Figure 12-6: Molecular view of solution.

NOTE

Molecular View of Nonideal Effects

In a solution of two components, a molecule is surrounded by a mix of similar and dissimilar molecules and experiences a combination of self- and cross-interactions, as shown schematically in Figure 12-6. The total energy of interaction depends on the average number neighbors and on how many of them are of the same kind. If self and cross interactions are identical in strength and the two components have similar molecular sizes, we obtain an ideal solution: a molecule is surrounded by the same number of neighbors on average, whether in pure liquid or in solution, and its total interaction with its neighbors does not depend on how many of them are of similar or dissimilar kind. If self and cross interactions are different, the solution environment surrounding a molecule is quite different from the environment in the pure liquid. This causes deviations from ideal-solution behavior. Difference in molecular size is also a source of nonidealities because the arrangement of neighbors around a molecule is affected. In the limit $x_i \to 1$, component i approaches ideal-solution behavior because it, interacts almost exclusively with molecules of the same type (component i is the majority component at this limit). In this solution the minority component is found at its infinite dilution limit: a molecule of the minority component is completely surrounded by dissimilar molecules and experience cross interactions only. The activity coefficient shows its maximum deviation from 1 at the infinite dilution limit.

Contributions to nonideality that are caused by differences in molecular size are called *combinatorial* and are related to the arrangement of molecules in space. Contributions that are caused by molecular interactions are called *residual*. The goal of solution theories is to provide suitable approximations for these two sources of nonideal behavior.

12.4 Activity Coefficient and Phase Equilibrium

To perform VLE calculations, the starting point is the equality of the fugacity of component in the two phases:

$$f_i^V = f_i^L.$$

For the fugacity of the vapor we use the general expression

$$f_i = y_i \phi_i^V P,$$