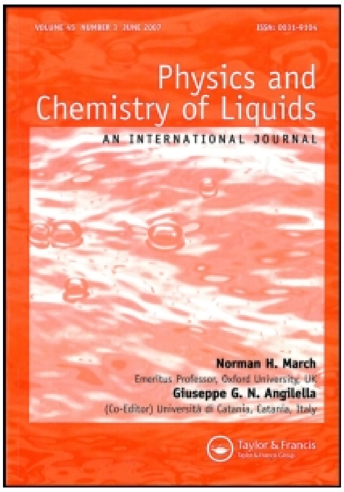

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Critical Properties of n-Alkanes and the Relevance of Polymer Models to the Heavy Fluid Metals Rb and Cs

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CRITICAL PROPERTIES OF n-ALKANES AND THE RELEVANCE OF POLYMER MODELS TO THE HEAVY FLUID METALS Rb AND Cs

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n-alkane critical constants as determined experimentally for n $\leq$ 18 are first compared and contrasted with the predictions of various models. Qualitative accord is found, but only one quantitative prediction, that of Wertheim's model for the critical temperature T_c, is found to fit the experimental data over the admittedly limited range of n available.

Reference is then made to critical properties of the heavy fluid alkali metals, and especially Rb and Cs, where some evidence is cited for the existence of long chains of alkali atoms. The relative constancy of the product of the critical pressure P_c and the critical volume V_c for the three heaviest alkalis is noted, a fact consistent with one of the more recent 'polymer' models.

Keywords: n-alkanes; Critical properties; Scaling; Alkali metals

I. BACKGROUND AND OUTLINE

It has been recognized for a long time that an interesting question concerns the critical properties of long polymer chains. Experimentally, it is established that conventional polymers normally decompose at temperatures below their critical point, making the critical point unattainable in such experiments (see *e.g.*, Refs. [1,2]). But engineering applications often use the critical properties of such long polymers as a

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means of estimating liquid densities at low temperatures, so the problem is of interest to study theoretically.

The outline of the paper is as follows. In Section 2 immediately below, experimental data on the critical properties of the n-alkanes is analyzed. Then in Section 3, early model studies and their predictions are summarized and brought into contact with the facts presented in Section 2. The important model of Wertheim is discussed in Section 4, and especially for the variation of the critical temperature T_c with the number n of monomers. Then in Section 5, the model predictions are, very briefly, compared and contrasted with the experimental facts for the alkali fluid metals at the critical point. Section 6 constitutes a summary plus some suggestions for future experimental studies.

II. EXPERIMENTAL DATA ON CRITICAL PROPERTIES OF n-ALKANES

The more recent experimental studies on the critical properties of the n-alkanes include those of Anselme *et al.* [2] and of Steele (as reported by Tsonopoulos and Tan [3]). The experimental data of Anselme *et al.* [2] covers values for n up to 18 and indicates that the critical mass density $\rho_c(n)$ goes up to a maximum at $n = 6, 7$ and then continues to decrease linearly for larger n-values. The data of Steele [3] however, although only for values of n up to 12, shows a continuous increase of $\rho_c(n)$ with increasing n and there is no evidence of a maximum. Smit *et al.* [4] applied a combination of the Gibbs-ensemble technique and the configurational-bias Monte Carlo method on a new model for the n-alkanes and found very good agreement with the experimental data of Anselme [2].

The experimental data from Anselme *et al.* [2] is plotted in Figure 1 together with the best possible fit of the decreasing 'tail'. This tail is described well by the linear relation:

$$\rho_c(n) = -0.00156n + 0.244 \tag{1}$$

Of course, since the critical monomer number density, say $\rho_c^m(n)$, can roughly be defined by

$$\rho_c^m(n) = \frac{1}{M(CH_2)}\rho_c(n) \tag{2}$$

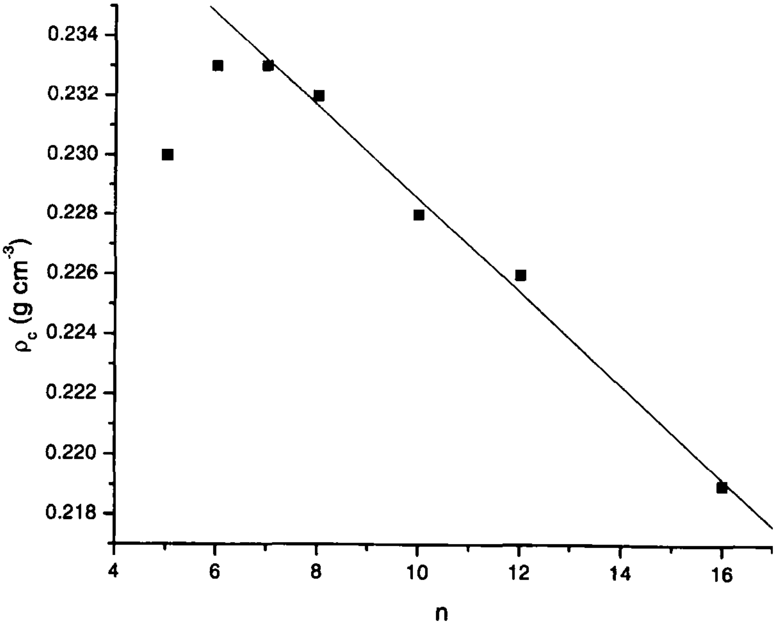

FIGURE 1 Mass density ρ_c of the n-alkanes *versus* n for $5 \leq n \leq 16$, taken from experiment. Straight line drawn is appropriate for $7 \leq n \leq 16$, and is represented by Eq. (1).

with $M(CH_2)$ the mass of the monomer, (we neglect the extra hydrogen atoms at both ends of the n-alkane) a similar linear relation holds for $\rho_c^m(n)$.

The critical polymer number density, say $\rho_c^p(n)$, is obtained by dividing the critical mass density $\rho_c(n)$ by the mass of the polymer chain, say M(chain), which is for the n-alkanes given by

$$\begin{aligned} M(chain) &= M(CH_2)(n-2) + 2M(CH_3) \\ &= M(CH_2)n + 2M(H) \end{aligned} \tag{3}$$

And since the mass of the hydrogen atom is small compared to that of the CH_2 molecule, this roughly amounts to dividing by n (up to a proportionality constant). Figure 2 shows $\rho_c^p(n)$ as a function of n together with the best possible fit of the form a^*n^b. A least squares fitting procedure leads to the result

$$\rho_c^p(n) = 0.0103\, n^{-1.03} \tag{4}$$

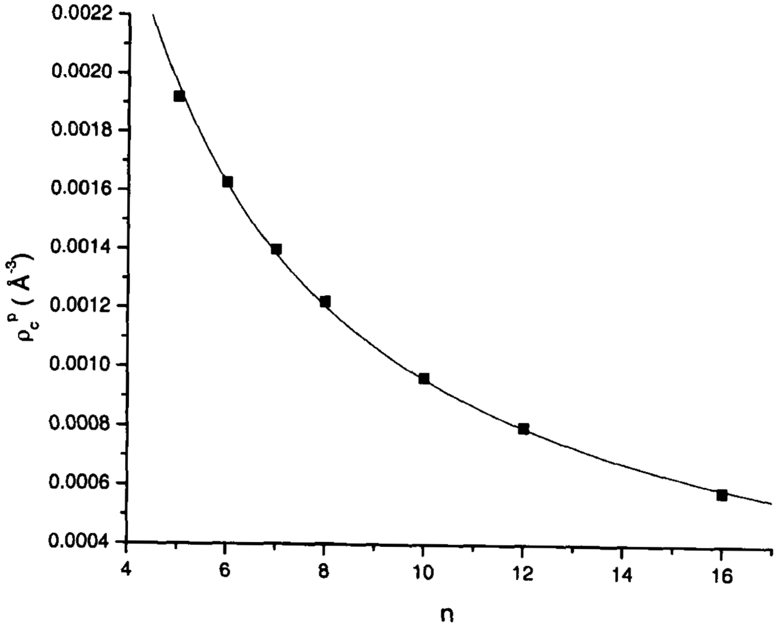

FIGURE 2 Critical polymer density ρ_c^p *versus* n. Curve drawn through points is a least squares fit given by Eq. (4). Note that ρ_c^p is accurately proportional to n^{-1} over the accessible range $n \leq 16$.

The exponent is very close to -1, and this reflects the fact that, although there is a clear tendency, the dependence of the critical mass density ρ_c and the critical monomer density ρ_c^m on chain length is actually very weak (to go from mass density to polymer number density one divides by n, thereby introducing the exponent -1). In fact, on the basis of less precise experimental data, it was concluded some forty five years ago that the monomer density at which the system becomes critical (ρ_c^m), was independent of the length of the chains formed from those monomers [5].

The experimental data for the critical pressure P_c for the n-alkanes together with the best possible fit of the form a^*n^b is shown in Figure 3. The data is described well by the relation

$$P_c(n) = 11.7\,n^{-(3/4)} \tag{5}$$

with pressure in units of MPa. The last three points however follow a slightly different curve, indicating a somewhat lower power law for

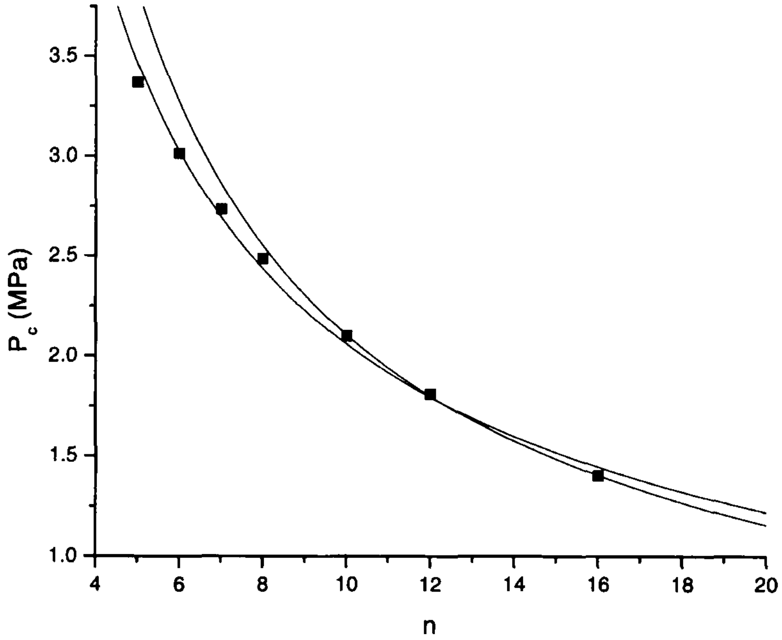

FIGURE 3 Critical pressure from experiment *versus* n. Curve through the experimental points is given by Eq. (5). Note that for $n \leq 12$ lower curve is an excellent fit to experiment with dependence $n^{-(3/4)}$. Other curve (lower for $n > 12$) is fitted to last three points only and magnitude of exponent is then increased somewhat from 0.75 to 0.86.

larger n-values given by

$$P_c(n) = 15.35 n^{-0.86} \tag{6}$$

III. EARLY THEORETICAL INVESTIGATIONS

One of the first fundamental approaches on the basis of an extension of the cell method was undertaken by Prigogine [6] whose treatment of n-mers predicted that ρ_c^m scales as $n^{-(1/2)}$:

$$\rho_c^m \propto n^{-(1/2)} \tag{7}$$

Interestingly, the Flory-Huggins (FH) theory for polymer solutions [7–10] also predicts this behaviour of ρ_c^m indicating that, if Prigogine's prediction is correct, the vapor–liquid equilibria of pure polymers can be regarded as a solution of rod-like polymers in a solvent of small molecules. This assumption was made by Kurata and Isida [5].

However this scaling behaviour of ρ_c^m leads to the prediction that

$$\rho_c^p(n) \propto n^{-(3/2)} \tag{8}$$

Comparison with the experimental relation (4) makes it clear that neither of the above theories is qualitatively applicable to the n-alkanes.

A few years later, Flory, Orwell and Vrij [11] developed a continuum theory which was fairly recently applied successfully by Tsonopoulos and Tan [3] to describe experimental data. Returning briefly to Prigogine's work, it also predicted that the critical temperature T_c scales as

$$T_c \propto \frac{n}{(n^{(1/2)}+1)^2} \tag{9}$$

thus reaching a constant asymptotic value T_c^∞ for infinitely long chains $n \rightarrow \infty$. The agreement of this formula with recent experimental data is for convenience discussed in the next paragraph. No results concerning the critical pressure or compressibility ratio are forthcoming from Prigogine's method or FH theory.

IV. THERMODYNAMIC PERTURBATION MODEL OF WERTHEIM

The simplest of the present day theories that approach polymer liquids from liquid state theory is the thermodynamic perturbation theory from Wertheim [12–15]. Although originally developed to describe model fluids consisting of associating hard spheres, it was realised that the theory could be used just as well to describe attractive monomers [16].

Interestingly Wertheim's model gives back the original predictions of both the Prigogine and the FH theories in the sense that it again predicts (analytically) a decrease of the critical monomer density ρ_c^m proportional to $n^{-(1/2)}$ in the limit of large n.

Very recently, an extensive numerical comparison was made by MacDowell *et al.* [17] between results from Wertheim's perturbation model and 'exact' Monte Carlo simulations (using essentially the same techniques as Smit *et al.* [4], but a different polymer model) for the behaviour of a given n-mer model along the liquid-vapour coexistence curve. Simulations were done for n-mers containing up to 60 monomers and good overall agreement was found between the results from both methods.

Two important conclusions relevant to our work are apparent.

(i) They found that the critical monomer density $\rho_c^m(n)$ decreases with increasing chain length n but the maximum for $n = 6.7$ is not recovered by MacDowell *et al.*, and is thus not a universal feature of n-mers but depends on the model. However in contrast, as was already noted by Smit *et al.* [4], the decrease of $\rho_c^m(n)$ with (large) increasing n does seem to be a more general property since MC simulations by Mooij *et al.* [18] of a polymeric bead-spring model also revealed this behaviour.

(ii) More importantly, MacDowell *et al.*, found that over chain lengths up to 60 monomers the critical properties are still far from reaching their predicted asymptotic behaviour. As a matter of fact, over the assessed range, the MC results for the critical monomer density ρ_c^m as a function of the chain length n were well fitted by the relation

$$\rho_c^m(n) = 0.452\,n^{-0.264} \tag{10}$$

So we have roughly that $\rho_c^m \sim n^{-(1/4)}$ instead of Eq. (7). For the critical temperature T_c, Wertheim's theory predicts for large values of n a law of the form

$$T_c(n) = T_c^{\infty} + bn^{-(1/2)} + cn^{-1} + \cdots . \tag{11}$$

with T_c^{∞} the asymptotic value of the critical temperature for infinitely long chains. The MC results, on the other hand, are described well by the relation

$$\frac{k}{\varepsilon} T_c(n) = 3.3 - 2.44\,n^{-0.27} \tag{12}$$

with k the Boltzmann constant and ε an energy parameter of the applied non-bonding pair potential (a truncated and shifted Lennard-Jones).

Surprisingly however, we found that the experimental values for the critical temperature T_c of the n-alkanes [2] are fitted excellently by the large-n form (11) predicted by Wertheim's model even though the chain lengths only go up to a value $n = 16$! A fit of the form (12) was found to describe the experimental results reasonably, but certainly less well than Wertheim's large-n formula. Figure 4 shows the experimental results taken from the work of Anselme *et al.* [2] together with the best possible fit using Wertheim's large-n formula. Clearly Wertheim's form gives the best fit and the resulting expression is

$$T_c(n) = 1290.5 - 2830\,n^{-(1/2)} + 2227,4\,n^{-1} \qquad (13)$$

thus predicting a critical temperature for alkanes of infinite length of about 1290 K. The resulting formula using an exponent of -0.27

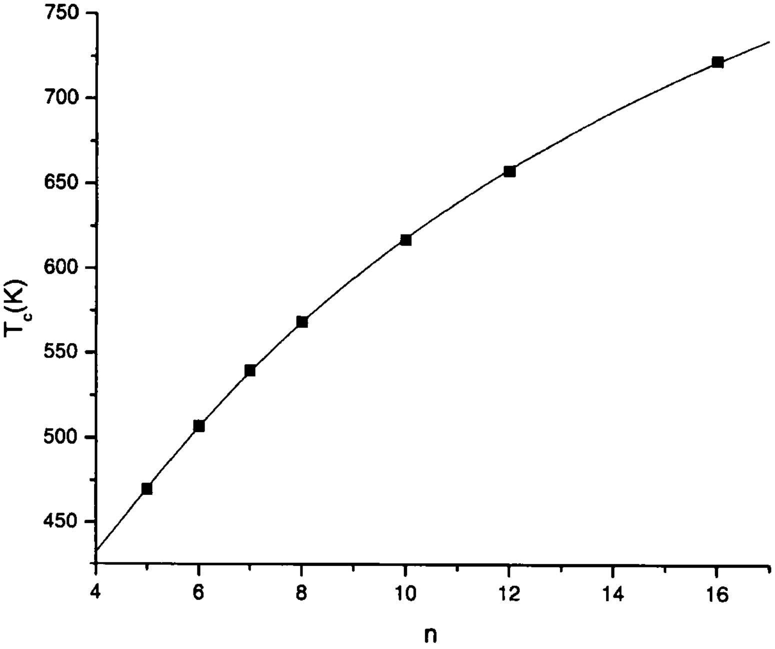

FIGURE 4 Critical temperature from experiment *versus* n for n-alkanes. Curve is prediction of Wertheim's model discussed in Section 4: see especially Eqs. (10) and (12). Note that while Eq. (10) is strictly a large n expansion, with the choice of coefficients as in Eq. (12) the data is fitted to experimental accuracy for $5 \leq n \leq 16$.

is given by

$$1401.34 - 1450.6n^{-0.27}$$

thus leading to a value for T_c^{∞} of about 1400. The scaling formula (9), on the other hand, is not appropriate to describe the available experimental data on T_c for the n-alkanes.

The obvious conclusion from this is that the range of n-values where the predicted large-n forms of Wertheim's theory are valid depends to some extent on the chosen system. Moreover, as mentioned before, the experimental values of the critical monomer density of the n-alkanes are not well described by the power law $n^{-(1/2)}$, so the range of validity of the large n-forms depends also on the particular critical constant under consideration (if indeed the models are directly applicable to experiment at all).

Wertheim's theory also predicts that the critical compressibility ratio of the chain liquid reaches a constant value of (1/3) in the limit of large n;

$$Z_c = \frac{P_c}{\rho_c^p k_B T_c} \rightarrow \frac{1}{3} \tag{14}$$

Figure 5 shows the predictions from the experiments of Anselme *et al.* [2] for the critical compressibility ratio of the n-alkanes as a function of n. The dependence on n for $n \lesssim 20$ is seen to be rather weak and can be fitted by the linear relation

$$Z_c(n) = 0.28 - 0.0025n \tag{15}$$

If we insert the empirical relations for $T_c(n)$, $\rho_c^p(n)$ and $P_c(n)$ into the formula for Z_c Eq. (14) we obtain the following empirical formula

$$Z_c(n) = 0.117\frac{n^{(1/4)}}{(1290 - 2830n^{-(1/2)} + 2227n^{-1})} \tag{16}$$

Although the agreement of this formula with experiment is clearly less convincing than that of the linear relation (15) it is important to note that it exhibits a minimum at about n = 17 and then continues to increase with increasing n. The empirical relation (16) for $Z_c(n)$ does not reach a constant asymptotic value at large n but continues to increase proportional to $n^{(1/4)}$ so obviously the present empirical

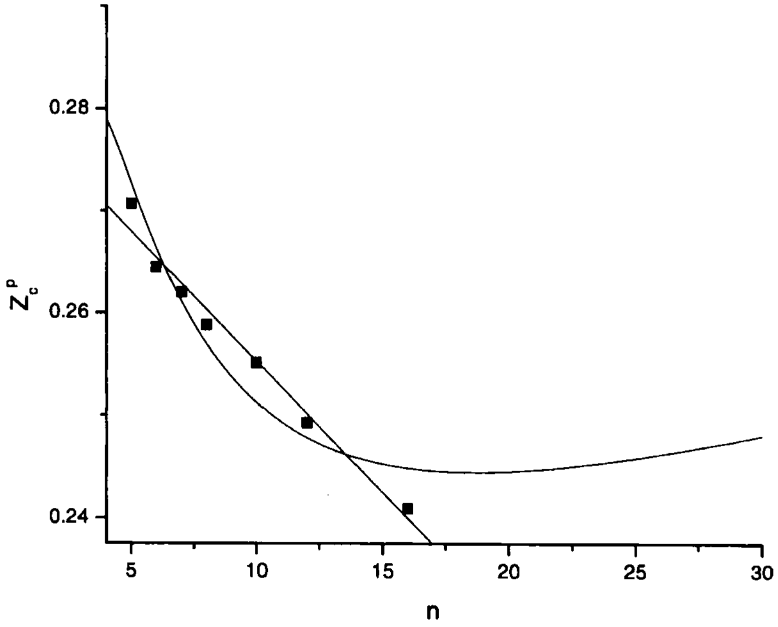

FIGURE 5 Critical compressibility ratio Z_c for the n-alkanes *versus* n. Note relatively small variation of Z_c with n, which is roughly linear in n for $6 \leq n \leq 16$. Curved fit is represented by Eq. (16) and is obtained by combining the empirical relations found for P_c, ρ_c and T_c into expression (14) for Z_c.

relations cannot be extended to very large n-values if Wertheim's model predictions are be to found correct.

Since Wertheim's theory predicts that both $Z_c(n)$ and $T_c(n)$ reach a constant asymptotic value in the limit of large n, it follows from the elementary relation

$$P_c = Z_c(\rho_c^p k_B T_c) \tag{17}$$

that in the limit of large n, $P_c(n)$ will have the same asymptotic behaviour as $\rho_c^p(n)$ and since roughly $\rho_c^p(n) = (1/n)\rho_c^m(n)$ we obtain

$$P_c(n) \propto \rho_c^p(n) \propto n^{-(3/2)} \tag{18}$$

From relations (4) and (5) it is clear that this is not valid for the n-alkanes over the observable range of n-values. However fitting only the last three experimental points for $P_c(n)$ did bring the exponent from a value of -0.75 down to a value of -0.86 thus increasing slightly the agreement with the exponent of $\rho_c^p(n)$. And of course, since our fit for T_c for the n-alkanes goes off to a constant asympotic value, but $P_c(n)$ and $\rho_c^p(n)$ behave differently, combining these empirical relations to predict the behaviour of Z_c for large n (see relation (16)) cannot lead to a constant asymptotic value as was already noted above.

V. COMPARISON WITH CRITICAL BEHAVIOUR OR ALKALI METALS

Winter *et al.* [19] obtained the near neighbour (nn) distance and the first coordination number z for a number of different thermodynamic states of liquid Rb and Cs along the liquid-vapour coexistence curve from neutron diffraction experiments. One of us [20] fitted their data for the coordination number z by

$$z = a\rho + b \tag{19}$$

This leads to a coordination number of about two at the critical point. The values for the nn distance on the other hand remained relatively constant along the liquid-vapour coexistence curves of both Rb and Cs thus lending support to the interpretation that a chemical bond is the basic building block in these expanded liquid states and that 1-D chainlike configurations are formed as one approaches the critical point. Freeman and March [21] have compared the (likely) chains in the Cs fluid metal near T_c with results for low concentrations of Cs adsorbed on semiconductor surfaces. There the work of Whitman *et al.* [22] suggests chains of about a 1000 Å in length, which should roughly correspond to a number of momomers n in the chain $\gtrsim 150$.

In contrast with the n-alkanes where the length of the chains is constant and equal to n, the length of the assumed chains in, for instance, liquid Rb, may have a certain distribution within a given thermodynamic state. Assuming however that a certain length is predominant near criticality, denoted by, say, n_c^{Rb} *and* n_c^{Cs}, it is of interest to inquire whether the (clearly present) trends in the critical constants of the alkali metals (and the heavy alkali metals in particular) can be described by power laws similar to those appropriate for the n-alkanes.

For instance do the following relations hold for Rb and Cs (with C_1 and C_2 of course the same for both elements)?

$$T_c^{Rb} = C_1 * (n_c^{Rb})^{C_2}$$
$$T_c^{Cs} = C_1 * (n_c^{Cs})^{C_2}$$

(And similar relations for the critical pressure, critical density and compressibility ratio.) For convenience the experimentally determined critical constants for five alkalis are given in Table I (values taken from [23]).

To the authors knowledge at the time of writing, only the experiment of Whitman *et al.* [22] has revealed any information concerning the order of magnitude of the number of atoms (building blocks) in the alkali chains. Whether this number can be transferred into the bulk liquid state remains an open question at the moment. However, on the basis of the results of Whitman *et al.*, it is reasonable to assume that the alkali chains contain an order of magnitude more 'building blocks' than do the n-alkanes whose critical properties are presently accessible to experiment. More importantly, since the information from Whitman *et al.*, concerns only one alkali metal, namely Cs, nothing can be said from experiment as to whether the above mentioned power laws hold and new experiments of the same type with Rb or even K are of considerable interest.

Clearly the results obtained from Wertheim's thermodynamic perturbation theory cannot simply be transferred to the alkali metals. For instance, Wertheim's theory predicts that both the critical monomer density and the critical pressure decrease with increasing chain length. If this trend also holds for the heavy alkalis, then it is clear from Table I that the length of the chains must increase in going

TABLE I Observed critical constants of alkali metals

Element	$P_c(MPa)$	$10^4 V_c(m^3/mol)$	$T_c(K)$	$P_cV_c^*(10^{-3}eV)$
Li	30.4	0.588	3344	17.9
Na	25.22	1.09	2497	27.5
K	15.95	2.04	2239	32.5
Rb	12.45	2.93	2017	36.5
Cs	9.25	3.51	1924	32.5

*The approximate constancy of the product P_cV_c in Table I would be consistent with Wertheim's asymptotic predictions for really long chains if the chains assumed to exist at the critical point were about the same length from Na through to Cs.

from Rb to Cs. However Wertheim's theory also predicts an increase in critical temperature towards an asymptotic value with increasing chain length and this is clearly not the case in going from Rb to Cs. One could argue that the difference between T_c^{Rb} and T_c^{Cs} is rather small, invoke experimental error and point to the fact that, because of the assumed relatively large n-values (~ 150), the heavy alkali metals are already in the asymptotic regime where, according to Wertheim's theory, the critical temperature reaches a constant. However in that respect it must be said that both Rb and Cs correlate very well with the lighter alkalis and that the decrease in T_c with increasing atomic number of the alkalis is quite clear.

On the other hand, the ratio (P_c/ρ_c), or equivalently the product P_cV_c is remarkably constant throughout the alkalis except for Li, as is clear from Table I, and this correlated behaviour of P_c and ρ_c is also predicted from Wertheim's model in the limit of large n. However, whereas in Wertheim's theory this correlation follows simply from the fact that in the large n regime, both T_c and Z_c, reach a constant asymptotic value, this is clearly not the case for the heavy alkalis as was already discussed for T_c above.

VI. SUMMARY AND FUTURE DIRECTIONS

Available experimental data on the n-alkanes has here been brought into close contact with a number of theoretical models. The most striking success is then found to be the prediction of Wertheim's model for the critical temperature T_c, as shown in Figure 4. Even there, however, it must be borne in mind that the number of monomers n is less than 20, and there is currently no certainty that this is in the 'asymptotic regime of large n'. Data on P_c shown in Figure 3 and represented usefully by the power law (5) is consistent with the model prediction that the critical pressure should tend to zero as $n \to \infty$. However, for $n < 20$, the exponent is roughly $-(3/4)$ according to Eq. (5), whereas Wertheim's model leads to the asymptotic prediction $-(3/2)$ as $n \to \infty$. As Figure 5 shows, the variation of the critical compressibility ratio Z_c with n for $n < 16$ is quite small (from ~ 0.27 to 0.24), and roughly linear with n and there is no possibility of predicting any finite limit $n \to \infty$.

Turning briefly to the possible relevance of 'chain' models to the heavy alkalis, the experiments of Whitman *et al.* [22] on Cs suggest, but of course do not prove, for the critical region, chains which are much longer than the n-alkanes currently available to experiment. The available chain model predictions that $P_c V_c$ tends to a constant are at least roughly consistent with the entries in the final column of Table I, if one omits the lightest alkali Li. However, it is plainly premature from the present considerations to claim that long chains exist in Rb and Cs especially near the critical point, and alternative models such as those suggested by the work of Pilgrim *et al.* [24] and of Ross *et al.* [25] deserve fuller investigation in relation to such long chain models. Finally, further experiments on the alkali metals are clearly of considerable interest for the future. Thus, as already mentioned, it would be of obvious interest if Rb and K could be investigated on semiconductor substrates, following the experimental studies of Whitman *et al.* [22] on Cs deposited on InSb and GaAs. Also, though we recognize the critical point is less accessible, experimental studies on K fluid metal using techniques developed by Hensel and co-workers, should prove illuminating.

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