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Critical Scaling Laws and an Excess Gibbs Energy Model

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ABSTRACT

Excess Gibbs energy models which are widely used in modelling thermodynamic properties of multicomponent liquid phases are based on the assumption that long-range density or concentration fluctuations can be neglected. This assumption is no longer valid near a system's critical point, where large density or concentration fluctuations effectively mask the identity of the system and produce universal phenomena which have been well studied in simple liquid-vapor and liquid-liquid systems. Based on the Landau-Ginzburg-Wilson theory of fluctuations we have developed a crossover procedure to incorporate the effects of critical fluctuations into a classical excess Gibbs energy model. As an example we have applied our crossover procedure to the Non-Random Two-Liquid (NRTL) excess Gibbs energy model. This crossover procedure involves the use of transformed variables for temperature and concentration and adding a fluctuation term to the classical excess Gibbs energy. The resulting transformed Gibbs energy has the universal scaling behavior near the consolute critical point and has a smooth crossover to classical behavior far away from the consolute critical point.

KEY WORDS: critical phenomena; Gibbs free energy; isobaric binary mixtures; liquid-liquid equilibrium; NRTL model.

1. INTRODUCTION

Liquid-liquid equilibria play an important role in the chemical industry. In an attempt to describe liquid-liquid equilibria in fluids, various phenomenological and semi-theoretical models have been proposed in the chemical engineering literature. Some commonly used models are the regular solution model, the Wilson model, the NRTL model, and UNIQUAC [1]. All these models are classical (mean-field) in nature and they fail to account for the effects of long-range concentration fluctuations in the vicinity of a consolute critical point. Classical models predict power-law behavior with classical critical exponents and these draw backs are now well understood [2].

In an attempt to describe both the critical region and the region remote from the critical point, various modifications of classical equations have been proposed. De Pablo and Prausnitz [3] have proposed a phenomenological correction to classical equations and have shown good representation of liquid-liquid equilibria in some binary and ternary systems. To account for non-classical behavior, De Pablo and Prausnitz [4, 5] have also have applied a transformation proposed by Fox [6], and extended it to binary and ternary system. Since Fox's method uses field variables explicitly, the methodology is less transparent and it is computationally intense [4, 5]. In addition this transformation fails to reproduce correct universal amplitude ratios asymptotically close to the critical point [7].

A systematic way of incorporating long-range fluctuations into a classical equation can be developed on the basis of renormalization-group theory [8]. Specifically, Chen and coworkers have shown how long-range fluctuations can be incorporated in a Landau-type expansion [9, 10, 11]. The simplicity and the physical appeal of this method is its transformation of the temperature and the order-parameter variable. The approach has been extended to the Carnahan-Starling-DeSantes equation of state [12, 13]. In this paper, a general transformation of the temperature and the mole

fraction variable in Gibbs energy models for liquid-liquid equilibria is proposed. This transformation can be applied to any classical Gibbs energy model. The transformed Gibbs energy model has the correct singular behavior in the vicinity of the consolute critical point and has a smooth crossover to classical behavior far away from the consolute critical point.

2. THERMODYNAMIC POTENTIAL

For a binary liquid mixture containing components 1 and 2, the molar Gibbs free energy satisfies a differential relation of the form

$$dg = -sdT + vdp + \mu_1 dx_1 + \mu_2 dx_2, \tag{1}$$

where s is the molar entropy, T is the temperature, v is the molar volume, p is the pressure, μ_i is the chemical potential of component i, and x_i is the mole fraction of component i. For a system at constant pressure Eq. (1) can be written as

$$dg = -sdT + \mu_{21} dx_2, \tag{2}$$

where $\mu_{21} = \mu_2$-μ_1. Here the thermodynamic potential, the molar Gibbs free energy $g(T, x_2)$, is a function of a density x_2 and a field T.

Binary liquid-liquid mixtures near a consolute point and pure fluids near a vapor-liquid critical point belong to the same universality class as the 3-dimensional Ising model [2, 14]. Close to the critical point, large density or/and concentration fluctuations effectively mask the microscopic identity of the system and produce universal phenomena. Near a consolute point of a binary mixture, the difference in the concentration of either component in the two coexisting liquid phases at constant pressure asymptotically behaves as:

$$x^{''} - x^{'} = \pm 2B \left| \frac{T - T_{\mathrm{c}}}{T_{\mathrm{c}}} \right|^{\beta} \tag{3}$$

where T_c is the consolute temperature, β is a critical exponent and B is a system dependent coefficient. Another property that is readily accessible to experiments is the osmotic susceptibility, which is defined as:

$$\left(\frac{\partial x_1}{\partial \mu_1}\right)_{P,T} = -\left(\frac{\partial x_2}{\partial \mu_1}\right)_{P,T} = \left\{x_2 \left(\frac{\partial^2 g}{\partial x_2^2}\right)_{P,T}\right\}^{-1}, \tag{4}$$

and which diverges asymptotically as

$$x_2 \left(\frac{\partial x_1}{\partial \mu_1}\right)_{P,T} = \pm\Gamma \left|\frac{T - T_c}{T_c}\right|^{-\gamma} \quad \text{along} \quad x = x_c \quad \text{as} \quad T \to T_c. \tag{5}$$

Here γ is a critical exponent, x_c is the critical concentration and Γ is a system-dependent coefficient.

3. EXCESS GIBBS FUNCTION

In this work the reduced molar Gibbs energy of mixing $\Delta g/RT$ is used as a generating function:

$$\frac{\Delta g}{RT} = x_1 \ln x_1 + x_2 \ln x_2 + \frac{g^{\mathrm{E}}}{RT} \tag{6}$$

where R is the universal gas constant and g^{E} is the excess Gibbs energy. One g^{E} model which is widely used to describe partially miscible systems is the NRTL equation [15]:

$$\frac{g^{\mathrm{E}}}{RT} = x_1 x_2 \left[\frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_1 + x_2 G_{12}}\right] \tag{7}$$

$$\tau_{21} = \frac{g_{21} - g_{11}}{RT} \quad , \quad \tau_{12} = \frac{g_{12} - g_{22}}{RT}$$
$$G_{21} = \exp(-\alpha_{12}\tau_{21}) \quad , \quad G_{12} = \exp(-\alpha_{12}\tau_{12}). \tag{8}$$

Here g_{ij} is an energy parameter characteristic of the i-j interaction. The parameter α_{12} is related to the nonrandomness in the mixture. When α_{12} is zero, the mixture is completely random and Eq.(7) reduces to the regular solution model. This equation has three parameters τ_{21}, τ_{12}, and α_{12}, but α_{12} is generally fixed at a value between

0.2 to 0.470.

4. CLASSICAL MOLAR GIBBS FREE-ENERGY OF MIXING

For a complete specification of the thermodynamic properties, the reduced molar Gibbs free-energy of mixing as a function of mole fraction and temperature is considered here. All variables used here are made dimensionless.

$$\tilde{T} = -\frac{T_{\rm c}}{T}, \qquad \tilde{x} = \frac{x}{x_{\rm c}}, \qquad \tilde{g} = \frac{g}{RT}, \qquad \tilde{\mu} = \frac{\mu}{RT}$$
$$\Delta\tilde{T} = \tilde{T} + 1, \qquad \Delta\tilde{x} = \tilde{x} - 1. \tag{9}$$

In terms of these reduced variables, the NRTL parameters in Eq. (8) can be rewritten as:

$$\tau_{21} = \frac{g_{21} - g_{11}}{RT} = \tilde{a}(1 - \tilde{b}\Delta\tilde{T})$$
$$\tau_{12} = \frac{g_{12} - g_{22}}{RT} = \tilde{c}(1 - \tilde{d}\Delta\tilde{T}) \tag{10}$$

By applying the conditions of incipient immiscibility at the consolute point

$$\left(\frac{\partial^2 \Delta g}{\partial x^2}\right)\Big|_{x=x_{\rm c}} = \left(\frac{\partial^3 \Delta g}{\partial x^3}\right)\Big|_{x=x_{\rm c}} = 0, \tag{11}$$

the number of parameters can be reduced by two. For the NRTL equation, $\tilde{a} = 1.3474$ and $\tilde{c} = 0.94366$.

This classical molar Gibbs free-energy of mixing is valid everywhere except near the consolute point. Near this point, the thermodynamic properties calculated from classical equation exhibit power-laws, Eqs. (3) and (5), with classical exponent values $\beta = 0.5$ and $\gamma = 1.0$. Experiments and renormalization group calculations show $\beta = 0.325$ and $\gamma = 1.24$ [16]. In order to reproduce the correct singular behavior the free-energy is separated into a regular and a singular part.

$$\Delta\tilde{g}(\tilde{x}, \tilde{T}) = \Delta\tilde{g}_{\rm reg}(\tilde{x} = 1, \tilde{T}) + \Delta\tilde{g}_{\rm sing}(\tilde{x}, \tilde{T}) \tag{12}$$

The regular part is an analytic function of $\tilde{T}$ and the singular part is responsible for the non-analytic behavior near the critical point.

This separation of the Gibbs free-energy of mixing can be accomplished by expanding $\Delta\tilde{g}$ around the consolute point:

$$\Delta\tilde{g}(\tilde{x},\tilde{T}) = \Delta\tilde{g}(\tilde{x}=1,\tilde{T}) + \frac{\partial}{\partial\tilde{x}}(\Delta\tilde{g})\Big|_{\tilde{x}=1}(\tilde{x}-1) + \frac{1}{2!}\frac{\partial^2}{\partial\tilde{x}^2}(\Delta\tilde{g})\Big|_{\tilde{x}=1}(\tilde{x}-1)^2 + \cdots \quad (13)$$

In this expansion, the terms second and higher order in $\tilde{x}$ are combined to form $\Delta\tilde{g}_{\rm sing}$:

$$\Delta\tilde{g}_{\rm sing}(\tilde{x},\tilde{T}) = \Delta\tilde{g}(\tilde{x},\tilde{T}) - \Delta\tilde{g}(\tilde{x}=1,\tilde{T}) - \frac{\partial}{\partial\tilde{x}}(\Delta\tilde{g})\Big|_{\tilde{x}=1}(\tilde{x}-1). \quad (14)$$

The crossover procedure described in the next section is applied to $\Delta\tilde{g}_{\rm sing}$.

5. RENORMALIZED MOLAR GIBBS FREE-ENERGY OF MIXING

The classical molar Gibbs free-energy of mixing $\Delta\tilde{g}$ has to be transformed close to the critical point to take into account the effects of critical fluctuations. One such transformation has been developed by Chen et al. [9] for the Helmholtz free-energy density of a one-component fluid near the vapor-liquid critical point, where the order parameter is to be identified with the density. In incompressible liquid mixtures the order parameter is to be identified with the concentration x and we consider the Gibbs energy as a function of T and x as the appropriate potential

$$\Delta\tilde{g}_{\rm x} = \Delta\tilde{g}_{\rm sing}(\Delta\tilde{T}_{\rm x},\Delta\tilde{x}_{\rm x}) - \frac{1}{2}\Delta\tilde{T}^2\mathcal{K} \quad (15)$$

with

$$\Delta\tilde{T}_{\rm x} = \Delta\tilde{T}\mathcal{T}\mathcal{U}^{1/2} \quad (16)$$

$$\Delta\tilde{x}_{\rm x} = \Delta\tilde{x}\mathcal{D}^{1/2}\mathcal{U}^{1/4} \quad (17)$$

The rescaling functions $\mathcal{T}$,$\mathcal{D}$,$\mathcal{U}$ and $\mathcal{K}$ in these transformations are defined as:

$$\mathcal{T} = Y^{\frac{2\nu-1}{\nu\omega}} \quad , \quad \mathcal{U} = Y^{\frac{1}{\omega}},$$
$$\mathcal{D} = Y^{\frac{-\eta}{\omega}} \quad , \quad \mathcal{K} = \frac{\nu}{\alpha\bar{u}\Lambda}\left(Y^{-\frac{\alpha}{\nu\omega}} - 1\right), \quad (18)$$

where α, η, ν, and ω are critical exponents. The exponents β and γ in Eqs. (3) and (5) are related to the above set of exponents through the exponent relations $\gamma = (2-\eta)\cdot\nu$ and $\alpha + 2\beta + \gamma = 2$ [2, 16]. The function Y in Eq. (18) is a crossover function, which is defined implicitly as:

$$1 - (1-\bar{u})Y = \bar{u}\left[1 + \left(\frac{\Lambda}{\kappa}\right)^2\right]^{\frac{1}{2}} Y^{\frac{1}{\omega}}. \tag{19}$$

The variable κ^2, defined by

$$\kappa^2 = \left(\frac{\partial^2 \Delta\tilde{g}}{\partial \Delta\tilde{x}^2}\right)_{P,T} (\Delta\tilde{T} = \Delta\tilde{T}_{\mathrm{x}}, \Delta\tilde{x} = \Delta\tilde{x}_{\mathrm{x}}) Y^{\frac{1}{2\omega}} \tag{20}$$

serves as a measure of the distance from the critical point. The expression for κ^2 can also be written in terms of $\Delta\tilde{g}$ with the aid of Eq. (4). As $\kappa^2 \to 0$, $Y \to 0$ and one recovers from Eq. (15) the universal scaled asymptotic critical behavior [13]. As $\kappa^2 \to \infty$, $Y \to 1$, and $\Delta\tilde{g}_{\mathrm{x}}$ reduces to $\Delta\tilde{g}$ the classical free-energy of mixing. The crossover behavior of $\Delta\tilde{g}_{\mathrm{x}}$ is governed by two system-dependent constants $\bar{u}$ and Λ. The inverse "length" Λ reflects the discrete structure of matter and $\bar{u}$ is an effective coupling constant.

6. RESULTS AND DISCUSSION

We now demonstrate the applicability of the renormalized NRTL equation to a simple liquid-liquid system with both molecules of approximately the same size. One such system that has been studied close to the consolute point is n-heptane + acetic anhydride. Nagarajan et al. [17] have measured the coexistence curve of the above system by observing the transition temperature of 76 samples over a wide range of compositions. The coexistence data when plotted as mole fraction versus temperature seem to be more symmetric than when plotted as volume fraction versus temperature. The value of the critical parameters as measured by Nagarajan et al. [17] are $T_{\mathrm{c}} =$ 341.658 K. (when converted into ITS-90) and x_{c}(n-heptane) $= 0.4707$. Even though the

authors have taken into account the effects of gravity in the experimental data, Vnuk [18] has found some inconsistency in the data close to critical point. He attributes this inconsistency to gravity effects. In the present analysis of the experimental data a similar inconsistency was noted. In fitting the renormalized NRTL model we have kept the values

$$T_{\rm c} = 341.658 \text{ K}, \qquad x_{\rm c}(\text{n-heptane}) = 0.4707, \tag{21}$$

as determined by Nagarajan et al., but we omitted data points between $T_{\rm c}$ and 341.258 K.

The optimized NRTL parameters, crossover parameters, along with critical exponents that are used in our analysis are listed in Table I. The non-randomness parameter α_{12} is fixed at 0.2 . Figure 1 shows a comparison of the phase boundary calculated from the renormalized NRTL equation with the experimental data. In this figure the calculated phase boundary of the classical NRTL equation is also shown. The parameters of the classical NRTL equation have been determined from the experimental data far away from the consolute point. For α_{12}=0.2 the parameters are found to depend on temperature as:

$$\begin{aligned} g_{12} - g_{22} &= 2.092T + 4.7554, \\ g_{21} - g_{11} &= -6.2T + 3136.7. \end{aligned} \tag{22}$$

The calculated classical critical parameters are $T_0 = 360.658$ K and $x_0 = 0.4845$. In Fig. 2 $\log(x^{''} - x^{'})$ is shown as a function of $\Delta\tilde{T}$. Asymptotically close to the critical point we recover the power law given by Eq. (3) with β=0.325 and $B = 1.8$. This value of B is comparable to the value $B = 1.85$ found by Nagarajan et al. [17] from an asymptotic scaling analysis.

7. CONCLUSIONS

A procedure for transforming Gibbs energy models to reproduce the universal scaling behavior in the vicinity of the critical point is presented. This illustrates how the crossover procedure can be extended to an isobaric incompressible liquid-liquid system which belongs to the universality class of the 3-dimensional Ising model. Even though we have applied the procedure to a molecular mixture of approximately the same size, it can be extended to molecular mixtures of different sizes. This can be done by mixing of the field variables $\Delta\tilde{T}$ and $\Delta\tilde{\mu} = \tilde{\mu}(\tilde{T}) - \tilde{\mu}(x_{\mathrm{c}}, \tilde{T})$. For systems with molecules of very different sizes, the volume fraction is a better choice of order parameter than the mole fraction. Hence, it is advantageous to develop classical Gibbs energy models in terms of volume fraction. For practical applications, it is also possible to predict caloric properties like h^{E} and C_p^{E} along isotherms and $C_{p,x}$ along constant compositions from the NRTL model. Simultaneous prediction of both the phase boundary and the calorific properties is also possible with our transformed NRTL model. Further research towards these goals is in progress.

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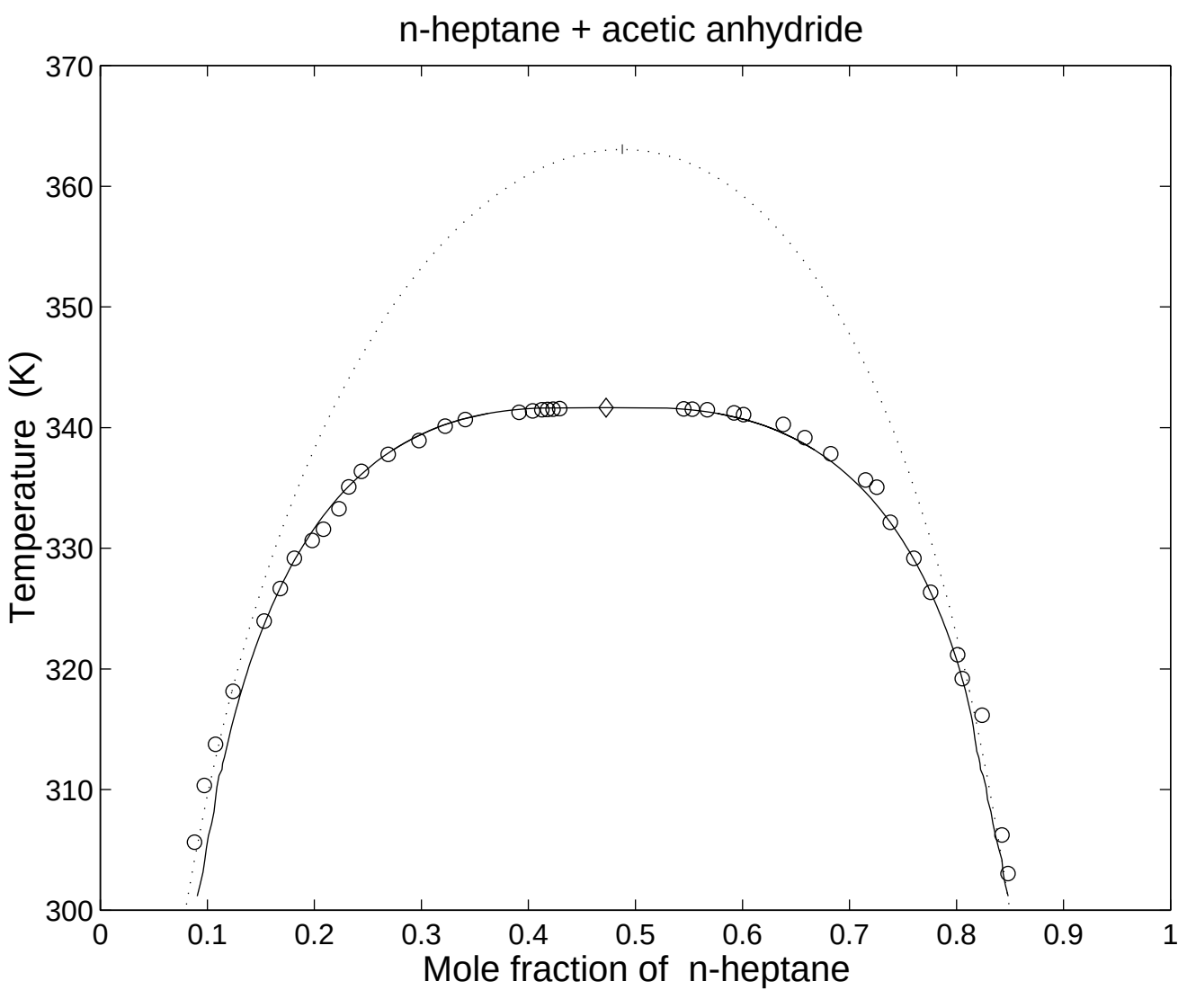
Table I. Parameters and Constants in the Renormalized NRTL Equation.

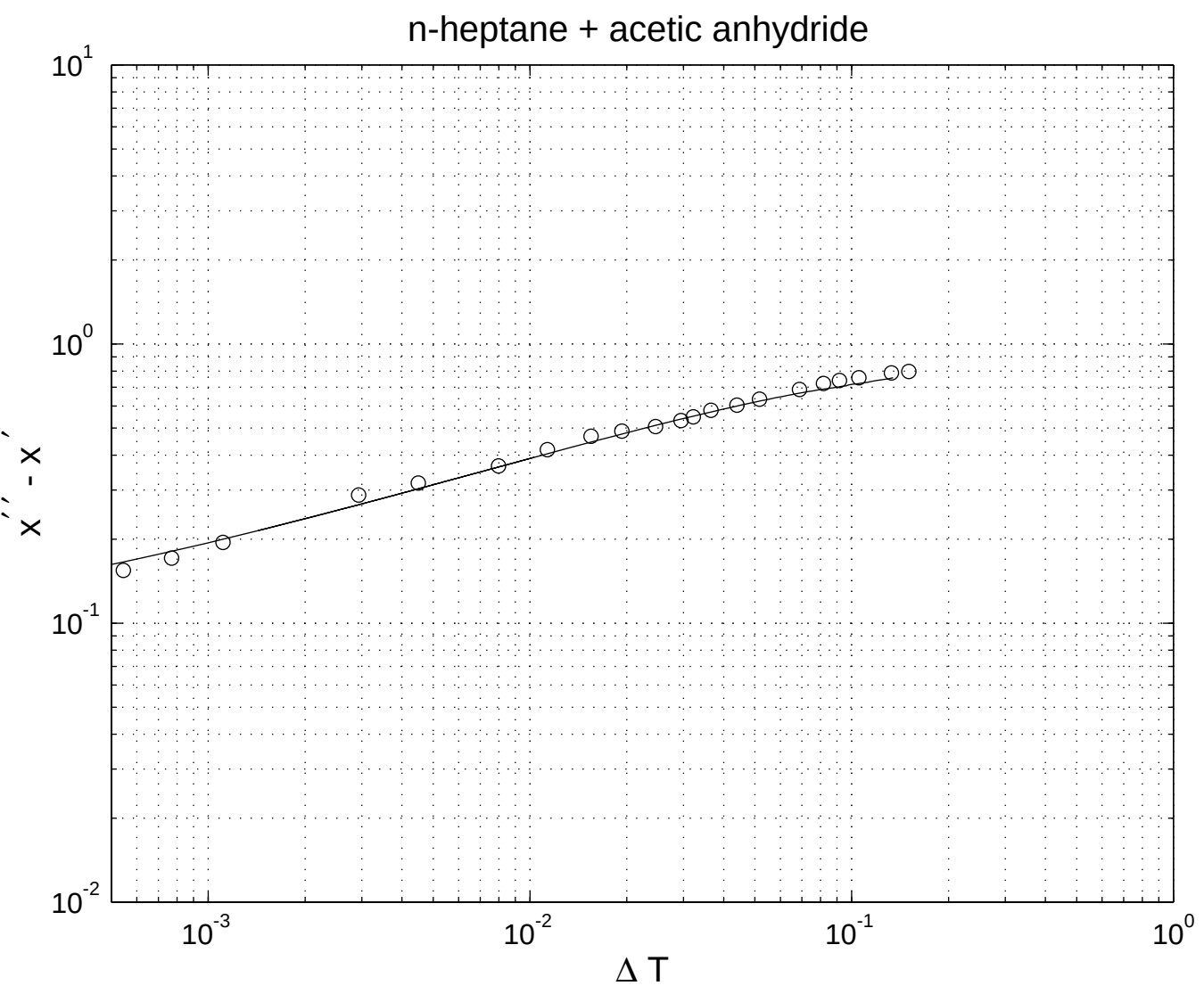
	Universal critical exponents		
α=0.110	η=0.0333	ν=0.630	ω=0.80952
	Critical parameters		
	$T_{\mathrm{c}} = 341.658$ K	x_{c}(n-heptane)=0.4707	
	Crossover parameters		
	$\bar{u} = 0.5546$	$\Lambda = 1.0302$	
	NRTL parameters		
$\tilde{a} = 1.347424$	$\tilde{b} = 3.982667$	$\tilde{c} = 0.944626$	$\tilde{d} = 1.973628$

Figure captions

Fig. 1. Coexistence curve for the system n-heptane + acetic anhydride at constant pressure. The circles $\circ$ indicate experimental phase boundary data, the solid curve represents the phase-boundary calculated from the transformed NRTL equation and the dashed curve represents the phase boundary calculated from the original classical NRTL equation. $\bullet$ indicates the classical critical point and $\diamond$ indicates the actual critical point.

Fig. 2. Log-log plot of the concentration difference $x^{''} - x^{'}$ in the two phases as a function of $\Delta T = (T - T_{\mathrm{c}})/T_{\mathrm{c}}$. The curve represents the values calculated from the renormalized Gibbs energy model.


n-heptane + acetic anhydride
Temperature (K)
Mole fraction of n-heptane
370
360
350
340
330
320
310
300
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1


n-heptane + acetic anhydride
10^{1}
10^{0}
10^{-1}
10^{-2}
$x'' - x'$
10^{-3}
10^{-2}
10^{-1}
10^{0}
ΔT