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The vapour–liquid equilibrium of *n*-alkanes

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Abstract. The vapour–liquid equilibrium of short *n*-alkanes is considered by using perturbation theory. This requires as a previous step obtaining an equation of state (EOS) for hard flexible models. An EOS for hard-*n*-alkane models which shows excellent agreement with computer simulation of hard-*n*-alkane models with up to 100 carbon atoms is proposed. This EOS is combined with a mean-field term and the vapour–liquid equilibrium of *n*-alkanes is computed. When theoretical critical densities and pressures are plotted as a function of the number of carbon atoms, a maximum is found. This is in agreement with experiment. The conditions for the appearance of such a maximum in general chain models are established. Some ways of improving the mean-field theory are suggested.

1. Introduction

The vapour–liquid equilibrium of *n*-alkanes is a problem of great practical interest since they are involved in a number of refinery processes. Moreover, understanding the vapour–liquid equilibrium of flexible molecules such as *n*-alkanes can be considered as a challenge for the liquid-state theory. In the last few years a considerable amount of work has been devoted to the problem of the vapour–liquid equilibrium of *n*-alkanes. On the experimental side new measurements are now available for the critical properties of *n*-alkanes up to C₂₄H₅₀ [1–3]. The presence of a maximum in the critical density when plotted versus the number of carbon atoms is now clearly established. Since *n*-alkanes are thermally unstable for temperatures higher than $T = 650$ K the study of the vapour–liquid equilibrium and critical properties for the longer members of the series presents important difficulties. Computer simulations using the Gibbs-ensemble methodology [4] have been recently performed for *n*-alkane models and a maximum in the critical density has also been found [5]. In spite of this progress theoretical studies on *n*-alkanes are somewhat scarce. Two theoretical treatments commonly used in chemical engineering for *n*-alkanes are the simplified perturbed hard-chain theory (SPHCT) [6] and the statistical associated-fluid theory (SAFT) [7]. These two theories are quite successful in reproducing the experimental data on *n*-alkanes but do not provide an explanation of the appearance of the maximum in the critical density. In this work we focus on the development of a perturbation theory for *n*-alkanes. Our goal is not to provide a quantitative theory for *n*-alkanes but rather to propose a very simple treatment able to describe and explain the appearance of a maximum in the critical density for *n*-alkanes. The development of the theory requires a good equation of state (EOS) for the corresponding hard model. Such an equation is now available [8, 9]. When combined

with a mean-field treatment of the attractive forces it shows that the maximum in the critical density of *n*-alkanes can be easily explained [10]. The condition for the appearance of this maximum in a chain model is established. We give some hints on how to go beyond the mean-field approach.

2. The potential model and perturbation theory of *n*-alkanes

Our model of *n*-alkanes uses the united-atom approach. Methylene and methyl groups are modelled by an interaction site located on the position of the carbon atom. The torsional potential of Ryckaert and Bellemans [11] is used for describing the interaction between carbons three bonds apart. Each site on one molecule interacts with all the sites of another molecule and with sites separated by at least four C–C bonds within the same molecule. The Lennard-Jones (LJ) potential is used for describing the inter- and intra-site–site interaction. We used $\sigma = 3.923 \text{ \AA}$ for all of the sites of the molecule. The choice of the CH₃–CH₃ and CH₂–CH₂ interaction energies $\epsilon_{CH_3-CH_3}$ and $\epsilon_{CH_2-CH_2}$, respectively, is not arbitrary. In fact, we have recently shown that the choice $\epsilon_{CH_3-CH_3}/k = 104 \text{ K}$ and $\epsilon_{CH_2-CH_2}/k = 49.7 \text{ K}$ provides a very good description of the experimental second virial coefficients of *n*-alkanes [12, 13]. This large difference in the energy parameter is needed when the same volume is assigned to the CH₃ and CH₂ groups. If a larger volume is assigned to the CH₃ group then the difference in the interaction energies is much smaller [12, 13]. The Lorentz–Berthelot rule will be used for determining $\epsilon_{CH_3-CH_2}$.

The site–site LJ potential will be split into a reference u_0 and a perturbation term u_1 by using the Weeks–Chandler–Andersen (WCA) criterion [14]. The residual free energy of the *n*-alkane will be obtained by using perturbation theory truncated at first order:

$$A = A_0 + A_1 \quad (1)$$

where A_0 is the residual free energy of the reference system (an *n*-alkane chain interacting through the site–site WCA potential) and A_1 is the first-order perturbation term. Therefore, a full implementation of the perturbation theory requires the knowledge of the thermodynamic properties (A_0) and structural properties of the reference system. The properties of the reference system A_0 will be related to those of a hard system by assigning a hard diameter given by the Barker–Henderson prescription [15] to each interaction site. We shall use for the hard-*n*-alkane model the EOS proposed by Wertheim and Chapman *et al* for chains of tangent hard spheres [16, 17]. This is done by assigning to the *n*-alkane model made up of n interaction sites an effective number of tangent hard spheres m_e . In this way the compressibility factor of the reference system Z_0 is given by

$$Z_0 = m_e \frac{1 + y + y^2 - y^3}{(1 - y)^3} - (m_e - 1) \frac{1 + y - 0.5y^2}{(1 - y)(1 - 0.5y)} \quad (2)$$

where $y = \rho V_{av}$ is the volume fraction given by the product of the number density of the *n*-alkane, ρ , and the average molecular volume V_{av} (different configurations of the chain may have different volumes). The expression for A_0 can be easily obtained by integrating equation (2) (see reference [8] for details). The second virial coefficient, B , arising from equation (2) is given by

$$B/V_{av} = 1.5m_e + 2.5. \quad (3)$$

We shall obtain m_e by imposing the condition that the second virial coefficient of the hard-*n*-alkane model is matched. Since the exact determination of B for a hard-*n*-alkane model is involved, we shall obtain it in an approximated way. First, the rotational-isomeric-state

(RIS) approximation will be used [18]. The *n*-alkane is now regarded as a multicomponent mixture of different conformers. By using convex body geometry and some reasonable approximations one obtains [9]

$$B/V_{av} = 1 + 3 \sum x_i \frac{R_i S_i}{V_i} \quad (4)$$

where x_i , R_i , S_i and V_i are the molar fraction, mean radius of curvature, surface and volume of conformer i , respectively. Values of S_i and V_i will be obtained exactly whereas the value of R_i will be taken from that of a parallelepiped with the same principal moments of inertia as conformer i [9]. The value of m_e is obtained from equations (3) and (4). This procedure for obtaining m_e was first proposed by Boublik [19].

To obtain A_1 we shall use the mean-field approximation. When this is done, A_1 is given for *n*-alkanes heavier than ethane by [10]

$$\frac{A_1}{N} = -\rho\sigma^3 \left(\frac{10\pi\sqrt{2}}{2} + \frac{2\pi(\sqrt{2}-1)}{3} \right) (4\epsilon_{CH_3-CH_3} + (n-2)^2\epsilon_{CH_2-CH_2} + 4(n-2)\epsilon_{CH_3-CH_2}). \quad (5)$$

To compute the vapour–liquid equilibrium we add the ideal free energy to the residual part. By equating pressure and chemical potential of the two coexisting phases the vapour–liquid equilibrium is obtained.

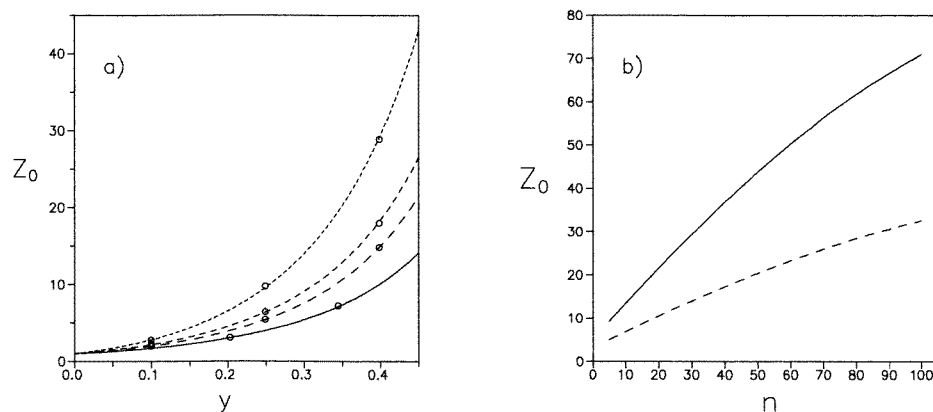


Figure 1. The compressibility factor Z_0 for the WCA version of the *n*-alkane model of Ryckaert and Belleman. Results were obtained for $T = 366.88$ K. (a) Z_0 versus y . Symbols are MD results and lines are the theoretical results as obtained from equation (2). The lines from top to bottom correspond to C_{30} ($m_e = 6.368$), C_{16} ($m_e = 3.732$), C_{12} ($m_e = 2.942$) and C_6 ($m_e = 1.770$). The values of m_e are taken from reference [9]. (b) Z_0 versus n as obtained from equation (2) for $y = 0.4$ (solid line) and $y = 0.3$ (dashed line).

3. Results

In figure 1(a), the EOS for repulsive *n*-alkanes as obtained from molecular dynamic simulations and from equation (2) is presented. As can be seen the agreement is quite good even for long chains. Therefore, a good EOS is now available for the WCA version of the Ryckaert–Belleman model. This is certainly an important step towards the implementation

of perturbation theories of n -alkanes. An extension of equation (2) to n -alkane mixtures has also been performed and again good agreement with simulation was found [9]. Changes in conformational population with density can be also analysed in the context of the theory by minimizing the free energy with respect to the relative population of the different conformers [20]. At high densities more spherical conformers are favoured with respect to more elongated (i.e. the all-*trans*) ones. That provokes a decrease in the *trans*-population at high densities. However, this decrease is found to be small [20]. In figure 1(b) the theoretical compressibility factor of repulsive n -alkanes is plotted as a function of n for fixed values of the volume fraction. As can be seen the behaviour of Z_0 with n is not linear (although it is approximately linear when a small range of values of n is considered). This is in contrast with the behaviour found for a fluid of tangent hard spheres [21].

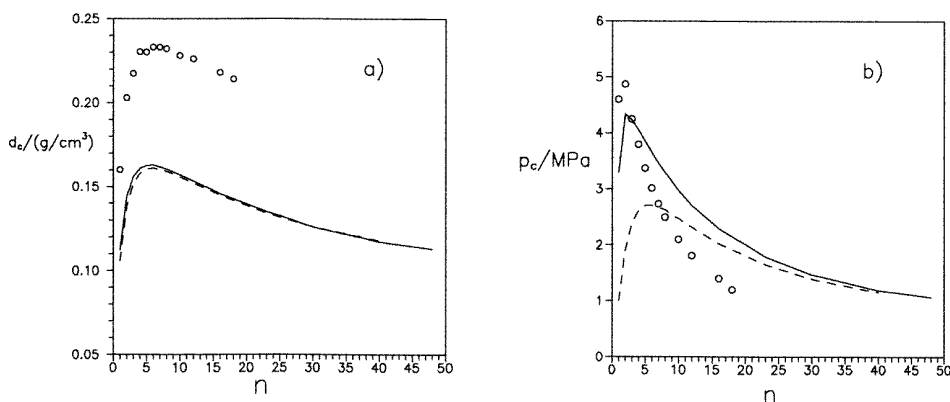


Figure 2. Critical properties of n -alkanes as functions of the number of carbons n . Open symbols are experimental results as obtained from references [1–3]. Results from mean-field perturbation theory with $\epsilon_{\text{CH}_3-\text{CH}_3}/k = 104$ K and $\epsilon_{\text{CH}_2-\text{CH}_2}/k = 49.7$ K are represented by solid lines and those with $\epsilon_{\text{CH}_3-\text{CH}_3}/k = 49.7$ K and $\epsilon_{\text{CH}_2-\text{CH}_2}/k = 49.7$ K are represented by dashed lines. (a) The critical density in g cm^{-3} . (b) The critical pressure in MPa.

We have computed the vapour–liquid equilibrium of n -alkanes by using the perturbation theory described in the previous section. The mean-field approximation for A_1 and the expression for A_0 obtained from equation (2) were used along with the LJ parameters described in the previous section. In figure 2(a) we present the critical density of n -alkanes as obtained from theory and from experiment. In figure 2(b) results are presented for the critical pressure. Obviously, the agreement is only qualitative due to the use of the mean-field approximation. However, the mean-field theory predicts correctly the appearance of a maximum in the critical density for n -hexane and in the critical pressure for ethane. By analysing the theory we learn that neither differences in interaction energy nor differences in mass between CH_3 and CH_2 are responsible for the appearance of the maximum in the critical density. The condition for the appearance of such a maximum is the existence of overlapping between contiguous interaction sites of the chain [10]. The maximum in critical density shifts to shorter chains as the overlapping between constituting sites decreases. In fact, no maximum in the critical density is expected for a model of tangent interaction sites. The existence of a maximum in the critical pressure does also require the presence of overlapping between contiguous interaction sites [10]. It shifts to shorter chains as the overlapping between interaction sites decreases. However, in this case the difference in the interaction energy between CH_3-CH_3 and CH_2-CH_2 groups does play an important role.

In fact, as this difference increases the maximum in the critical pressure shifts to shorter chains. If the interaction energy of CH_3 and CH_2 groups was the same, the maximum in the critical pressure would appear in *n*-hexane. The appearance of this maximum in ethane is due to the large difference between $\epsilon_{\text{CH}_3-\text{CH}_3}$ and $\epsilon_{\text{CH}_2-\text{CH}_2}$.

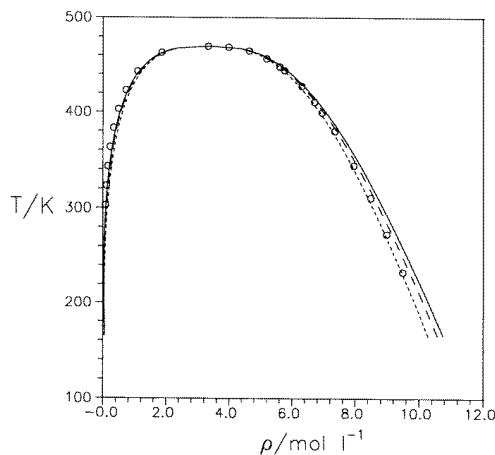


Figure 3. Coexistence densities of the vapour–liquid equilibrium of *n*-pentane as obtained from experiment (symbols) and from the perturbation theory of reference [24] for the following conformers: *trans*–*trans* (solid line), *trans*–*gauche* (dashed line) and *gauche*–*gauche* (short-dashed line).

The results presented so far illustrate two important points. The first is that an EOS is now available for realistic models of hard-*n*-alkane models. The second is that many experimental features of the vapour–liquid equilibrium of *n*-alkanes can be explained by using a simple mean-field perturbation theory. Obviously the use of the mean-field approximation prevents a quantitative description but it is quite useful for obtaining an understanding of the critical properties of *n*-alkanes. How do we go further? Obviously, the mean-field approximation should be replaced. One possibility is to use structural information coming from the PRISM (polymer reference interaction site model) integral equation to evaluate the first-order perturbation term [22]. Progress along this line can be anticipated. A different approach would be to replace the problem of the multicomponent mixture constituted by the *n*-alkane (each conformer represents a different component) by that of a pure fluid. One could choose a simple geometry to describe the *n*-alkane. For instance, Boublik and co-workers [23] take a spherocylinder to approximately describe the shape of the *n*-alkane. Another possible choice is to take a representative conformer of the *n*-alkane mixture in order to approximately describe its shape [24]. There are now available successful perturbation theories for molecular fluids [25–27] interacting through the Kihara [28] potential (note that the treatment described in section 2 applies to the site–site interaction model only). Therefore, one could apply these theories to the pure fluid (either the spherocylinder or the chosen conformer) and obtain in this way an approximation to the properties of the *n*-alkane. In figure 3 the vapour–liquid equilibrium of *n*-pentane as obtained from experiment and from the perturbation theory of Kihara fluids described in reference [24] is shown. Results for the *trans*–*trans*, *gauche*–*gauche* and *trans*–*gauche* conformers of *n*-pentane are presented. Although it is not possible to determine the vapour–liquid equilibrium of each *n*-pentane conformer experimentally, this can be done easily

with perturbation theory. Potential parameters of each *n*-pentane conformer were obtained from the experimental critical temperature and density. Note that the results of figure 3 were obtained using a different potential model and a theory different to that described in section 2 of this work (details may be found in reference [24]). It is clear that the *tg*- and *gg*-conformers provide a satisfactory description of the vapour–liquid equilibrium of *n*-pentane.

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