# Critical temperature of infinitely long chains from Wertheim's perturbation theory

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Wertheim's theory is used to determine the critical properties of chains formed by $m$ tangent spheres interacting through the pair potential $u(r)$. It is shown that within Wertheim's theory the critical temperature and compressibility factor reach a finite non-zero value for infinitely long chains, whereas the critical density and pressure vanish as $m^{-1.5}$. Analysing the zero density limit of Wertheim's equation or state for chains it is found that the critical temperature of the infinitely long chain can be obtained by solving a simple equation which involves the second virial coefficient of the reference monomer fluid and the second virial coefficient between a monomer and a dimer. According to Wertheim's theory, the critical temperature of an infinitely long chain (i.e. the $\Theta$ temperature) corresponds to the temperature where the second virial coefficient of the monomer is equal to 2/3 of the second virial coefficient between a monomer and dimer. This is a simple and useful result. By computing the second virial coefficient of the monomer and that between a monomer and a dimer, we have determined the $\Theta$ temperature that follows from Wertheim's theory for several kinds of chains. In particular, we have evaluated $\Theta$ for chains made up of monomer units interacting through the Lennard-Jones potential, the square well potential and the Yukawa potential. For the square well potential, the $\Theta$ temperature that follows from Wertheim's theory is given by a simple analytical expression. It is found that the ratio of $\Theta$ to the Boyle and critical temperatures of the monomer decreases with the range of the potential.

## 1. Introduction

In the early 1980s Wertheim developed a theory to deal with the thermodynamic properties of fluids with association forces [1–4], for example hydrogen bonding fluids. It was soon realized that the formalism proposed could lead to an approximate equation of state for a completely different system, namely, that formed by chain molecules. The reason for this surprising relation arises from the fact that chains are formed from a fluid of associating monomers when the strength of the association becomes infinitely strong. This interesting finding was discovered independently by Wertheim [5] and by Chapman et al. [6]. It can be stated than since the publication of these two papers a new era has been born for the statistical mechanics of flexible molecules. In the simplest implementation of the theory, which is commonly denoted as the first order perturbation theory, the only information required to build an approximate equation of state for the chain fluid is the equation of state and the pair correlation function at contact of the monomer fluid. In the first order perturbation theory,

the properties of the chain fluid are independent of the torsional state of the molecule and of the bond angle between three consecutive beads. For hard spheres, both the equation of state (EOS) and the pair correlation at contact are well known, and therefore, it is simple to derive an equation of state for chains of tangent hard spheres. This is the reason why the first application of Wertheim's theory of association to flexible molecules was performed on hard flexible chains [5, 6]. Further development followed in the early 1990s. Zhou and Stell [7] and Smith et al. [8] reformulated Wertheim's theory of association in a different language: namely that of the equilibrium constant. Chapman [9] showed that Wertheim's formalism could also be applied to systems with attractive forces. The work of Johnson et al. [10, 11] has shown that Wertheim's formalism yields quite a good description for Lennard-Jones (LJ) chains, provided that the EOS and pair correlation function of the reference LJ fluid is known accurately. Gil-Villegas et al. have shown that the same holds true for square well chains [12] and recently the same has been shown for Yukawa chains [13]. One can summarize by saying that a good EOS of chain molecules interacting through a given pair potential can be obtained if the EOS and

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pair correlation function of the monomer fluid are known accurately. We should mention that the integral equation theory, known as the Reference Hypernetted Chain (RHNC), provides a highly satisfactory description of both thermodynamic and structural properties for most spherical pair potentials [14, 15]. Therefore, an approximate but reliable description of flexible chains can be obtained nowadays in a rather straightforward way. Since the message seems a little bit enthusiastic we should temper our expectations by mentioning that Wertheim's theory describes fluids made up of tangent monomer units, without any restriction in the bond angle or in the torsional energy. We shall denote models like these as fully flexible models. However, from a chemical point of view the models of real interest are those in which the bond angle is fixed, there is a torsional potential and the monomers are not tangent but overlap when forming the chain. For these more realistic models Wertheim's theory is not yet successful thus the situation is far from satisfactory.

In recent years Wertheim's theory has been used to predict the vapour–liquid equilibrium of fully flexible molecules. Critical properties as obtained from Wertheim's theory have been compared to simulation results. This has been done by Escobedo and de Pablo for Lennard-Jones (LJ) and square well (SW) chains [16], and by Blas and Vega for LJ chains [17]. The theory performs a reasonable job in estimating the coexistence envelope and the critical properties of chain fluids. One interesting question is the behaviour of the critical point of infinitely long polymers. Experimentally, polymers usually decompose at temperatures below the critical point, making the critical point unreachable [18–20]. Thus we turn to theory to provide an indication of the behaviour of the critical properties of long chains. Engineering correlations typically use the critical properties of these long polymers in order to estimate the liquid densities at low tempereatures so the problem is also interesting from the point of view of applications. The elegant Flory–Huggins theory [21, 22], although originally derived for polymer–solvent mixtures, can equally well be applied to a pure polymer system. After all, the solvent never appears in the Flory–Huggins theory so it may be replaced by holes without difficulty. The Flory–Huggins theory predicts that for infinitely long chains, the critical temperature reaches a finite value, and the volume fraction tends to zero with a power law of $m^{-1/2}$. Therefore, the critical density (expressed in mass per unit volume) should go to zero. No prediction for the critical pressure is obtained from the Flory–Huggins theory. Since the Flory–Huggins theory is developed for lattice polymers, it is not clear what happens in a continuous three-dimensional polymer.

For $n$-alkanes, it seems that the critical temperature reaches a finite value, and although it was thought for three decades that the critical density (in units of mass per volume) reaches a finite non-zero value [23], the discovery of the existence of a maximum in the critical density [18, 19, 24, 25] seems to strongly suggest that the critical density goes to zero. A relatively simple study by Vega and MacDowell [26] showed that a simple mean field theory is able to predict that the critical density and pressure should go to zero for long chains in general, and for polyethylene in particular. Experimental and theoretical work by Nikitin supports this idea [20]. This is in contrast to some theories [23, 27–29] which suggest that the critical density and pressure approach asymptotic non-zero values. Since Wertheim's theory is one of the most successful theories for flexible chains, it is interesting to check the predictions of this theory concerning the critical properties of long chains. This is one of the goals of this work. The second goal is to analyse the factors determining the value of the critical temperature of infinitely long chains, the so-called $\Theta$ temperature. It will be shown that according to Wertheim's theory, the $\Theta$ temperature is simply related to the second virial coefficient of the monomer and of the monomer–dimer models.

## 2. Brief description of Wertheim's perturbation theory

We shall summarize the main ideas contained within Wertheim's theory by following the thermodynamic cycle introduced by Zhou and Stell [7]. Let us assume that we have a certain number of spherical particles $N^{ref}$ which will be denoted as monomers within a certain volume $V$ at a temperature $T$. These spherical particles interact through a spherical pair potential $u(r)$. We shall denote this fluid as the reference fluid and the properties of this reference fluid will be labelled by the superscript 'ref'. Let us also assume that in another container of volume $V$ and temperature $T$, we have $N = N^{ref}/m$ fully flexible chains of $m$ monomers each. By fully flexible chains we mean chains of $m$ monomers, with a fixed bond length of $L = \sigma$, and no other constraints (i.e. there is no restriction in either bonding or in the torsional angles). Each monomer of a certain chain interacts with all the other monomers in the system (i.e. in the same molecule or in other molecules) with the pair potential $u(r)$. The variable $\sigma$ is a value of $r$ for which the function $u(r)$ starts to increase strongly towards positive values. The chain system described so far will be denoted as the chain fluid.

The Helmholtz free energy of the reference fluid $A^{ref}$ can be divided into an ideal and a residual part as follows:

$$\frac{A^{\text{ref}}}{N^{\text{ref}}kT} = \frac{A^{\text{ref}}_{\text{ideal}}}{N^{\text{ref}}kT} + \frac{A^{\text{ref}}_{\text{residual}}}{N^{\text{ref}}kT} = \ln\left(\rho^{\text{ref}}\right) - 1 + \frac{A^{\text{ref}}_{\text{residual}}}{N^{\text{ref}}kT},$$
(1)

where $\rho^{\text{ref}}$ is the number density of the reference fluid. The residual term represents the difference between the reference fluid and that of a system without intermolecular interactions at the same temperature and density.

The free energy of the chain fluid $A$ can also be divided into an ideal and a residual part as follows:

$$\frac{A}{NkT} = \frac{A_{\text{ideal}}}{NkT} + \frac{A_{\text{residual}}}{NkT} = \ln\left(\rho\right) - 1 + \frac{A_{\text{residual}}}{NkT},$$
(2)

where $\rho$ is the number density of chains. Thermodynamic properties without any superscript refer to the chain fluid.

The residual term represents the difference between the chain fluid and an ideal gas of chains at the same temperature and number density. In the ideal gas of chains there are no intermolecular interactions, whereas intramolecular interactions are still present. Let us assume at this point that the properties (thermodynamic and structural) of the reference fluid are known. Can we obtain an approximation for $A_{\text{residual}}$ of the chain fluid from the properties of the monomer fluid? Following Zhou and Stell let us transform the reference fluid into the chain fluid in a three step thermodynamic process as illustrated in figure 1:

*Step* 1. From the reference fluid to an ideal gas. Change in free energy:

$$\Delta A_{\text{step 1}} = -A^{\text{ref}}_{\text{residual}}.$$
(3)

*Step* 2. From an ideal gas to an ideal chain. By using the potential of mean force concept [30, 31] and taking into account that the change in free energy is the work required to bring together two particles at constant $T$ and $V$, we obtain:

$$\Delta A_{\text{step 2}} = -NkT \ln\left[\exp\left(-\beta U_{\text{intra, chain}}\right)\right],$$
(4)

where $U_{\text{intra, chain}}$ is the intramolecular energy of the chain for the chosen configuration and $\beta = 1/(kT)$.

*Step* 3. From an ideal gas of chains to the real fluid of chains. The change in free energy is given by:

$$\Delta A_{\text{step 3}} = A_{\text{residual}}.$$
(5)

So far no approximations have been introduced. The chain in free energy to take the system from the reference fluid to the chain fluid is given exactly by:

$$\Delta A_{\text{step 1}} + \Delta A_{\text{step 2}} + \Delta A_{\text{step 3}}$$

$$= -A^{\text{ref}}_{\text{residual}} - NkT \ln\left[\exp\left(-\beta U_{\text{intra, chain}}\right)\right]$$

$$+ A_{\text{residual}}.$$
(6)

The work to form one, and only one chain in the reference fluid (the change in free energy to form a single chain) is given exactly by:

$$-kT \ln\left[g(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_m; N^{\text{ref}}, 0)\right],$$
(7)

where $g(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_m)$ is the $m$-body correlation function between monomers in the mixture constituted by $N^{\text{ref}}$ monomers and zero chains. Once this chain is formed we have a fluid of $N^{\text{ref}} - m$ monomers and one chain. The work to form a second chain in this fluid is given by:
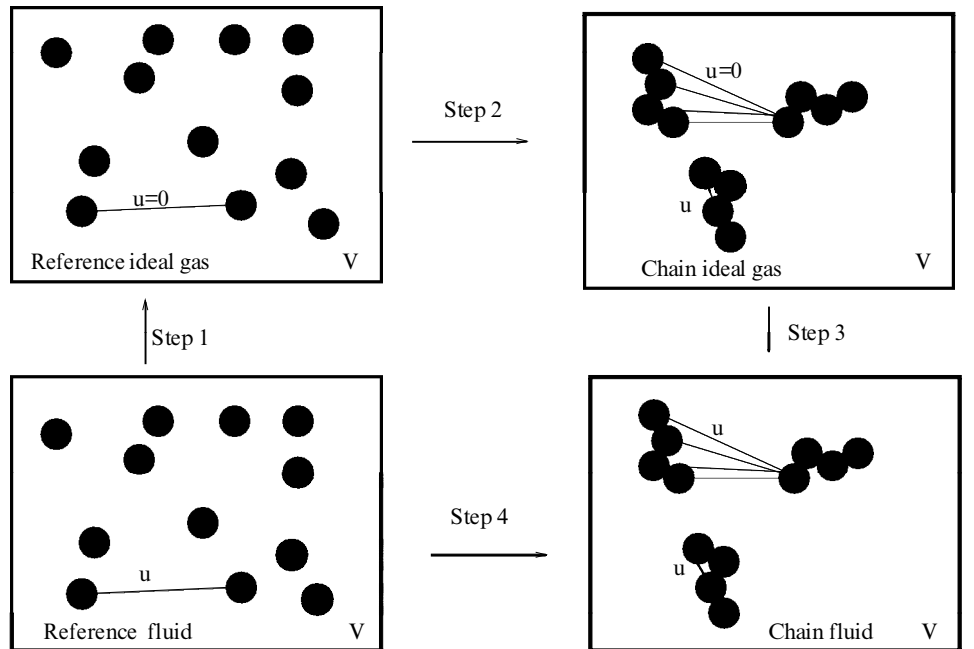


Figure 1. Thermodynamic cycle involved in Wertheim's theory.

$$-kT \ln[g(\mathbf{r}_1, \mathbf{r}, \ldots, \mathbf{r}_m; N^{\text{ref}} - m, 1)], \qquad (8)$$

where the numbers following the semicolon ';' $N^{\text{ref}} - m, 1$ reflects the composition of the system. Finally, the work to form the last chain molecule is given by:

$$-kT \ln[g(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_m; m, N - 1)]. \qquad (9)$$

We shall now make the following approximation:

*Approximation* 1. We shall assume that the $m$-body correlation function between the monomers in the mixture of monomers and chains, at any composition, can be approximated by the $m$ correlation function of the reference monomer fluid. That is:

$$g(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_m; N_1, N_2) = g(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_m; N^{\text{ref}}, 0). \qquad (10)$$

We shall use this approximation to estimate $\Delta A_{\text{step 4}}$.

*Step* 4. From the reference fluid to the chain fluid. The change in free energy is given approximately by:

$$\Delta A_{\text{step 4}} \approx -NkT \ln[g(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_m; N^{\text{ref}}, 0)]. \qquad (11)$$

Obviously, Step 4 is equivalent to the sum of Steps 1, 2 and 3, so that

$$\Delta A_{\text{step 4}} = \Delta A_{\text{step 1}} + \Delta A_{\text{step 2}} + \Delta A_{\text{step 3}}. \qquad (12)$$

Therefore, we obtain for the free energies:

$$-NkT \ln[g(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_m; N^{\text{ref}}, 0)]$$
$$= -A_{\text{residual}}^{\text{ref}} - NkT \ln\left(\exp\left(-\beta U_{\text{intra, chain}}\right)\right)$$
$$+ A_{\text{residual}}. \qquad (13)$$

The $m$-body background correlation function, $y$, is defined as:

$$g(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_m; N^{\text{ref}}, 0)$$
$$= \exp\left(-\beta U_{\text{intra, chain}}\right) y(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_m; N^{\text{ref}}, 0). \qquad (14)$$

Substituting equation (14) into equation (13) one obtains:

$$A_{\text{residual}} = A_{\text{residual}}^{\text{ref}} - NkT \ln[y(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_m; N^{\text{ref}}, 0)]. \qquad (15)$$

The $m$ background correlation function of the reference fluid is unknown so that another approximation is required.

*Approximation* 2. We shall approximate the $m$ body background correlation function of the reference fluid by the following approximation [7]:

$$y(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_m; N^{\text{ref}}, 0)$$
$$= y(r_{12}; N^{\text{ref}}, 0) y(r_{23}; N^{\text{ref}}, 0) \ldots y(r_{m-1,m}; N^{\text{ref}}, 0)$$
$$= y^{\text{ref}}(r_{12}) y^{\text{ref}}(r_{23}) \ldots y^{\text{ref}}(r_{m-1,m}). \qquad (16)$$

By substituting equation (16) into equation (15) and taking into account that the value of the bonding distance is $\sigma$, one obtains:

$$A_{\text{residual}} = A_{\text{residual}}^{\text{ref}} - N(m-1)kT \ln[y^{\text{ref}}(\sigma)]. \qquad (17)$$

Therefore, the free energy of the chain fluid is given by:

$$\frac{A}{NkT} = \ln(\rho) - 1 + \frac{A_{\text{residual}}^{\text{ref}}}{NkT} - (m-1) \ln[y^{\text{ref}}(\sigma)]. \qquad (18)$$

Therefore, to know the free energy of the chain fluid it is sufficient only to know the residual free energy of the reference fluid and the pair background correlation function of the reference fluid at the bonding distance of the chain. The equation of state which follows from equation (18) is given by:

$$Z = \frac{p}{\rho kT} = 1 + mZ_{\text{residual}}^{\text{ref}} - (m-1)\rho \frac{\partial \ln[y(\sigma)]}{\partial \rho} \qquad (19)$$

or simply:

$$Z = mZ^{\text{ref}} - (m-1)\left(1 + \rho^{\text{ref}} \frac{\partial \ln[y(\sigma)]}{\partial \rho^{\text{ref}}}\right) \qquad (20)$$

where we have defined $Z^{\text{ref}}$ as $Z^{\text{ref}} = p/(\rho^{\text{ref}}kT)$. We shall denote equation (20) as Wertheim's EOS [4, 6]. It has been shown that for chains of tangent spheres, equation (20) performs very well [32].

## 3. Critical properties of long chains from Wertheim's perturbation theory

MacDowell *et al.* [15] have recently analysed the critical properties of very long chain molecules using Wertheim's theory. We shall describe briefly the main ideas. It will be assumed that for very long chains, the critical density goes to zero. If this is so, then a truncated virial expansion will correctly describe the equation of state at low densities (i.e. the proximities of the critical point). From the virial expansion one obtains:

$$\frac{p}{kT} = \rho + B_2(T)\rho^2 + B_3(T)\rho^3, \qquad (21)$$

where $B_2(T)$ and $B_3(T)$ are the virial coefficients of the chain fluid.

By applying the conditions for the critical point of pure fluids (i.e. setting to zero the first and second derivatives of the pressure with respect to number density) one obtains the following set of equations for the critical temperature and density:

$$B_2(T_c) + [3B_3(T_c)]^{1/2} = 0, \qquad (22)$$

$$\rho_c = \frac{1}{[3B_3(T_c)]^{1/2}}. \qquad (23)$$

The second and third virial coefficients of a chain molecule with $m$ monomer units that follow from Wertheim's EOS (i.e. equation (20)) are:

$$B_2 = m^2 \left( B_2^{\text{ref}} - \frac{m-1}{m} a_2 \right),$$

$$B_3 = m^3 \left( B_3^{\text{ref}} - \frac{m-1}{m} a_3 \right), \qquad (24)$$

where $B_2^{\text{ref}}$ and $B_3^{\text{ref}}$ are the second and third virial coefficients of the reference fluid of non-bonded monomers. The coefficients $a_2$ and $a_3$ are just the first and second derivatives of $\ln y(\sigma)$ with respect to $\rho^{\text{ref}}$ evaluated at zero density (i.e. $a_2$ is just $\partial \ln y(\sigma)/\partial \rho^{\text{ref}}$ evaluated for $\rho^{\text{ref}} = 0$). Of course, $a_2$ and $a_3$ are chain length independent.

Let us assume now that there is a finite asymptotic critical temperature in the limit of infinite chain length, which we shall call $\Theta$. Then let us perform a series expansion of $B_2$ and $B_3$ in powers of $\Delta T = \Theta - T$ and let us truncate this expansion in first order. By replacing this truncated expansion in equation (24) one obtains in the limit of large $m$:

$$B_2(T) = m^2(C_2 - C_2' \Delta T),$$

$$B_3(T) = m^3(C_3 - C_3' \Delta T), \qquad (25)$$

where $C_2 = B_2^{\text{ref}}(\Theta) - a_2(\Theta)$ and $C_3 = B_3^{\text{ref}}(\Theta) - a_3(\Theta)$, while $C_2'$ and $C_3'$ are the corresponding derivatives with respect to temperature. Substitution of the linearized virial coefficients into the condition for the critical temperature leads to a quadratic equation for $\Delta T$. Solving this equation yields $\Delta T_c(m)$, defined as $\Theta - T_c(m)$:

$$\Delta T_c(m) - \frac{C_2}{C_2'} = \pm \frac{1}{2C_2'^2} \left( 12C_2'^2 C_3 - 12C_2 C_2' C_3' \right.$$

$$\left. + 9C_3'^2 \frac{1}{m} \right)^{1/2} \frac{1}{m^{1/2}} - \frac{3C_3'}{2C_2'^2} \frac{1}{m}. \qquad (26)$$

In the limit of large $m$ the right-hand side of equation (26) vanishes. Therefore the critical temperature of the infinitely long polymer becomes $\Theta$ (i.e. $\Delta T_c(m) = 0$) only if the coefficient $C_2$ vanishes. According to equation (25) the second virial coefficient at $T = \Theta$ in the limit of $m$ going to infinity is given by:

$$\lim_{m \to \infty} B_2(\Theta) = m^2 C_2(\Theta). \qquad (27)$$

Therefore the coefficient $C_2$ vanishes at $T = \Theta$ only when the second virial coefficient of the infinitely long

polymer becomes zero at that temperature. We arrive at the conclusion that indeed $C_2$ must vanish at the Boyle temperature of the infinitely long polymer (where the second virial coefficient vanishes), thus identifying the $\Theta$ temperature with the Boyle temperature of the infinitely long polymer. From the definition of $C_2$, we see that this temperature is attained when the following condition is satisfied:

$$B_2^{\text{ref}}(\Theta) - a_2(\Theta) = 0. \qquad (28)$$

Note also that the leading terms of the expansion are of order $m^{-1/2}$ and $m^{-1}$, just as predicted by the Flory–Huggins (FH) theory.

The case of the critical density is much simpler. Substitution of the expression for $B_3$ in the condition for the critical density shows that:

$$\rho_c \propto m^{-3/2}, \qquad (29)$$

so that the critical mass density decreases with a lower law proportional to $m^{-1/2}$, as predicted by the FH theory. Equation (29) is consistent with our initial assumption of a vanishing critical density for long chains. In other words, by assuming that the critical density goes to zero, so that a truncated virial expansion is valid, we obtain the result that the critical density goes to zero, which is consistent with our initial assumption.

It is important to note that the above arguments apply regardless of the specific form in which the reference fluid (thermodynamics and structure) is described. Recently, Nikitin *et al.* [33, 34] have proposed a simple EOS for chain fluids. It is simple to show that Nikitin's treatment is equivalent to taking $y(\sigma)$ to be a constant independent of density, so that $a_2 = 0$ for all temperatures. However, equation (28) shows that this simple version still predicts an asymptotic critical temperature which must obey the condition $B_2^{\text{ref}}(\Theta) = 0$. Obviously, this condition is obeyed for the Boyle temperature of the reference fluid.

Let us now analyse the behaviour of the compressibility factor at the critical point of infinitely long chains that follows from Wertheim's theory. It can be shown that at the critical point besides equation (23), it must also hold that $\rho_c = -B_2(T_c)/[3B_3(T_c)]$. Using this expression for the critical density in the linear term of equation (21) and equation (23) in the quadratic term, it is seen that both terms exactly cancel each other out. Dividing the resulting expression for the pressure by the critical density (equation (23)) we obtain:

$$Z_c = \frac{p_c}{\rho_c k T_c} = \frac{1}{3} + \frac{B_4}{(3B_3)^{1.5}} + \cdots. \qquad (30)$$

For the particular case of Wertheim's EOS (i.e. equation (20)) one finds that $B_4$ scales as $m^4$ and $B_3$ scales as $m^3$

(see equation (24)) so that the ratio $B_4/B_3^{1.5}$ tends to zero when $m$ goes to infinity. Therefore, Wertheim's EOS predicts a limiting value of the compressibility factor at the critical point of infinitely long polymers of 1/3.

Once it has been shown that for very long polymers the critical temperature reaches an asymptotic finite value, the compressibilty factor reaches an asymptotic finite non-zero value and that the critical number density goes to zero, it must be concluded that the critical pressures goes to zero with the same power law than the density (i.e. $m^{-1.5}$), so that the ratio between pressure and density remains finite.

To summarize, Wertheim's theory predicts for the critical properties of very long chains:

  (i) a finite critical temperature;
 (ii) a compressibility factor of 1/3; and
(iii) a vanishing number density and pressure with the scaling law (i.e. $m^{-1.5}$).

It should be mentioned that the scaling laws of Wertheim's theory are identical to the predictions obtained by a theory which combines Wertheim's EOS for hard chains with a mean field contribution due to attractive forces [26].

At this point let us analyse in more detail the scaling laws of Wertheim's theory for the virial coefficients of chains. Wertheim's theory predicts for any type of chain (flexible or rigid, with attractive forces or of hard type) that $B_2$ scales as $m^2$ and $B_3$ scales as $m^3$. For hard chains this was shown by Boublik [35]. Is this correct? The answer is no. Let us show why. Very little is known of the behaviour of $B_2$ and $B_3$ in chains with attractive forces. Therefore we cannot test the accuracy of Wertheim's treatment for these kinds of chains. However for chains of hard spheres a little more is known. For hard spherocylinders Onsager [36] and Frenkel [37] have shown [38] that $B_2$ scales as $m^2$ and $B_3$ scales as $m^3 \ln(m)$. This scaling holds also for hard linear rigid chains [39, 40]. For hard flexible chains scaling laws are different. In fact it is well known [41–44] that $B_2$ scales as $m^{3\nu}$ and $B_3$ scales [40, 45] as $m^{6\nu}$ where $\nu$ is the exponent defining the radius of gyration under good solvent conditions (i.e. $\nu = 0.588$). Therefore scaling laws of $B_2$ and $B_3$ are different for linear rigid and flexible hard chains. The scaling of Wertheim's treatment is not exact either for rigid or hard flexible chains. Wertheim's theory predicts correctly the scaling law of $B_2$ of linear rigid chains only. Nothing else. This is not surprising. Wertheim's theory is not particularly accurate in the low density limit. This point has received little attention although evidence for this is increasing [46]. In this paper we analyse the critical properties of long chains that follow from Wertheim's theory. Even though the scaling laws for the virial coefficients of Wertheim's

theory are wrong the theory has the merit of predicting a finite value of the critical temperature and compressibilty factor at the critical point for very long chains, and predicts a vanishing value for the critical density and pressure. Notice that these trends are in agreement with the more recent experimental data on the critical properties of n-alkanes [20]. Therefore the theory seems to be describing qualitatively the main trends in the critical properties of chains. Can a theory with wrong predictions in the scaling laws of the virial coefficients provide qualitative undersanding of the critical properties of chains? We believe that the answer to that question is yes. The Flory–Huggins theory [21, 22] is used commonly to describe the fluid–fluid separation that occurs when a polymer dissolves into a solvent. The Flory–Huggins theory predicts that the osmotic virial coefficients, second and third, scale respectively [47] as $m^2$ and $m^3$ (i.e. the same as those which are obtained from Wertheim's theory). It is well known that this scaling is wrong. However, the Flory–Huggins theory predicts qualitatively the existence for long chains of a finite critical temperature and that the polymer critical density vanishes as the chain gets longer. In a few words the theory predicts the trends correctly even though it made incorrect predictions on the scaling laws of the virial coefficients. Our view is that Wertheim's theory describes qualitatively main trends in the behaviour of the critical properties of chains, but is incorrect in the scaling predicted for the virial coefficients. The same holds for the Flory–Huggins theory. Not surprisingly Flory developed a more sophisticated theory to predict correctly the osmotic second virial coefficient of polymers [48]. Probably a similar route could be undertaken within Wertheim's formalism.

Let us now investigate further equation (28), which is an implicit equation for the critical temperature of the infinitely long chain (i.e. the $\Theta$ temperature). $B_2^{\mathrm{ref}}$ is simply the second virial coefficient of the monomer fluid. The coefficient $a_2$ is given by

$$a_2 = \left( \frac{\partial \ln[y(\sigma)]}{\partial \rho^{\mathrm{ref}}} \right)_{\rho^{\mathrm{ref}} = 0}. \tag{31}$$

Obviously, this is identical to:

$$a_2 = \left( \frac{\partial \ln[g(\sigma)]}{\partial \rho^{\mathrm{ref}}} \right)_{\rho^{\mathrm{ref}} = 0}. \tag{32}$$

Therefore, the coefficient $a_2$ is the derivative of the logarithm of the pair correlation function ($g$ or $y$) of the reference fluid evaluated at zero density and $r = \sigma$. The density expansions of $g$ and $y$ are well known in terms of diagrams [49]. By using the low density diagrams of the expansion of $y$ it can be proved easily that $a_2$ is given by the diagram presented in figure 2.
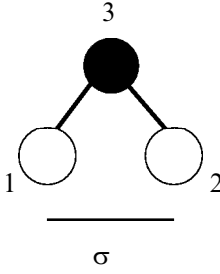
Figure 2. Diagram corresponding to the term denoted as $a_2$.

In this diagram, the distance between the two white circles should be $\sigma$ (i.e. the bond distance). Solid lines of the diagram represent Mayer functions, black circles indicate integration with respect to the coordinates of that molecule and white circles indicate that no integration with respect to their coordinates should be performed. It should be mentioned that all molecules of the graph represent monomers, so that the Mayer function is given simply by $f = \exp\left[-\beta u(r)\right] - 1$. The graph plotted previously is a concise way of writing the following integral:

$$a_2 = \int f(1,3)f(2,3)\,d\mathbf{r}_3, \qquad (33)$$

where the distance between the monomers 1 and 2 is fixed to $\sigma$. After some algebra this integral can be written as:

$$a_2 = 4B_2^{\text{ref}} - 2B_2^{\text{monomer–dimer}}, \qquad (34)$$

where $B_2^{\text{monomer–dimer}}$ is the second virial coefficient between a monomer and a dimer. The dimer is formed by two monomers rigidly bonded at a distance $\sigma$. Therefore, the physical meaning of the coefficient $a_2$ is quite simple: it is the difference between four times the virial coefficient of the monomer and two times the virial coefficient of the monomer–dimer. Let us show with an example that equation (34) is correct. For hard spheres, one can obtain the value of $g(\sigma)$ from the Carnahan–Starling [50] EOS. By taking logarithms and evaluating the derivative of $\ln\left[g(\sigma)\right]$ with respect to $\rho^{\text{ref}}$ for $\rho^{\text{ref}} = 0$, one finds that for hard spheres, $a_2 = 1.3089$. Let us now evaluate $a_2$ from equation (34). The second virial coefficient of a hard sphere is well known. The second virial coefficient between a monomer and a dimer is just one half of the volume of a hard dumbbell with reduced bond length $L^* = 0.5$ which is also well known [51]. Evaluating now equation (34) one finds $a_2 = 1.3089$, which is identical to the value obtained via the other route.

Substituting equation (34) into equation (28) one obtains:

$$B_2^{\text{ref}}(\Theta) - \tfrac{2}{3}B_2^{\text{monomer–dimer}}(\Theta) = 0. \qquad (35)$$

Equation (35) tell us that the critical temperature of the infinitely long chain (i.e. the $\Theta$ temperature) that follows from Wertheim's theory is the temperature where the second virial coefficient of the monomer becomes 2/3 of the second virial coefficient between the monomer and the dimer. Equation (35) is amazingly simple and provides a way of obtaining the $\Theta$ temperature that follows from Wertheim's theory for a certain type of chain fluid. All that is required are two second virial coefficient calculations. We shall illustrate this in the following section.

Let us finish this section by mentioning that there is a variant of Wertheim's theory which is known as Wertheim's dimer theory [52]. In this theory the reference fluid is made up of dimers, and chains are formed by joining several dimers. The steps desribed before can be easily applied to this new case by replacing $m$ by $m/2$ in our previous derivation and replacing the thermodynamic properties and structure of the monomer reference fluid by the thermodynamic properties and structure of the dimer reference fluid. The scaling laws of the critical properties derived before still hold for Wertheim's dimer theory.

## 4. Results

In this section we shall show results for the $\Theta$ temperature of long chains that follows from Wertheim's theory. We shall analyse several types of chains which differ in the pair potential between the monomer units. Let us start with the LJ chain fluid (i.e. chains formed by LJ monomers at the bonding distance $\sigma$). The Lennard-Jones potential is given by:

$$u(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]. \qquad (36)$$

First let us focus on the evaluation of $a_2$ for the LJ fluid. We shall evaluate $a_2$ via two different numerical procedures. In the first procedure we shall numerically evaluate $B_2^{\text{ref}}$ and $B_2^{\text{monomer–dimer}}$ for several temperatures, so that $a_2$ can be evaluated from equation (34). $B_2^{\text{ref}}$ is evaluated from a simple Simpson's integration. $B_2^{\text{monomer–dimer}}$ is obtained by fixing the dimer in the $z$ axis (with the centre of mass at the origin of coordinates) and performing integration over $r$ and $\theta$ (the distance and polar angle of the monomer) using Simpson's rule. The evaluation of $a_2$ using this procedure requires about 20 s of CPU time on a personal computer. In figure 3, the value of $a_2 = 4B_2^{\text{ref}} - 2B_2^{\text{monomer–dimer}}$ as obtained from this procedure is shown as a solid line.

The second procedure for estimating $a_2$ is more involved. We shall use the definition of $a_2$ from equation (32). For a given temperature we shall perform Monte Carlo simulations of the LJ fluid for reduced densities in the range (0–0.10). The value of $g(\sigma)$ will be evaluated
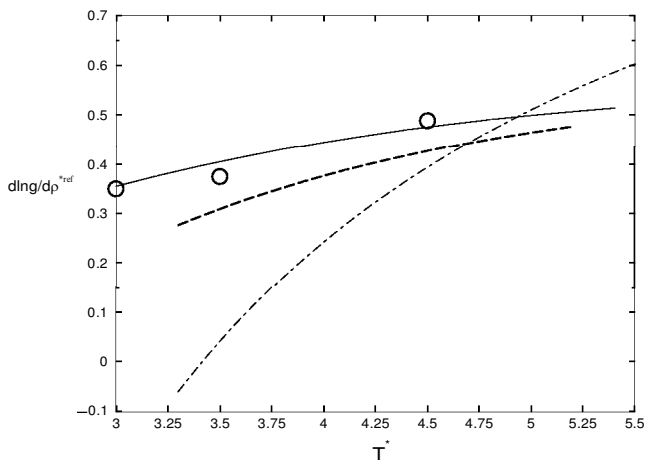
Figure 3. Second virial coefficient of the LJ monomer fluid $B_2^{\text{ref}}$ (dashed–dotted line), and the coefficient $a_2$ as estimated from virial coefficient calculations and equation (34) (solid line), from Monte Carlo simulations of this work (open circles) and from the parametrization provided by Johnson and Gubbins (dashed line).
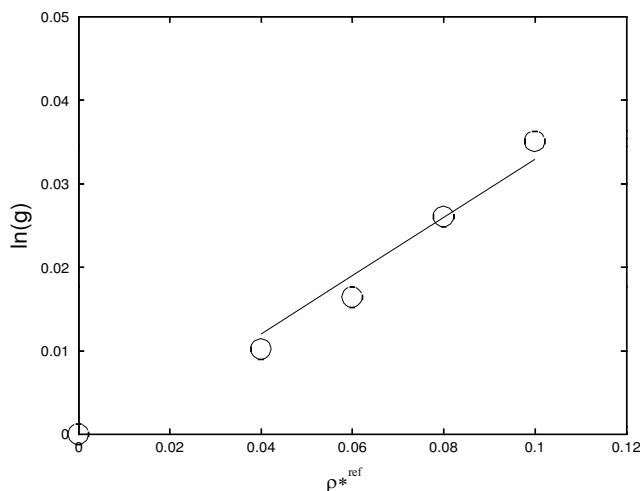


Figure 4. The pair correlation $g(\sigma)$ of the LJ monomer fluid for $T^* = 3$ as a function of the reduced density as obtained from the Monte Carlo simulations of this work.

from the simulation. We typically used systems of 256 molecules and runs of 200 000 cycles for equilibration and 400 000 cycles for collecting averages. The grid used to determine $g(\sigma)$ has a width of $0.02\sigma$. For each temperature, a plot is made of $\ln(g)$ versus reduced number density and then the results are fitted to a straight line. In figure 4, a plot of $\ln(g)$ versus density is shown for the LJ fluid with $T^* = T/(\varepsilon/k) = 3$. In this case, a linear square fit yields a slope of 0.3495 and this is the second estimate of $a_2$ for $T^* = 3$. It may appear that the numerical uncertainty of $g(\sigma)$ presented in figure 4 is too large. To illustrate the origin of the problem, we shall mention that for $T^* = 3$, $g(\sigma) = 1$ for $\rho^* = 0$ and $g(\sigma) = 1.04$ for $\rho^* = \rho\sigma^3 = 0.10$. In other words, $g(\sigma)$ increases by 0.004 when the reduced density increases by 0.01. Therefore, it is important to have an accuracy of about 0.001 in $g(\sigma)$. This is difficult to achieve at low densities. In figure 3, the values of $a_2$ obtained from this second procedure are shown as white circles. It can be seen there is good agreement between $a_2$ evaluated from both procedures. However, the numerical uncertainty of $a_2$ obtained from molecular simulations is rather large and therefore the estimate of $a_2$ from the second virial coefficients provides higher numerical accuracy (in this case, the simplest and fastest is also the best). Therefore, in what follows we shall use the second virial coefficient calculations to determine $a_2$. A few years ago, Johnson et al. [10,11] performed molecular dynamics simulations for the LJ fluid and obtained simulation values of $g(\sigma)$ for a number of thermodynamic states (about 200). They then fitted the simulation values of $g(\sigma)$ to an empirical formula. From this empirical fit of $g(\sigma)$ and from equation (32), it is not difficult to obtain the value of $a_2$ that

corresponds to their fit. The estimate of $a_2$ that follows from the Johnson et al. fit [11] is shown in figure 3 as a dashed line. As can be seen, the estimate of Johnson et al. is close but certainly different from our estimate. The origin of the discrepancy is the following. For temperatures larger than $T^* = 3$, Johnson et al. [11] performed simulations for densities larger than $\rho^* = 0.10$. Therefore, the estimate of $a_2$ that follows from their work is not particularly accurate at high temperatures.

In figure 3, the values of $B_2^{\text{ref}}$ and $a_2$ are plotted as a function of the reduced temperature of the reference LJ fluid. According to equation (28), the temperature where both curves cross determines the $\Theta$ temperature. Therefore, the $\Theta$ temperature of LJ chains that follows from Wertheim's theory is $\Theta = T^* = 4.92$. The estimate of the $\Theta$ temperature obtained from Gibbs ensemble simulations is about 4.59 [53]. Therefore, Wertheim's theory overestimates the critical temperature of infinitely long LJ chains by about 7%. When the Johnson et al. values of $a_2$ are used, Wertheim's theory provides $T^* = 4.65$ as the estimate of the $\Theta$ temperature. This is in closer agreement with the simulation results. This improvement in the estimate of the $\Theta$ temperature is somehow fortuitous since it arises from a bad estimate of $a_2$ ($B_2^{\text{ref}}$ is evaluated properly when the Johnson et al. EOS of the LJ fluid is used). At this point we should emphasize an important aspect of the implementation of Wertheim's theory for the vapour–liquid equilibria of long chains and especially for the estimate of the critical properties of long chains. One requires good thermodynamic and structural data at low densities of the reference fluid. Otherwise, estimates of the critical properties of long chains can vary significantly between different implementations of Wertheim's theory.

Table 1.   Properties of SW fluids as a function of $\lambda$. $T_B^{\text{ref}}$ is the Boyle temperature of the reference fluid, $\Theta$ is the critical temperature of the infinitely long chain, obtained either from Wertheim's theory or from Monte Carlo (MC) results of [54, 55].

| $\lambda$ | $T_B^{\text{ref}}$ | $\Theta$ | $\Theta_{\text{MC}}$ | $\Theta/T_B^{\text{ref}}$ | $\Theta_{\text{MC}}/T_B^{\text{ref}}$ |
|------|-------|--------|-------|-------|-------|
| 1.10 | 0.72  | 0.705  | *     | 0.98  | *     |
| 1.25 | 1.394 | 1.424  | 1.35  | 1.021 | 0.968 |
| 1.5  | 2.846 | 3.351  | 3.12  | 1.177 | 1.096 |
| 1.75 | 4.842 | 6.935  | 5.95  | 1.43  | 1.228 |
| 2    | 7.489 | 13.233 | 10.74 | 1.77  | 1.434 |

Once we have described the results for the LJ system, we shall use the same procedure to estimate the critical temperature for other systems. An interesting system is the square well (SW). Starting from square well monomers interacting through the pair potential:

$$u(r) = \infty, \qquad r < \sigma. \tag{37}$$

$$u(r) = -\varepsilon, \qquad \sigma < r < \lambda\sigma, \tag{38}$$

$$u(r) = 0, \qquad r > \lambda\sigma, \tag{39}$$

where $\lambda$ is the range of the potential, one can form SW chains (chains with tangent bonded spheres interacting through a site–site SW interaction). In table 1 we present results for the critical temperature of infinitely long SW chains as a function of the range of the potential $\lambda$. The $\Theta$ temperature of SW chains (the model considered in this work) has been recently determined through second virial coefficient calculations of SW chains by Dautenhahn and Hall *et al.* [54] for $\lambda = 1.5$. For $\lambda = 1.25$, 1.75 and 2 Hall and Wichert have determind the $\Theta$ temperature for chains with intermolecular SW interactions but with intramolecular hard sphere interactions [55]. Although this is not the model studied in this work, one may expect that the effect of the intramolecular interactions on the virial coefficients is small. In table 1, the estimates of the $\Theta$ temperature of SW chains arising from the second virial calculations of Hall and co-workers [54, 55] are shown. By comparing the results of Wertheim's theory with the estimate of Hall and co-workers, it may be concluded that the error of the theory in determining the $\Theta$ temperature of SW chains is of about 5%, 7%, 16% and 23% for $\lambda = 1.25$, 1.5, 1.75 and 2 respectively. As can be seen, the error increases with the range of the potential. From the results of table 1 we can state that for usual ranges of pair interaction potentials (i.e. LJ, SW with $\lambda$ less than 1.5) Wertheim's theory can predict the $\Theta$ temperature with an accuracy better than 10%.
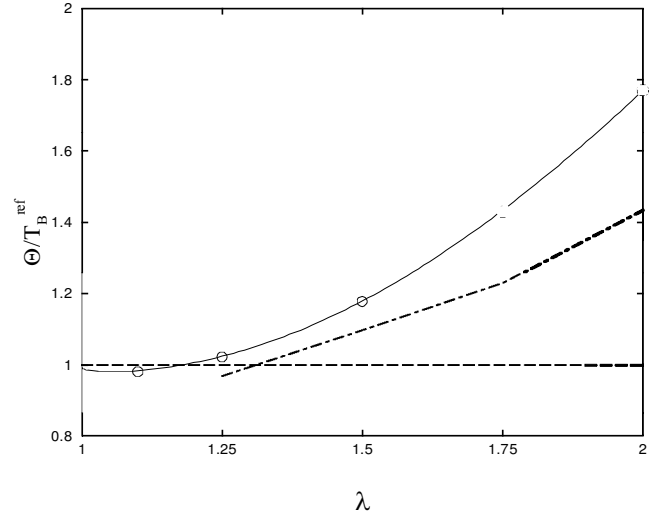


Figure 5.   Ratio between $\Theta$ and the Boyle temperature of the reference fluid $T_B^{\text{ref}}$ for SW chains as obtained from Wertheim's theory with numerical (open circles) or analytical (solid line) determination of $a_2$; from the theory of Nikitin *et al.* (dashed line) and from numerical simulations (dashed–dotted line).

Also in table 1 results for the Boyle temperature of the reference fluid, $T_B^{\text{ref}}$, are shown (i.e. the temperature at which the second virial coefficient of the reference fluid vanishes). As can be seen in table 1, $T_B^{\text{ref}}$ decreases as the range of the potential decreases. The conclusion is that both $T_B^{\text{ref}}$ and $\Theta$ decrease with the range of the attractive forces. One can understand easily that decreasing the range of attractive forces results in a decrease in the critical temperature and in the Boyle temperature. It is more interesting to analyse the value of the ratio $\Theta/T_B^{\text{ref}}$ in SW chains. This ratio is also shown in table 1. It can be seen that this ratio decreases strongly as the range of the potential decreases. In figure 5, this ratio as obtained from simulation and from Wertheim's theory is plotted as a function of $\lambda$ for the SW fluid. The value of this ratio for LJ chains estimated by simulations is of about 1.34, so that the LJ chains behave similarly to SW chains with $\lambda = 1.6$. According to the theory of Nikitin *et al.* [33, 34], the ratio of $\Theta/T_B^{\text{ref}}$ should be one for any chain fluid. It can be seen in figure 5 that this ratio is close, but not identical to one. Nikitin *et al.*'s theory provides a simple first estimate for the $\Theta$ temperature of a polymer made up of tangent spheres: the $T_B^{\text{ref}}$ of the monomer. This estimate will be especially good when the range of the attractive forces is small. The result of figure 5 has a number of practical applications. In fact, it indicates that second virial coefficient calculations of chains should be preferred to Gibbs ensemble simulations in order to determine the $\Theta$ temperature of chains formed by tangent spheres. This is so because $T_B^{\text{ref}}$ is already close to $\Theta$, so one may expect that by evaluating

the Boyle temperature of a short chain one can obtain quite a good estimate of $\Theta$. However, as will be shown later, the critical temperature of the monomer is typically two or three times smaller than the critical temperature of the infinitely long polymer, so one should determine the vapour–liquid equilibria for long chains in order to estimate properly the $\Theta$ temperature. Moreover, second virial coefficient calculations can be performed more easily than Gibbs ensemble calculations.

There is another issue. In figure 5 it is seen that Wertheim's theory predicts $\Theta$ temperatures smaller than $T_B^{\mathrm{ref}}$ for values of $\lambda$ smaller than $\lambda = 1.15$. The numerical determination of $\Theta$ becomes difficult for small values of $\lambda$. Therefore, it is difficult to establish from numerical methods the asymptotic behaviour of the ratio $\Theta/T_B^{\mathrm{ref}}$ when $\lambda$ tends to one. In the Appendix of this work it will be shown that for the SW system, the second virial coefficient between a monomer and a dimer can be determined analytically. Therefore, the solution of equation (35) for $\Theta$ at a certain value of $\lambda$ can be performed analytically (i.e. it amounts to solving a second order equation). The important conclusion is that for SW chains, the value of $\Theta$ arising from Wertheim's theory is given by a simple analytical expression. In figure 5, the value of this analytical expression is shown as a solid line. It can be seen that our numerical determination of $\Theta$ (open circles) agrees quite well with the analytical result. The behaviour of $\Theta/T_B^{\mathrm{ref}}$ that follows from Wertheim's theory can now be discussed in the limit of small values of $\lambda$. It turns out that Wertheim's theory predicts the existence of a minimum in the ratio $\Theta/T_B^{\mathrm{ref}}$ for values of $\lambda$ slightly larger than one and moreover that this ratio tends to one when $\lambda$ goes to one.

In table 2, $T_c^{\mathrm{ref}}$ (i.e. the critical temperature of the reference fluid) and $\Theta$ are presented for SW fluids with several values of $\lambda$. Results are also presented in figure 6. As can be seen, the ratio $\Theta/T_c^{\mathrm{ref}}$ decreases with the range of potential $\lambda$. The theory of Nikitin *et al.* predicts (when the van der Waals equation of state is used for the monomer) that this ratio is equal to 27/8.

At this point, we should mention an interesting issue. It is well known that for the SW monomer with $\lambda$ less than 1.3 the vapour–liquid equilibrium is metastable with respect to freezing [58]. For chains one may expect a similar result, the vapour–liquid equilibrium becoming metastable with respect to freezing when the range of the attractive forces becomes small. However, fluid–solid equilibrium is not considered in this paper and we cannot provide quantitative details on this issue.

Finally we shall consider the properties of chains with monomers interacting through the Yukawa potential. This potential is given by:
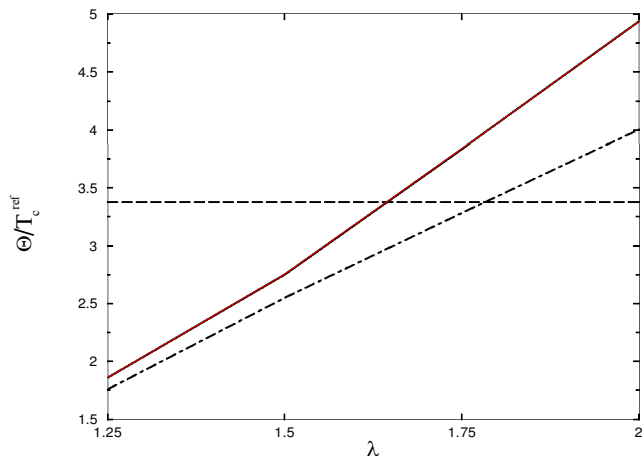


Figure 6. Ratio between $\Theta$ and the critical temperature of the reference fluid $T_c^{\mathrm{ref}}$ for SW chains as obtained from Wertheim's theory (solid line), the theory of Nikitin *et al.* (dashed line) and from numerical simulations (dashed–dotted line).

Table 2. Properties of SW fluids as a function of $\lambda$. $T_c^{\mathrm{ref}}$ is the critical temperature of the reference fluid taken from [56, 57]. $\Theta$ is the critical temperature of the infinitely long chain, obtained either from Wertheim's theory or from Monte Carlo (MC) results of [54, 55].

| $\lambda$ | $T_c^{\mathrm{ref}}$ | $\Theta$ | $\Theta_{\mathrm{MC}}$ | $\Theta/T_c^{\mathrm{ref}}$ | $\Theta_{\mathrm{MC}}/T_c^{\mathrm{ref}}$ |
|---|---|---|---|---|---|
| 1.25 | 0.764 | 1.424 | 1.35 | 1.86 | 1.76 |
| 1.5 | 1.219 | 3.351 | 3.12 | 2.75 | 2.55 |
| 1.75 | 1.811 | 6.935 | 5.95 | 3.83 | 3.28 |
| 2 | 2.684 | 13.233 | 10.74 | 4.93 | 4.00 |

$$u(r) = \infty, \qquad r < \sigma, \tag{40}$$

$$u(r) = -\frac{\varepsilon}{r/\sigma}\exp\left(-\gamma(r/\sigma - 1)\right), \qquad r > \sigma. \tag{41}$$

The parameter $\gamma$ controls the range of the potential. This potential has been studied recently by Davies *et al.* [13] using Wertheim's theory to obtain the vapour–liquid equilibrium of short chains. In table 3 and figure 7, results for $T_B^{\mathrm{ref}}$ and $\Theta$ temperatures are shown for the Yukawa chains as a function of the range of the potential (i.e. the inverse of $\gamma$). The dependence of $T_B^{\mathrm{ref}}$ and $\Theta$ with the range of the potential of the Yukawa chains is similar to that found for SW chains. The ratio $\Theta/T_B^{\mathrm{ref}}$ decreases as the range of the potential decreases. One can suspect from the results of the SW model that this ratio reaches a minimum for big values of $\gamma$ and then goes to one as $1/\gamma$ goes to zero. In table 4 and figure 8, results for $T_c^{\mathrm{ref}}$ and $\Theta$ temperatures are shown for the Yukawa fluids. Trends are similar to those found in SW systems.
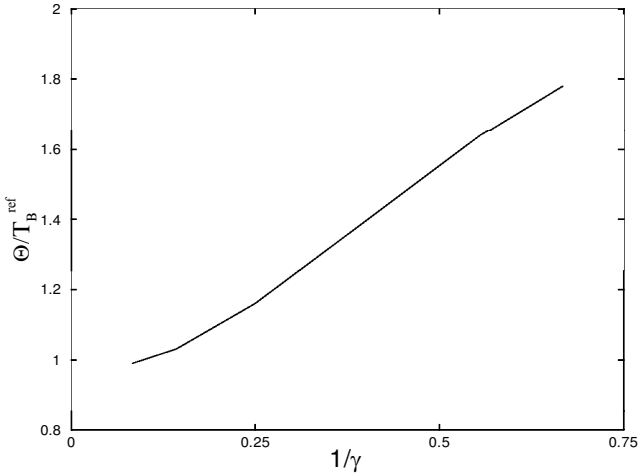
Figure 7.  Ratio between $\Theta$ and the Boyle temperature of the reference fluid $T_B^{ref}$ for Yukawa chains as obtained from Wertheim's theory.
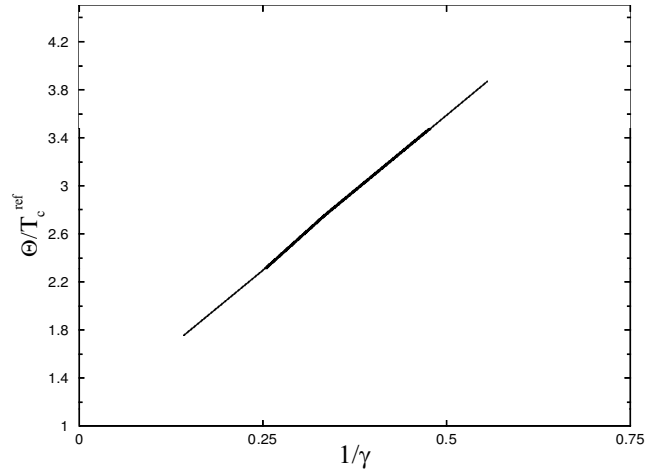


Figure 8.  Ratio between $\Theta$ and the critical temperature of the reference fluid $T_c^{ref}$ for Yukawa chains as obtained from Wertheim's theory.

Table 3.  Properties of Yukawa fluids as a function of $\gamma$. $T_B^{ref}$ is the Boyle temperature of the reference fluid, $\Theta$ is the critical temperature of the infinitely long chain, obtained from Wertheim's theory.

| $\gamma$ | $T_B^{ref}$ | $\Theta$ | $\Theta/T_B^{ref}$ |
|---|---|---|---|
| 1.5 | 3.49 | 6.22 | 1.78 |
| 1.8 | 2.76 | 4.53 | 1.64 |
| 3 | 1.525 | 1.97 | 1.29 |
| 4 | 1.14 | 1.32 | 1.16 |
| 7 | 0.705 | 0.725 | 1.03 |
| 12 | 0.49 | 0.485 | 0.99 |

Table 4.  Properties of Yukawa fluids as a function of $\gamma$. $T_c^{ref}$ is the critical temperature of the reference fluid taken from [59, 60]. $\Theta$ is the critical temperature of the infinitely long chain, obtained from Wertheim's theory.

| $\gamma$ | $T_c^{ref}$ | $\Theta$ | $\Theta/T_c^{ref}$ |
|---|---|---|---|
| 1.8 | 1.17 | 4.53 | 3.87 |
| 3 | 0.715 | 1.97 | 2.75 |
| 4 | 0.576 | 1.32 | 2.29 |
| 7 | 0.412 | 0.725 | 1.76 |

One final comment concerning the $\Theta$ temperature. Wertheim's theory assumes that the $\Theta$ temperature of chains made of flexible tangent monomers is independent of the bonding angle and the torsional potential. Obviously, this is an approximation. To illustrate that this is the case let us mention that for the LJ chains, the $\Theta$ temperature obtained from simulations of the fully flexible model is of 4.59 [53], whereas if the bond angle is fixed to the tetrahedral value and one imposes a torsional potential, then a value of 4.25 [61] is obtained. The introduction of bonding angle within Wertheim's theory requires knowledge of the three body distribution function of the reference fluid. Although for hard spheres the three body distribution function is well known, this is not the case for other fluids such as LJ, SW or Yukawa.

One can conclude that for fully flexible chains interacting through a pair potential with a usual range for the attractions (i.e. LJ, SW with lambda less than 1.6), Wertheim's theory predicts the $\Theta$ temperature with an accuracy of about 10%. Given the relative simplicity of

the theory, and the simple expresson predicted for $\Theta$, one can conclude that Wertheim's theory does a nice job indeed, and takes one step further the theory of polymers started by Flory and Huggins 60 years ago.

## 5.  Conclusions

In this paper Wertheim's theory has been used to determine the EOS for a chain fluid made up of monomers interacting through a pair potential $u(r)$. After deriving the equation, the critical properties obtained from this theory for long chains are analysed in detail. It is found that critical density and pressure vanish as $m^{-1.5}$. The compressibility factor tends to 1/3 and the critical temperature tends to a finite value. By analysing the critical properties of long chains that follow from Wertheim's equation of state it is concluded that the critical temperature of the infinitely long chain is also the temperature at which the second virial coefficient of the chain vanishes. By analysing the second virial coefficient of chain that follows from Wertheim's EOS, it is found it must vanish when a simple condition is satisfied. This condition is that the second virial coefficient of

the monomer reference fluid becomes equal to 2/3 of the second virial coefficient between a monomer and a dimer fluid. We have used this simple condition to determine the $\Theta$ temperature that follows from Wertheim's equation of state for several fluids, namely, the LJ, the square well and the Yukawa. For the LJ fluid, results are in good agreement with both simulation results and previous estimates of $\Theta$ obtained from the implementation of Wertheim's theory performed by Johnson *et al.* We notice, however, that when implementing Wertheim's EOS to obtain the $\Theta$ temperature of a long chain, good values of $\ln g/\mathrm{d}\rho^{\mathrm{ref}}$ are needed at low densities. Therefore, one should know precisely $g(\sigma)$ at low densities so that its derivative can be evaluated precisely. For SW chains, we have shown that the value of $\Theta$ arising from Wertheim's theory is given by an analytical expression (see the Appendix).

We have found that the ratio of $\Theta/T_{\mathrm{B}}^{\mathrm{ref}}$ decreases with the range of the potential, reaching a minimum for short ranged potentials and then approaching unity as the range of the potential vanishes. For tangent spheres this ratio is of the order of one for the usual ranges of attractive forces. Notice that when the polymer is made up from overlapping spheres, different conclusions can be obtained. For instance for polyethylene, the $\Theta$ temperature seems to be located [62] at about 1600 K, whereas the Boyle temperature of the monomer (methane) is of about 300 K, so that in this case the ratio $\Theta/T_{\mathrm{B}}^{\mathrm{ref}}$ is of the order of 5. Therefore, the rule of thumb that the $\Theta$ temperature is similar to the Boyle temperature of the monomers is only valid for chains formed by tangent monomer spheres. We have also found that the ratio of $\Theta/T_{\mathrm{c}}^{\mathrm{ref}}$ decreases with the range of the potential.

In summary, this work shows that to evaluate the critical temperature of infinitely long chains, which follows from Wertheim's theory, one just needs the second virial coefficient of the monomer and that between the monomer and the dimer. Once these are known $\Theta$ is obtained from the condition $B_2^{\mathrm{ref}}(\Theta) - 2/3 B_2^{\mathrm{monomer-dimer}}(\Theta) = 0$. This is by far simpler than knowing the equation of state of the reference fluid at any temperature and density, the value of $g(\sigma)$ of the reference fluid at any temperature and density, solving for the critical conditions (i.e. $\mathrm{d}p/\mathrm{d}\rho = 0$ and $\mathrm{d}^2p/\mathrm{d}\rho^2 = 0$) for large $m$ and then taking the limit of $m$ going to infinity. Moreover, for the SW both $B_2^{\mathrm{ref}}$ and $B_2^{\mathrm{monomer-dimer}}$ can be obtained exactly so that it is shown that Wertheim's theory predicts analytically the value of $\Theta$ for SW chains. This is a quite interesting result. For polymers made of tangent spheres with a normal range of the attractive forces, the $\Theta$ temperature is close to the Boyle temperature of the reference monomer fluid.

## Appendix

In this appendix we shall derive the formula for the $\Theta$ temperature of SW chains that follows from Wertheim's theory. For that purpose, we shall first determine the second virial coefficient between a monomer and a dimer when the interaction between the monomer and each of the two sites of the dimer is given by the square well potential given by equations (37)–(39). In the following, we shall set the value of $\sigma$ to one and this is equivalent to taking $\sigma$ as the unit of length. According to this, the bond length of the dimer is one. The two distances from the monomer to the interaction sites of the dimer will be denoted as $r_1$ and $r_2$, respectively. The potential between the monomer and the dimer can adopt only four different values. The first possible value is infinite, and it occurs when any of the two variables $r_1$ or $r_2$ is less than one. The second possible value is $-\varepsilon$, and it occurs when $r_1 > \lambda$ and $1 < r_2 < \lambda$ or when $r_2 > \lambda$ and $1 < r_1 < \lambda$. The third value is $-2\varepsilon$ and it results when $1 < r_1, r_2 < \lambda$. The fourth value is zero and it occurs when $\lambda < r_1, r_2$. The second virial coefficient of a pair of molecules is given by the formula

$$B_2 = \frac{-1}{2}\int\left(\exp\left(-\beta u\right) - 1\right)\mathrm{d}\mathbf{r}_{12}\,\mathrm{d}\Omega_1\,\mathrm{d}\Omega_2, \qquad \text{(A 1)}$$

where $\mathbf{r}_{12}$ is the vector connecting the centre of mass of the two molecules and $\Omega_1$ and $\Omega_2$ are the coordinates needed to define the orientation of molecules 1 and 2, respectively. Taking into account equation (42) and that for the SW monomer–dimer problem the pair potential may adopt four different values only, the second virial coefficient of the SW monomer–dimer is given by:

$$B_2 = \tfrac{1}{2}[V_1 - V_2(x - 1) - V_3(x^2 - 1)], \qquad \text{(A 2)}$$

where $V_1$, $V_2$ and $V_3$ are the volumes of the regions where the pair potential adopt the values $\infty$, $-\varepsilon$ and $-2\varepsilon$ respectively while $x$ is given by:

$$x = \exp\left(1/T^*\right) \qquad \text{(A 3)}$$

and the reduced temperature is $T^* = T/(\varepsilon/k)$.

The values of $V_1$, $V_2$ and $V_3$ can be computed exactly. The shape of the regions $V_1$, $V_2$ and $V_3$ is shown in figure A1. We need some basic formulae before providing the exact result. The volume of a diatomic molecule formed by two hard spheres (hard dumbbell) of diameter $d_{\mathrm{A}}$ and $d_{\mathrm{B}}$ which are a distance $L$ apart, $V_{\mathrm{HD}}(L, d_{\mathrm{A}}, d_{\mathrm{B}})$, is given by [63, 64]:
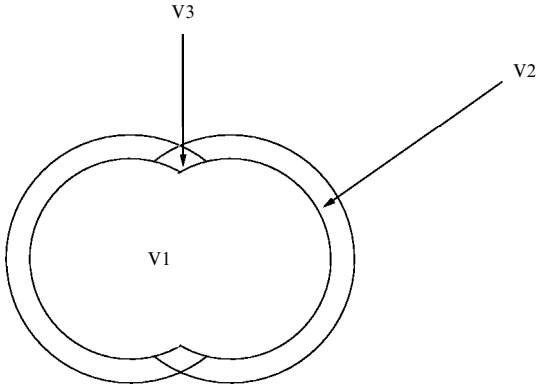
Figure A1. The three different regions contributing to the second virial coefficient between a monomer and a dimer with bond length $L = \sigma$ when the monomer presents a SW interaction with each of the sites of the dimer.

$$V_{\mathrm{HD}}(L, d_{\mathrm{A}}, d_{\mathrm{B}}) = \frac{\pi}{12}(d_{\mathrm{A}}^3 + d_{\mathrm{B}}^3 + 3d_{\mathrm{A}}^2 a$$
$$+ 3d_{\mathrm{B}}^2 b - 4a^3 - 4b^3), \quad (A\,4)$$

with the constants $a$ and $b$ given by:

$$a = \frac{1}{2}\left(L + \frac{d_{\mathrm{A}}^2 - d_{\mathrm{B}}^2}{4L}\right) \quad (A\,5)$$

$$b = L - a. \quad (A\,6)$$

The volume of the region which belongs simultaneously to two spheres of diameters $d_{\mathrm{A}}$ and $d_{\mathrm{B}}$ which are a distance L apart, $V_{\mathrm{overlap}}(L, d_{\mathrm{A}}, d_{\mathrm{B}})$, is given by:

$$V_{\mathrm{overlap}}(L, d_{\mathrm{A}}, d_{\mathrm{B}}) = \frac{\pi(d_{\mathrm{A}}^3 + d_{\mathrm{B}}^3)}{6} - V_{\mathrm{HD}}(L, d_{\mathrm{A}}, d_{\mathrm{B}}).$$
$$(A\,7)$$

Once these formulae have been introduced it is simple to show by inspection of figure A1 that $V_1$, $V_2$ and $V_3$ are given by ($\sigma$ is taken as the unit of length):

$$V_1 = V_{\mathrm{HD}}(1, 2, 2), \quad (A\,8)$$

$$V_3 = V_{\mathrm{overlap}}(1, 2\lambda, 2\lambda) + V_{\mathrm{overlap}}(1, 2, 2)$$
$$- 2V_{\mathrm{overlap}}(1, 2\lambda, 2), \quad (A\,9)$$

$$V_2 = V_{\mathrm{HD}}(1, 2\lambda, 2S) - V_{\mathrm{HD}}(1, 2, 2) - V_3. \quad (A\,10)$$

Equation (A 2) along with equations (A 3)–(A 10) shows that the second virial coefficient between a monomer and a dimer can be computed analytically. The second virial coefficient between a pair of SW monomers can also be computed easily. Therefore, the $\Theta$ temperature of SW chains can be obtained by solving

the following equation (see equation (35) of the main text):

$$\frac{2\pi}{3}[1 - (\lambda^3 - 1)(x - 1)] - \frac{1}{3}[V_1 - V_2(x - 1)$$
$$- V_3(x^2 - 1)] = 0. \quad (A\,11)$$

This is just a quadratic equation, which for a given $\lambda$ can be solved analytically (taking the positive root), yielding the value of $x$ and hence the value of the $\Theta$ temperature of the polymer. When $\lambda$ goes to one, the solution of equation (A 11) for $x$ goes to infinity, and therefore the $\Theta$ temperature goes to zero (see equation (A 3)). The Boyle temperature of the SW monomer $T_{\mathrm{B}}^{\mathrm{ref}}$ is given by:

$$\frac{1}{T_{\mathrm{B}}^{\mathrm{ref}}} = \ln\left(\frac{\lambda^3}{(\lambda^2 - 1)}\right) \quad (A\,12)$$

Therefore, when $\lambda$ goes to one the Boyle temperature of the SW monomer, $T_{\mathrm{B}}^{\mathrm{ref}}$, goes to zero. By analysing the divergence of equation (A 12) and of the root of equation (A 11), it can be concluded that when $\lambda$ goes to one then:

$$\Theta \sim \frac{1}{-\ln[C(\lambda - 1)]}, \quad (A\,13)$$

$$T_{\mathrm{B}}^{\mathrm{ref}} \sim \frac{1}{-\ln[D(\lambda - 1)]}, \quad (A\,14)$$

where $C$ and $D$ are positive constants. From these two previous equations it is easy to show that when $\lambda$ goes to one, the ratio $\Theta/T_{\mathrm{B}}^{\mathrm{ref}}$ goes also to one. This is further illustrated in figure A2 where the $\Theta$ temperature of SW chains as given by Wertheim's theory (equation (A 11))
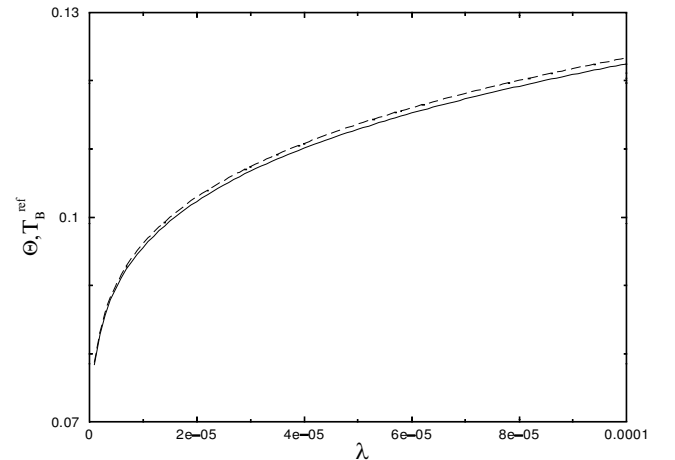


Figure A2. $\Theta$ temperature as given by Wertheim's theory (solid line) and $T_{\mathrm{B}}^{\mathrm{ref}}$ (dashed line) for SW chains in the limit of small values of $\lambda$.

and the Boyle temperature of the reference SW fluid, $T_{\mathrm{B}}^{\mathrm{ref}}$ are plotted for quite small values of $\lambda$.

Therefore, for SW chains the $\Theta$ temperature becomes the Boyle temperature of the monomer when the range of the attractive forces becomes arbitrarily small.

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