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# Influence of the Chain Length of Long Molecules on the Equation of State in Binary Gas–Liquid Mixtures

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The simple Flory–Huggins model can be combined with the lattice gas as was done by Tompa and others. Here the same method is used to obtain the van der Waals equation of state for a binary gas–liquid system containing a solute consisting of segmented molecules. The simplified equation of state developed here is useful for the study of the critical properties of such systems, in particular, the dependence of the various parameters on the chain length of the molecules.

**KEY WORDS:** Binary systems; gas–liquid systems; Tompa model; van der Waals equation.

## 1. THE EQUATION OF STATE

Let the number of sites occupied by solvent molecules be $n_1$ and assume that the number of chain molecules is $n_2$. Each molecule is made from $N$ segments; hence, the number of sites occupied by segments of the chain molecule is $Nn_2$. If the number of unoccupied sites is $n_0$, then total number of lattice sites will be $L = n_1 + Nn_2 + n_0$. The corresponding densities are $x_1 = n_1/L$, the density of the solvent, $x_2 = Nn_2/L$, the density of the polymer molecules, and $x_0 = n_0/L$, representing the density of the holes. These three variables also represent the probabilities in the molecular field approximation. Although $x_0$ is not an independent variable, it is often convenient to maintain it in the equations.

The interaction energy is given by

$$E = -L\left[\left(\frac{n_1}{L}\right)^2 w_1 + N\frac{n_1 n_2}{L^2} w_{12} + \left(\frac{Nn_2}{L}\right)^2 w_2\right] \tag{1}$$

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which leads to

$$E = -L(w_1 x_1^2 + w_{12} x_1 x_2 + w_2 x_2^2) \tag{1'}$$

The coefficient $w_{12}$ represents the interaction energy *per segment* between the solvent and the polymer molecule. The entropy is given by the logarithm of the probabilities multiplied by the number:

$$-S = n_1 \ln x_1 + n_2 \ln x_2 + (n_0 - L\sigma) \ln n_0 \tag{2}$$

The factor in the last term was modified to incorporate the van der Waals equation.(1) For $\sigma = 0$ one deals with the lattice gas (the Flory–Huggins–Tompa model,(2,3) and for $\sigma = 1$ with the modified van der Waals equation of state for chain molecules.

From the above equations one can construct the free energy

$$\begin{aligned} F/L = {} & -(w_1 x_1^2 + w_{12} x_1 x_2 + w_2 x_2^2) - \mu_1 x_1 - \mu_2 x_2 \\ & + T\left(x_1 \ln x_1 + \frac{x_2}{N} \ln x_2 + (x_0 - \sigma) \ln x_0\right) \end{aligned} \tag{3}$$

By differentiation with respect to $x_1$ and $x_2$ one finds the equations of state,(4),[2]

$$T\left[\ln\left(\frac{x_1}{x_0}\right) + \frac{\sigma}{x_0}\right] = 2w_1 x_1 + w_{12} x + \mu_1 \tag{4a}$$

$$T\left(\frac{\ln x_2}{N} - \ln x_0 + \frac{1}{N} - 1 + \frac{\sigma}{x_0}\right) = w_{12} x_1 + 2w_2 x_2 + \mu_2 \tag{4b}$$

Since the chemical potentials are usually not measured, it is customary to determine the pressure.(5) The accompanying equation (called the $q$ potential by van der Waals,(7) which is an expression for the difference in chemical potentials) is usually ignored.

In Appendix A it is shown that the definition of the pressure in a lattice system with $N$-segmented molecules is the same as before:

$$pV_0 = -F + x_1 \frac{\partial F}{\partial x} + x_2 \frac{\partial F}{\partial x_2} \tag{5}$$

Using this definition, we obtain

$$\begin{aligned} & pV_0 + w_1 x_1^2 + w_{12} x_1 x_2 + w_2 x^2 \\ & \quad = T\left[(\sigma - 1) \ln x_0 + \frac{x_1 + x_2}{x_0} \sigma + \frac{x_2}{N} - x_2\right] \end{aligned} \tag{6}$$

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[2] The $N$ dependence in Eqs. (3) and (6b) in ref. 4 is incorrect.

It is easy to see that for $N=1$ we regain the van der Waals equation if $\sigma=1$ and the lattice gas equation if $\sigma=0$. (The cell size is 1; see Appendix B.)

For $N\neq 1$ the equation has an extra term. Whether this term represents a physical reality is not clear *a priori.* For this reason the justification of the definition of the pressure is repeated in the Appendix.

## 4. CALCULATION OF THE CRITICAL LINE AND THE LIMIT OF STABILITY

In order to obtain the Hessian matrix of the free energy, which determines the condition for the spinodal temperature, I introduce the functions

$$\alpha_1 = T/x_1 - U_1 \tag{7a}$$

$$\alpha_2 = T/Nx_2 - U_2 \tag{7b}$$

$$\alpha_0 = [(1+\sigma/x_0)/x_0]\,T - U_0 \tag{7c}$$

with $U_1 = 2w_1 - w_{12}$, $U_2 = 2w_2 - w_{12}$, and $U_0 = w_{12}$. The spinodal is given by

$$\alpha_1\alpha_0 + \alpha_2\alpha_0 + \alpha_1\alpha_2 = 0 \tag{8}$$

In order to obtain the critical line, one differentiates and finds

$$\chi = \frac{x_1}{(T - x_1 U_1)^3} + \frac{x_2/N}{(T/N - x_2 U_2)^3} + \frac{x_0^3(2\sigma + x_0)/(x_0+\sigma)^3}{T - [x_0^2/(x_0+\sigma)]\,U_0} = 0 \tag{9}$$

After substitution of the previous equation to eliminate the $T$, one obtains an expression for the critical line in the form

$$\chi = \chi(x_1, x_2; w_1, w_2, w_{12}, N) \tag{10}$$

It is possible to express this as a polynomial in $x_1$ and $x_2$, depending on the parameters $w_1$, $w_2$, $w_{12}$, and $N$.

## 3. CONDITIONS FOR THE TRICRITICAL POINT

The tricritical point is determined by two conditions. The first is the condition that the critical line has a point at which metastability changes into unstability as given by

$$\Sigma = \frac{\partial \chi}{\partial x_1}\alpha_2 + \frac{\partial \chi}{\partial x_2}\alpha_1 = 0 \tag{11}$$

and second that two of these points coincide:

$$\frac{\partial \Sigma}{\partial x_1}\alpha_2+\frac{\partial \Sigma}{\partial x_2}\alpha_1=0 \tag{12}$$

As indicated in ref. 8, the tricritical point may or may not be a critical double point. This is of practical interest since double points are easier to evaluate. Regions around the double point can be explored effectively using expansions.

## 4. APPLICATION

Peters *et al.*(9) noted that, when comparing solutions of alkane molecules of different lengths, the logarithm of the concentration in the gas phase depended on the length of the chains in a linear fashion in the interval $8<N<24$.

Using the modified equation of state for the segmented molecules, we find, omitting all terms of second and higher order in the density variables, since we consider the gas phase only,

$$pV_0=T[(x_1+x_2)+(1/N-1)\,x_2] \tag{13}$$

Hence, at constant temperature and pressure one might compare the concentration $c=x_2/(x_1+x_2)$ as a function of $N$, the number of segments, as follows:

$$1-\frac{pV_0}{\rho T}=\left(1-\frac{1}{N}\right)c \tag{14}$$

For large $N$ this can be written as

$$\ln c=\frac{1}{N}+\ln\left(1-\frac{pV_0}{\rho T}\right) \tag{15}$$

If the last term is kept constant, this leads to a linear dependence on $1/N$. In the interval considered, this is approximately Peters' observation.

## APPENDIX A. THE DEFINITION OF THE PRESSURE IN A LATTICE GAS

The definition of the pressure in a lattice gas is somewhat esoteric because there are no molecules flying around, hence it might be a good idea to go back to basics. Despite the fact that no kinetics is[3] involved, the

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[3] I know this will hurt you, Nico, but in English this is officially recognized as "plural construed as singular."

lattice gas does give the ideal gas result at low densities. The same holds for the modification of the lattice gas, where the hole entropy $x_0 \ln x_0$ is replaced by the expression $(x_0 - 1) \ln x_0$; it leads to the van der Waals equation of state for one component and for binary mixtures. In both cases the pressure was defined in various places in the literature^(5,10) as

$$pV_0 = -F + x\, \partial F/\partial x \tag{A1}$$

which led to the desired result, despite the lack of kinetics. The argument used to establish Eq. (A1) is repeated here in order to show that the introduction of segmented molecules does not affect the result.

Since the pressure is a force per unit area and since the force is the negative derivative of the thermodynamic energy, i.e., the free energy, it is natural to define the pressure as

$$pV_0 = -L\, \partial F/\partial L \tag{A2}$$

where $L$ is the number of lattice sites. Since the $L$ dependence of the free energy is, in the models used here, always of the form

$$F = Lf(n_1/L, n_2/L) \tag{A3}$$

where $f$ is a given function of the density variables $x_1 = n_1/L$ and $x_2 = n_2/L$, it follows immediately that

$$pV_0 = -L\left(f - x_1 \frac{\partial f}{\partial x_1} - x_2 \frac{\partial f}{\partial x_2}\right) \tag{A4}$$

and that the definition is independent of $N$.

## APPENDIX B

In the original van der Waals equation a volume $V_m$ was assigned to the space occupied by the molecules. Since this volume is proportional to the number of molecules, $V_m = bn$. The logarithmic term in the free energy can be written as

$$\ln(V - bn) = \ln[V(1 - n/L)] \tag{B1}$$

with $L = V/b$, the number of lattice sites available to the molecules. This subsequently leads to the term $T(x_1 + x_2)/x_0$ in the van der Waals equation of state. Using this approximation for the case of a system consisting of a solvent and a polymer, the same result is obtained provided one takes for $n = n_1 + Nn_2$, the total number of solvent molecules plus the total number of polymer segments. A major drawback of this model is, as is the case for any lattice type of description, that the volume occupied by the solvent molecule has been taken to be the same as the volume occupied by a polymer segment. Of course one is not bound to the lattice model, but if a concentration-dependent $b$ factor is introduced, one loses the advantage of a separable free energy.

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## NOTE ADDED IN PROOF

I was not aware that the problem of the $N$-dependence was addressed by Hijmans$^{(11)}$ in 1961.

## REFERENCES

1. D. Furman and R. B. Griffiths, *Phys. Rev. A* **17**:1139 (1978).
2. H. Tompa, *Trans. Faraday Soc.* **45**:1142–52 (1949).
3. K. Solc, L. A. Kleintjes, and R. Koningsveld, *Macromolecules* **17**:573 (1984).
4. P. H. E. Meijer, I. L. Pegg, M. Keskin, *J. Chem. Phys.* **88**:1976 (1988).
5. M. Coopersmith and R. Brout, *Phys. Rev.* **130**:2539 (1963).
6. J. D. van der Waals, *Natuurk. Verh. Kon. Akad. Amsterdam, Deel XX* (August 1880).
7. J. D. van der Waals and Ph. Kohnstamm, *Lehrbuch der Thermostatik*, Part II (Barth, Leipzig, 1927).
8. P. H. E. Meijer, *J. Chem. Phys.*, to appear.
9. C. J. Peters, J. de Swaan Arons, J. S. Galagher and J. M. H. Levelt Sengers, *A.I.Ch.E. Journal* **34**:834 (1988).
10. J. A. Schouten, C. A. ten Seldam, and N. J. Trappeniers, *Physica* **73**:556 (1974).
11. J. Hijmans, *Physica* **27**:433 (1961).