

Mutual Diffusion of Components in Liquid PAH-Water System in Mean Field Approximation

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Abstract

The model describing the properties of PAH-water system is proposed. The naphthalene-water system is taken as a particular example. The partial pressures are obtained by use of mean field approximation in lattice-gas model. The possibility of the existence of two stable condensed phases with different PAH fractions is shown. The binary phase diagram is constructed. The macroscopic dynamics of PAH diffusion in water and water diffusion in PAH is obtained by relaxation of free energy.

Introduction

The properties of PAH-water system especially liquid-gas phase transition are important for steam stripping of PAH (polycyclic aromatic hydrocarbons) from contaminated soils. The characteristic feature of PAH-water system is the wide miscibility gap, because of small interaction between PAH and water molecules in comparison with interaction between PAH-PAH or water-water molecules. These interactions can be easily included into lattice-gas model, in such a way that water and PAH molecules can situate only at certain sites of the lattice (positions in the imaginary lattice). The interactions occur between molecules situated at neighbouring sites. The size of the organic PAH molecule is much larger than that of water. This can be considered assuming that PAH molecule occupies several sites while water molecule occupy only one. Examples of two-dimensional simulations of such a system at two different temperatures are shown in Fig. 1.

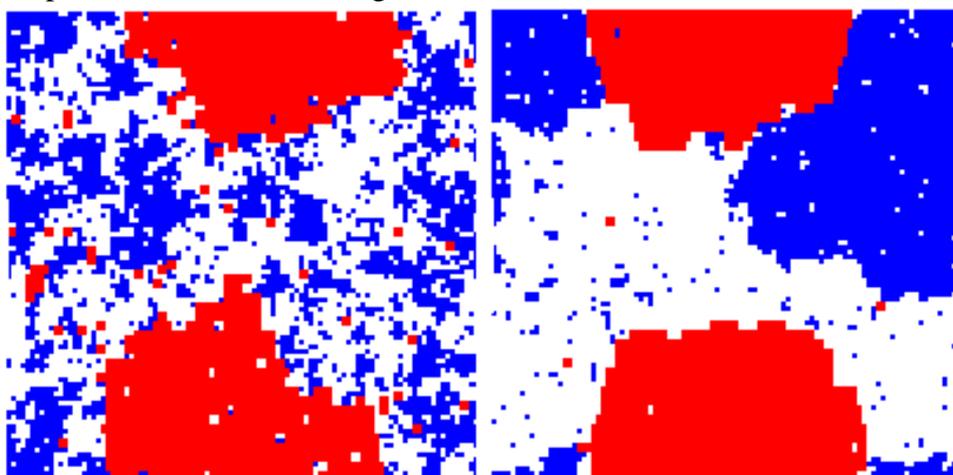


Fig. 1. Monte-Carlo simulations of PAH-water system near equilibrium. Larger molecules: PAH, smaller: water. Left figure at temperature 400 K, right one $T=300$ K. Periodic boundary conditions

As can be seen from Fig.1, PAH molecules condense at higher temperature in given mixture as the boiling temperature of PAH is higher than of water. However, the boiling temperature of the mixture depends on the fraction of both components in the system. The

analysis of phase transitions will be made using mean field approximation [1]. It neglects the correlations in the system.

1. Stationary Case

It is almost impossible to find the accurate expression of entropy if the size of one molecule is larger than another. In order to simplify the analysis, it is assumed that larger molecules can occupy only fixed positions in the lattice which guarantees that each PAH molecule do not edge into another. These positions are chosen in a way that there is left no free site in a pure PAH system. Free energy F^l of such a liquid phase in the mean field approximation [2] neglecting the presence of vacancies is

$$F^l = -\frac{1}{2N} [l_{11}\alpha N_1^2 + l_{12}(\alpha+1)N_1N_2 + l_{22}N_2^2] + kT \left[N_1 \ln \frac{\alpha N_1}{N} + \frac{N_2}{\alpha} \ln \frac{N_2}{N} \right], \quad (1)$$

where $N \equiv \alpha N_1 + N_2$ is the number of sites in the system, N_1, N_2 are numbers of PAH and water molecules, respectively; l_{11}, l_{12}, l_{22} are binding energies between PAH-PAH, PAH-water and water-water, respectively; α is the ratio of volumes between molecule of PAH and water. The values of the molar masses and densities of pure components show that the volume ratio α is 6.77 for naphthalene, while $\alpha = 8.83$ for pyrene. The lattice-gas model has to be used also for gaseous phase. The free energy here is

$$F^g = kT \left[N_1^g \ln \frac{N_1^g}{N^g} + \frac{1-\alpha}{\alpha} (N^g - \alpha N_1^g) \ln \frac{N^g - \alpha N_1^g}{N^g} + N_2^g \ln \frac{N_2^g}{N^g} + (N^g - \alpha N_1^g - N_2^g) \ln \frac{N^g - \alpha N_1^g - N_2^g}{N^g} \right], \quad (2)$$

where N^g is the number of sites in gas phase; N_1^g, N_2^g are numbers of PAH and water molecules in gas phase, respectively. The interaction in gaseous phase has been neglected as the concentrations here are very small $\alpha N_1^g + N_2^g \ll N^g$. In equilibrium case, the chemical potentials μ_1, μ_2 of components in both phases are equal:

$$\frac{\partial F^l}{\partial N_1} = \frac{\partial F^g}{\partial N_1^g} = \mu_1, \quad \frac{\partial F^l}{\partial N_2} = \frac{\partial F^g}{\partial N_2^g} = \mu_2. \quad (3)$$

The partial pressure for ideal gas is proportional to the density of respective component. This assumption allows to obtain equilibrium pressures at phase boundary:

$$P_1(T, C) = P_{1eq}(T)(1-C) \exp\left[\frac{sC^2}{2kT}\right], \quad P_2(T, C) = P_{2eq}(T)C^{1/\alpha} \exp\left[\frac{s(1-C)^2}{2\alpha kT}\right], \quad (4)$$

where $s = l_{11} - l_{12}(\alpha+1) + l_{22}\alpha$; $C = \frac{N_2}{N}$ is the volume fraction of water in condensed phase. The parameters l_{11}, l_{22} which depend on temperature are found in such a way that for pure substances one gets corresponding saturation pressures $P_{1eq}(T)$ and $P_{2eq}(T)$ found in literature [3]. The above mentioned approximation of entropy leads to impossibility of separate water molecule to enter in condensed PAH phase. Thus, the Henry's law is fulfilled in this model only for molecules with higher molecular volume - in our case PAH. However, the more accurate Monte-Carlo simulations show that Henry's law is fulfilled if the condensed phase contains vacancies. The partial pressure of PAH vs. water is shown in Fig. 2. Below the

temperature of azeotrope T_e , the pressure curve crosses itself and the cross-point corresponds to phase transition. In this case it is solubility limit. The equality of pressures follows from (3) as the chemical transformation does not occur at phase transition. The parameter s is taken as independent on temperature. Its value is estimated from PAH solubility in water at T_e . At higher temperatures, the pressure of the system $P=1$ bar (dotted line) crosses the sum $P_1(T,C) + P_2(T,C)$ and the cross-points (hollow circles) are the boiling points of mixture. The molar fraction of water at dew points is the same as ratio between water pressure $P_2(T,C)$ in the hollow cross-point and total pressure P . That is the consequence of Dalton's law.

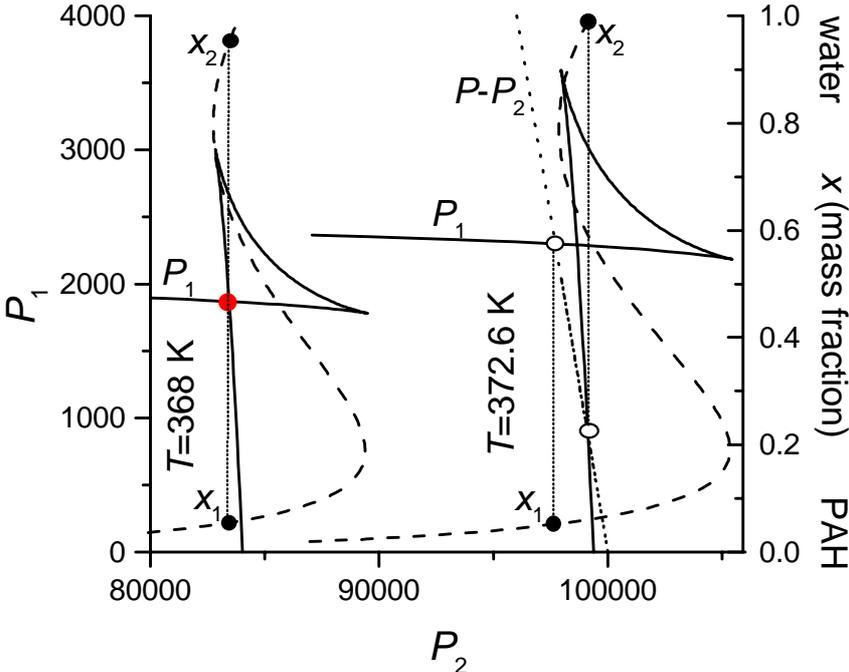


Fig. 2. Partial pressure of naphthalene vs. water (solid curve) at temperatures lower and higher than T_e . Dashed curve – mass fraction of water. x_1, x_2 : phase transition points

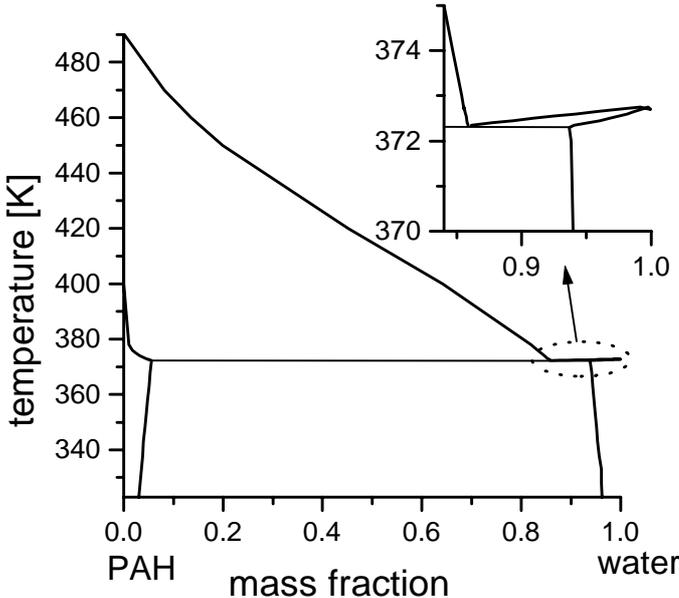


Fig. 3. Constructed phase diagram of naphthalene-water basing on partial pressures in Fig. 2

The graphically obtained phase transition points of Fig. 2 allow to build the phase diagram in Fig. 3. Rather high solubility of water in PAH is caused by the approximation of entropy for molecules with different sizes.

2. Mutual Diffusion in PAH-Water System

The diffusion like behaviour of condensed PAH-water system near equilibrium is of interest. Consider the on-dimensional case where the properties of this system vary only in segment with length l along x axis. The free energy (1) of the system is the integral

$$\frac{\alpha F^{11}[C]}{N} = \int_0^l dx \left\{ -\frac{1}{2} [l_{11}(1-C) + \alpha l_{22}C - sC(1-C)] + kT [C \ln C + (1-C) \ln(1-C)] \right\} dx, \quad (5)$$

where $C \equiv C(t, x)$. The free energy has a minimum at homogeneous distribution $C(t, x) = \text{const}$ at constant temperature if one-phase system is stable. Let us include a small perturbation by changing the homogeneous distribution. Such perturbation creates fluxes that for isolated system tends to equalise the distribution and thus decrease the free energy [4]. This flux is proportional to

$$j \sim -C(1-C) \frac{\partial}{\partial x} \left(\frac{\delta F^{11}}{\delta C(x)} \right) \sim -(kT - sC(1-C)) \frac{\partial C}{\partial x}, \quad (6)$$

where the multiplier $C(1-C)$ is added because the relaxation has diffusion like nature and its rate is proportional to the number of occupied sites and number of free sites. For small fraction C , the flux is $j = -D \frac{\partial C}{\partial x}$, where D is diffusion coefficient. Equation (6) shows that the interaction between components changes the diffusion coefficient to

$$D_{\text{eff}}(C) = D \left(1 - \frac{s}{kT} C(1-C) \right). \quad (7)$$

One notes that the effective diffusion coefficient could change the sign at a certain interval of C which would lead to instability of the numerical solution. The explanation for such a behaviour is that homogeneous distribution becomes unstable. Instability means that two-phase system is present. Neglecting the energy of phase boundaries, the free energy of locally relaxed system is

$$\frac{\alpha F^{12}[C]}{N} = \int_0^l dx \left\{ -\frac{1}{2} [l_{11}(1-C) + \alpha l_{22}C - sC_{eq}(1-C_{eq})] + kT [C_{eq} \ln C_{eq} + (1-C_{eq}) \ln(1-C_{eq})] \right\} dx, \quad (8)$$

where C is again the average volume fraction of water in the system; non-trivial two roots of

$$C_{eq} = \frac{1}{1 + \exp \left[\frac{s}{2kT} (1 - 2C_{eq}) \right]} \neq \frac{1}{2} \quad (9)$$

are the equilibrium fractions in two-phase system either of the solubility limit of water in PAH or vice versa. These values correspond to solubility curves in phase diagram Fig. 3. For convenience, let us take the root with $C_{eq} < \frac{1}{2}$, while the fraction in another phase is $1 - C_{eq}$.

Introducing the small perturbation for C in the system, one obtains that flux is zero at homogeneous temperature:

$$j \sim -C(1-C) \frac{\partial}{\partial x} \left(\frac{\delta F^{12}}{\delta C(x)} \right) = 0. \quad (10)$$

Resuming, the diffusion equations are

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \left(1 - \frac{s}{kT} C(1-C) \right) \frac{\partial C}{\partial x} \right), \quad C \leq C_{eq} \text{ or } C \geq 1 - C_{eq}, \quad (11)$$

$$\frac{\partial C}{\partial t} = 0, \quad C_{eq} < C < 1 - C_{eq}. \quad (12)$$

These macroscopic diffusion equations describe stable relaxation of the condensed phase as the effective diffusion coefficient is always positive. The only point where diffusion coefficient becomes zero is at critical temperature $T_c = \frac{s}{4k}$ and $C = \frac{1}{2}$, which is the consequence of such phenomena as critical opalescence. However, the critical temperature for PAH-water system at 1 bar pressure is much higher than temperature of azeotrope T_e . Therefore, the correction in effective diffusion coefficient plays a little role in the dynamics of condensed system. The mutual diffusion in naphthalene-water system is shown in Fig. 4, where the initial condition corresponds to separated components. The thickness of thinner layer with major PAH fraction decreases as the greater amount of PAH dissolves into water. The monotonous decrease of free energy is shown in Fig. 5.

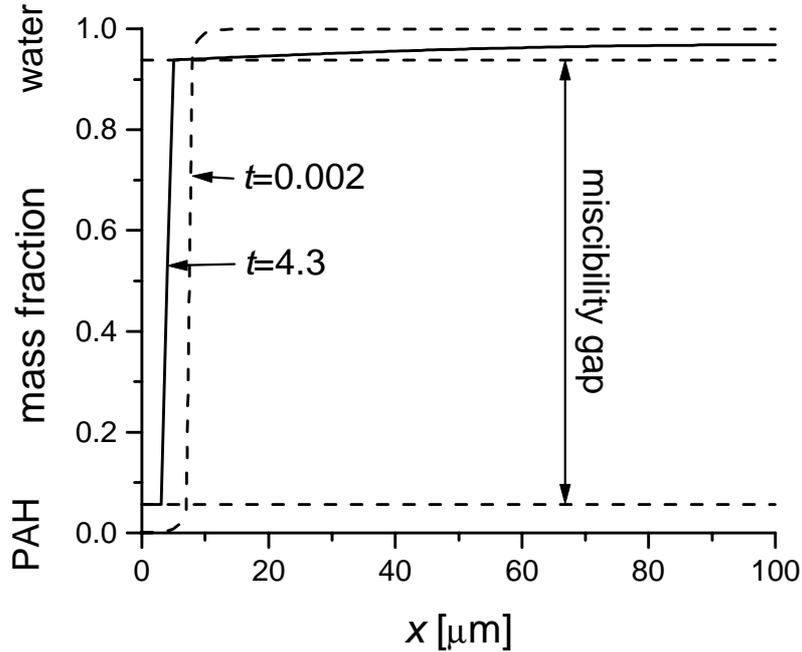


Fig. 4. Mutual diffusion in closed naphthalene-water system at 372 K

For inhomogeneous temperature, other gradient terms survive that leads to thermo-diffusion. Nevertheless, the temperature during steam stripping in condensed phase remains practically homogeneous close to T_e . Hence, thermo-diffusion can be neglected.

The inclusion of surface tension in free energy of two phase system by means of correcting C_{eq} for concave phase boundary would lead to instability. These instabilities are of

microscopic nature. The small change of the free energy by surface tension can be neglected for macroscopic description.

Conclusions

The mean field approximation of microscopic lattice-gas model allows to obtain the partial pressures of binary mixture if the saturation pressures of individual components are known. The wide miscibility gap in PAH-water system is caused by comparatively weak interaction between different molecules.

More accurate and time consuming Monte-Carlo simulations allows to test the model equations, particularly those concerning the phase equilibrium.

The variation of locally relaxed free energy leads to stable macroscopic dynamics of two-phase system neglecting the energy of phase boundaries.

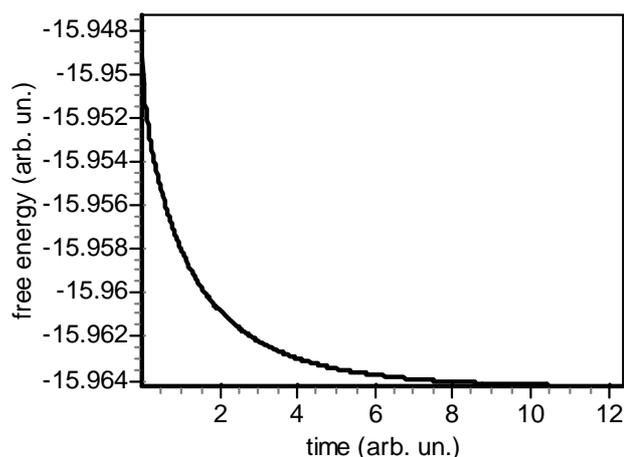


Fig. 5. Decrease of free energy in diffusion process of Fig. 4

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