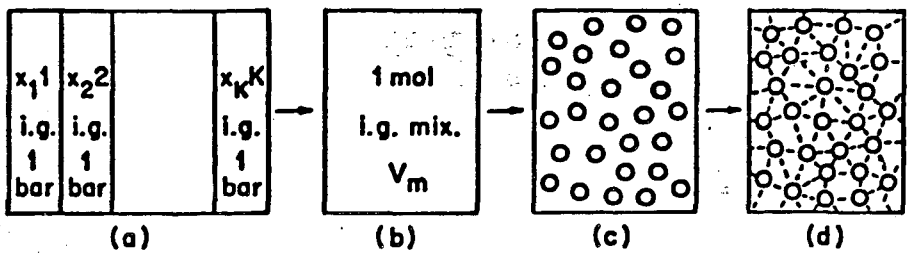



Figure 1

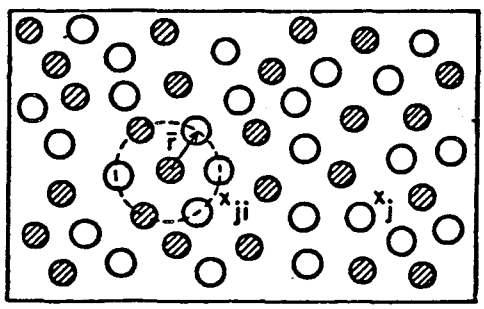



Figure 2

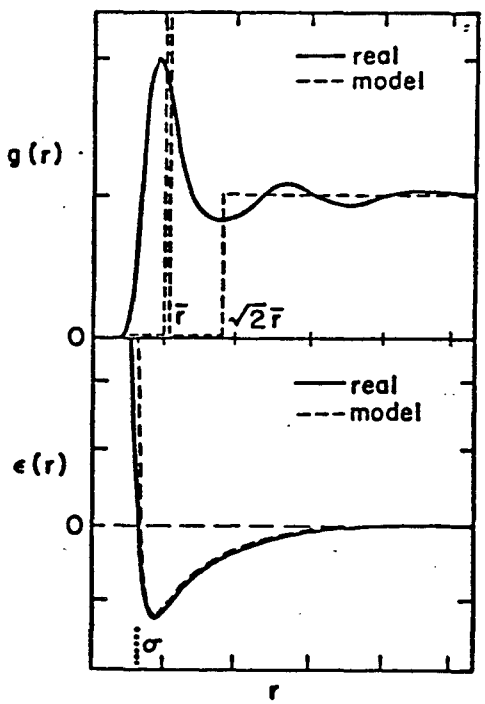
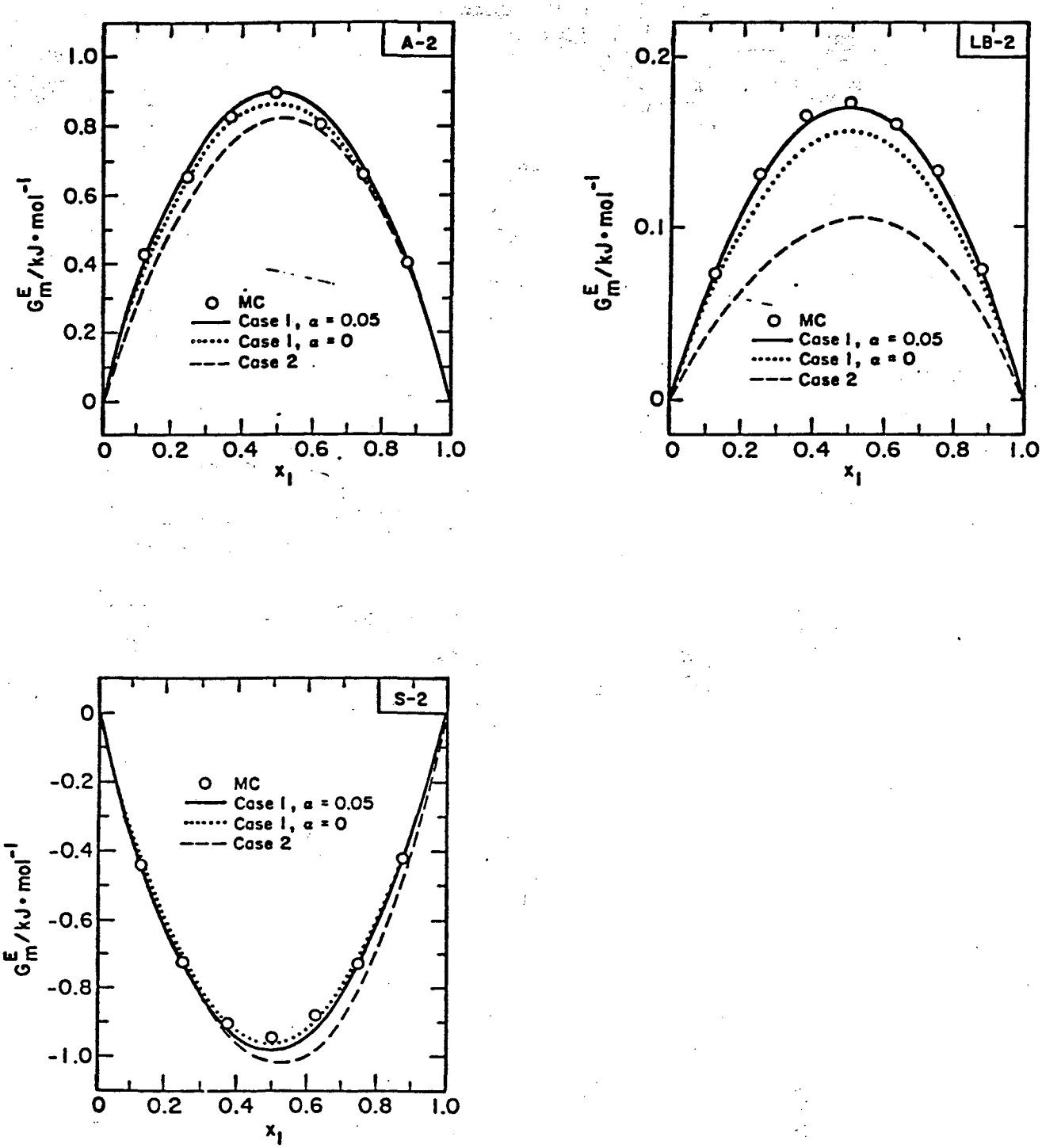



Figure 3

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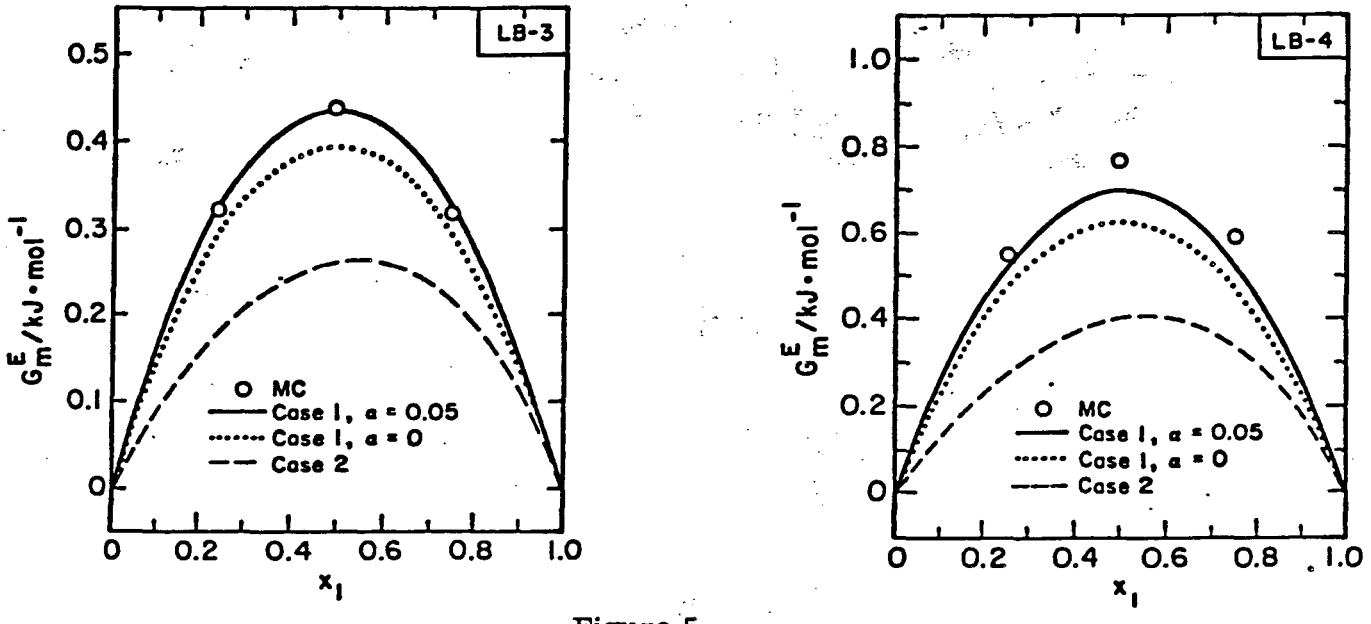
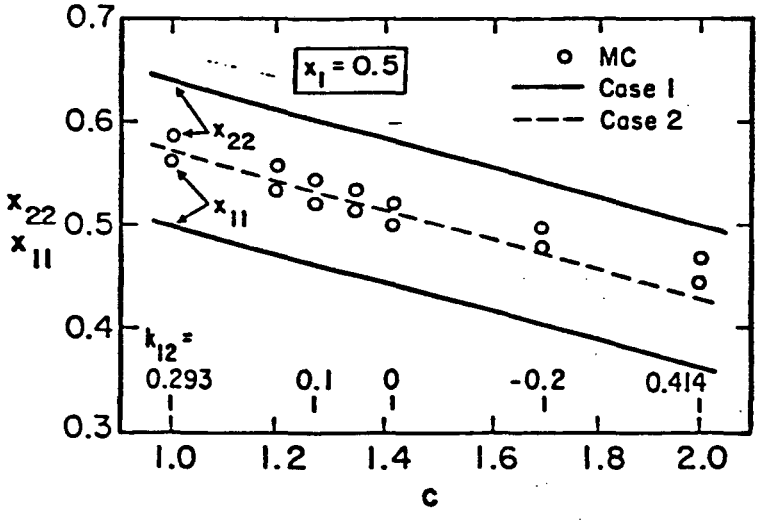



Figure 5

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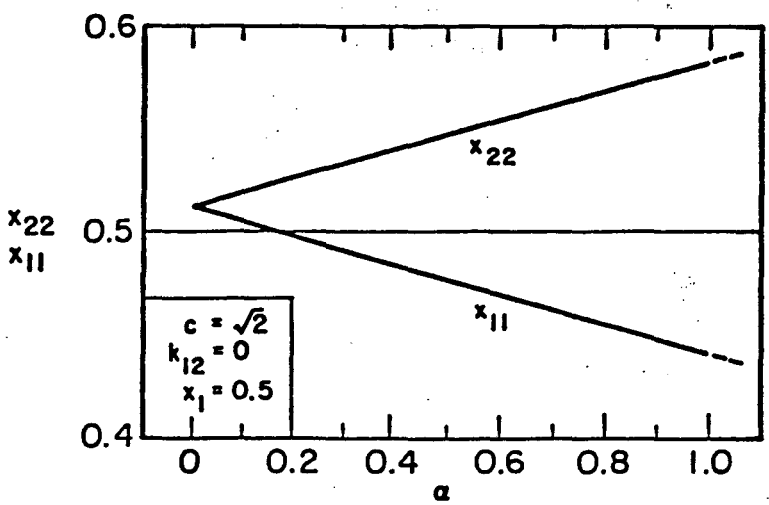


Figure 7

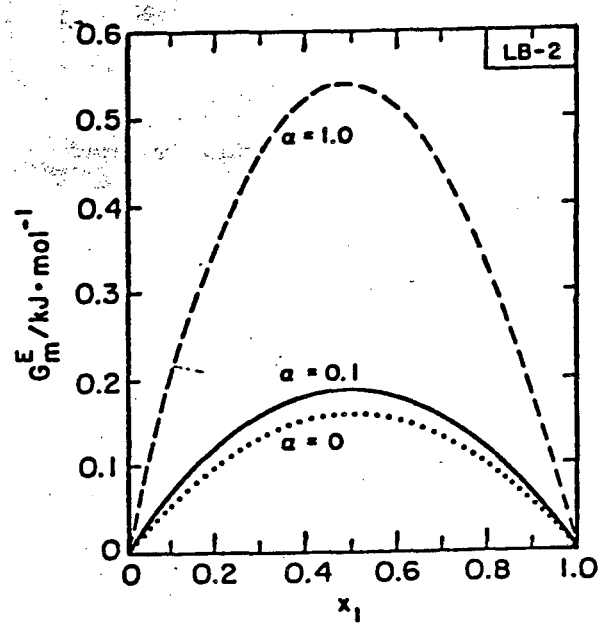


Figure 8

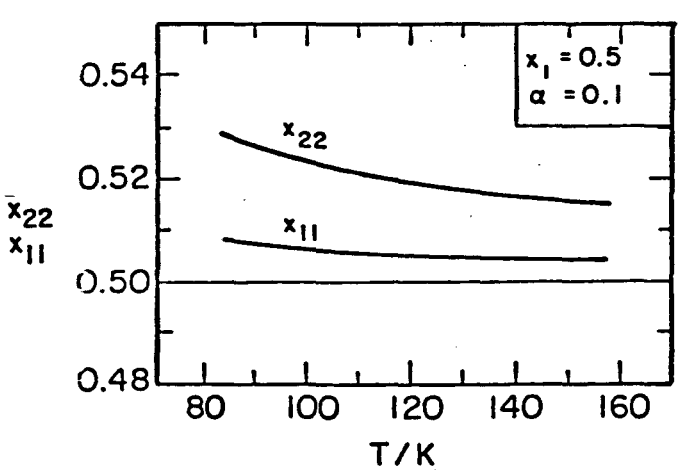


Figure 9

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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