Second virial coefficients, critical temperatures, and the molecular shapes of long *n*-alkanes

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(Received 5 March 1996; accepted 5 June 1996)

The second virial coefficient for a molecular model of *n*-alkanes with up to 200 carbon atoms has been computed for temperatures in the range of 1000 K$<T<$2000 K. The model used in the calculations is based on one which reproduces the experimental values of the second virial coefficient for short *n*-alkanes. The Boyle temperature of *n*-alkanes is not much affected by the length of the chain for *n*-alkanes with more than 100 carbon atoms. According to the Flory theory, for infinitely long chains the Boyle temperature and the critical temperature, denoted as the θ temperature are the same. On this basis using the present model we find $\theta=1620$ K as the critical temperature of polymethylene. Scaling laws for the square of the end-to-end distance and for the radius of gyration at several temperatures are analyzed. For high temperatures, the scaling laws correspond to good solvent conditions whereas at the θ temperature the scaling laws are those of an ideal chain. The shape of long *n*-alkanes at several temperatures is also analyzed. We find that the polymethylene chains present an anisotropy similar to that of a parallelepiped with a ratio of sizes of 1:1.7:3.6. © *1996 American Institute of Physics.* [S0021-9606(96)51634-X]

I. INTRODUCTION

The *n*-alkanes are compounds of great interest for the petrochemical industry. These compounds play an essential role in several refinery and related processes like separation of waxes. For light *n*-alkanes the thermodynamic properties are very well known through the whole phase diagram.[1–4] However, for heavy *n*-alkanes experimental data are rather scarce. Usually thermodynamic data of heavy *n*-alkanes are estimated by using the principle of corresponding states. For this reason the determination of the critical properties of heavy *n*-alkanes is of considerable interest.

For low weight *n*-alkanes the critical properties are well known. For longer *n*-alkanes some problems arise since *n*-alkanes are thermally unstable for temperatures larger than 650 K. However, quite recently there has been some progress[5–7] and the critical properties have been determined for *n*-alkanes up to tetraeicosane ($C_{24}H_{50}$). Basically, a fast heating of the sample is performed in these experiments, so that significant thermal decomposition does not take place. However, for longer chains there is no experimental data concerning critical properties. It is not likely that there would be data in the near future since very long *n*-alkanes are quite unstable at high temperatures.[7] In this paper we shall focus on the problem of the determination of the critical temperature of long chains.

To overcome this situation three possible routes are possible. The first is to propose a fitting function for the critical properties of *n*-alkanes and to obtain the parameters of the fit by using the low weight *n*-alkane data. Examples of that can be found in Refs. 8 and 9. The problem with this approach is that the fitting function is completely empirical and *ad hoc*, so that there is no guarantee that the extrapolation is reliable for long *n*-alkanes. The second is to use a semiempirical method with some theoretical ground and to obtain the needed parameters from the critical data of short *n*-alkanes. An example of this approach can be found in Refs. 9 and 10. The third approach is to use a molecular description of the problem and to use the methods of statistical thermodynamics for the estimation of properties. The parameters describing the interaction between molecules can be obtained from the short *n*-alkanes data. Examples of this third approach can be found in Refs. 11–13 where the critical properties of *n*-alkanes up to C_{48} were estimated by using computer simulation and in Refs. 14–17 where second virial coefficients of *n*-alkanes up to C_{16} were computed numerically. In this work this molecular route will be used.

Recently the second virial coefficient of *n*-alkanes has been computed.[15,16] The parameters of the intermolecular potential were obtained by using experimental data on the second virial coefficient of short *n*-alkanes.[15,16] By using computer simulation Smit *et al.* have shown[12] that it is possible to obtain a satisfactory description of the vapor–liquid equilibria of *n*-alkanes with a molecular model similar to that used in our second virial coefficient calculations. Therefore for *n*-alkanes a model is now available which correctly describes second virial coefficient data and vapor–liquid equilibria of short *n*-alkanes.

In this work the second virial coefficient (B_2) will be calculated numerically for *n*-alkanes with up to 200 carbon atoms. Our goal is twofold. First, we shall provide estimates of the second virial coefficient of long chains. Particular interest will be devoted to the determination of the Boyle temperature T_B (the temperature for which $B_2=0$). Second, we shall make contact with some well-known theories of polymer science. A long time ago Flory and Krigbaum developed a theory for dilute polymer solutions.[18,19] This theory predicts that for very long chains the second osmotic coefficient becomes zero at a temperature which is independent of the length of the chain. This assumption has been recently tested by several groups for the pearl-necklace model.[20–23] In this work this assumption will be tested for the relatively realistic n-alkane model of our previous work. Moreover, according to the Flory–Huggins theory[24,25] of polymer solutions the critical temperature of infinitely long chains, usually denoted as the θ temperature, is also the temperature where the second osmotic virial coefficient vanishes. In other words according to Flory the Boyle temperature and the θ temperature are the same for infinitely long chains. This point has been recently confirmed by using computer simulation for a polymer on a simple lattice[26] and for the pearl-necklace model.[22] In this work we shall assume that the identification between T_B and θ is valid for very long n-alkanes. On this basis an estimate of the critical temperature of polymethylene will be given. The importance of this value is that it could be used as an asymptotic limit in engineering correlations.

The organization of this paper is as follows. In Sec. II details concerning the pair potential and B_2 calculations will be given. In Sec. III results for B_2 will be presented. In Sec. IV some considerations concerning scaling relations for n-alkanes will be given. In Sec. V the main conclusions to this work will be presented.

II. SECOND VIRIAL COEFFICIENT CALCULATIONS

The n-alkane will be described within the rotational isomeric state[27] (RIS) approximation. For each torsional angle only three possibilities exist, *trans* (t), *gauche*$^+$ (g^+), and *gauche*$^-$ (g^-). The *gauche* configuration makes an angle of 120° with respect to the *trans*. The geometry of the chain as described by the carbon skeleton is given by a C–C bond length fixed to 1.53 Å and a C–C–C angle of 112°. The number of carbon atoms of the n-alkane will be denoted as n_c. Each CH_3 or CH_2 group will be modeled as one interaction site located at the position of the carbon atom. Therefore, in this work no explicit description of the hydrogen atoms is made.

The intramolecular energy of the chain can be divided into a short-range and a long-range contribution. The short-range contribution is given by

$$U_{\text{intra}}^{\text{short}}=E_c+\sum_{k=4}^{n_c-1}E_{ab,k}+\sum_{i=1}^{n_c-5}\sum_{j=i+5}^{j=i+5}4\epsilon_{ij}[(\sigma/r_{ij})^{12}-(\sigma/r_{ij})^{6}]. \tag{1}$$

The indexes i,j in Eq. (1) run over the interaction sites of the molecule numbered from one to n_c and r_{ij} is the distance between site i and site j. The variables a,b,c can take the values t, g^+, or g^-. The C–C bonds of the molecule are numbered from one to n_c-1. E_c is the conformational energy associated to the rotational state of the third C–C bond of the chain and it depends on the rotational state of this bond only. The index k in Eq. (1) runs over the C–C bonds of the molecule starting in the fourth. The energy $E_{ab,k}$ is appropriately regarded as the contribution to U_{intra} associated with assignment of bond k to state b, bond $k-1$ being in state a. We are basically following the notation established by Flory.[27] The following set of E_{ab} energies will be used:

$$E_{tt}=E_{g^+t}=E_{g^-t}=0;\quad E_{tg^+}=E_{tg^-}=E_{g^+g^+}=E_{g^-g^-}=E_1;\quad E_{g^+g^-}=E_{g^-g^+}=E_2. \tag{2}$$

The last term in Eq. (1) is a Lennard-Jones (LJ) potential between carbons separated by five bonds. With Eq. (1) the interaction energy between units separated by less than six bonds along the chain is being considered. The $U_{\text{intra}}^{\text{short}}$ energy described by Eqs. (1) and (2) can be easily obtained by multiplying the total number of *gauche* bonds of the molecule by E_1, adding the LJ energy between carbons separated by five bonds, and finally adding the energy due to g^+g^- or g^-g^+ sequences. This last contribution is obtained by counting the number of appearances of g^+g^- or g^-g^+ sequences in the chain and multiplying that by (E_2-E_1).

The long-range intramolecular energy is given by

$$U_{\text{intra}}^{\text{long}}=\sum_{i=1}^{n_c-6}\sum_{j=i+6}^{n_c}4\epsilon_{ij}[(\sigma/r_{ij})^{12}-(\sigma/r_{ij})^{6}]. \tag{3}$$

In this work σ will be set to $\sigma=3.923$ Å. We shall use different values of ϵ for $CH_3-CH_3(\epsilon_{CH_3-CH_3})$, $CH_2-CH_2(\epsilon_{CH_2-CH_2})$, and $CH_3-CH_2(\epsilon_{CH_3-CH_2})$ interactions. The Lorentz–Berthelot rule will be used so that

$$\epsilon_{CH_3-CH_2}=(\epsilon_{CH_3-CH_3}\epsilon_{CH_2-CH_2})^{1/2}. \tag{4}$$

According to Eqs. (1)–(4) a full description of the model requires the values of E_1, E_2, $\epsilon_{CH_3-CH_3}$, and $\epsilon_{CH_2-CH_2}$. The total intramolecular energy for a given rotational isomer i is given by

$$U_{\text{intra},i}=U_{\text{intra},i}^{\text{short}}+U_{\text{intra},i}^{\text{long}}. \tag{5}$$

The intermolecular energy between a pair of molecules is given by

$$U_{\text{inter}}=\sum_{i=1}^{n_c}\sum_{j=1}^{n_c}4\epsilon_{ij}[(\sigma/r_{ij})^{12}-(\sigma/r_{ij})^{6}]. \tag{6}$$

Within the RIS approximation, where the n-alkane is regarded as a multicomponent mixture, the second virial coefficient is given by

$$B_2=\sum_i\sum_j x_ix_jB_{ij}, \tag{7}$$

$$B_{ij}=\int[1-\exp(-U_{\text{inter}}/kT)]2\pi r^2 dr\, d\omega_i\, d\omega_j, \tag{8}$$

where x_i,x_j are the molar fraction of rotational isomers i and j, respectively, and B_{ij} is the second virial coefficient between rotational isomers i and j. Hereafter, we shall use the word conformer to denote a rotational isomer. In Eq. (8) r stands for the distance between the center of mass of the conformers i and j and ω_i and ω_j represent a set of orientational angles defining the orientation of conformers i and j

TABLE I. Potential parameters of n-alkanes used in this work (see the main text for details). The Boltzmann constant is denoted as k.

Model	E_1/(cal/mol)	E_2/(cal/mol)	$(\epsilon_{CH_3-CH_3}/k)$/K	$(\epsilon_{CH_2-CH_2}/k)$/K
M1	700	2000	104	49.7
M2	700	2000	104	47.5
M3	500	2000	104	47.5
M4	700	2000	13	13

and are normalized to one (i.e., $\int d\omega_i=1$). U_{inter} refers to the intermolecular energy between conformers i and j at the distance r and for the relative orientation given by ω_i and ω_j. The molar fraction of a given conformer is obtained as

$$x_i=\exp(-U_{\text{intra},i}/kT)\Bigg/\sum_j \exp(-U_{\text{intra},j}/kT). \tag{9}$$

Therefore the key equations for the B_2 calculations are Eqs. (7)–(9). Our numerical implementation of Eqs. (7)–(9) is as follows

(i) A Monte Carlo run of an isolated chain is performed. Intramolecular energies (short and long range) are considered in the Monte Carlo run of the isolated chain. The pivoting algorithm[28] (with three possible rotational states per bond) was used for generating the chain configurations. Metropolis criterion is adopted for accepting configurations within the Monte Carlo (MC) run.[29] Typically, the MC run involves 10^6 steps. The coordinates of 100 configurations obtained within the run are stored for later analysis.

(ii) With the 100 configurations (conformers) generated in the previous step, 100 pairs of conformers are chosen randomly.

(iii) For each pair of conformers the integral of Eq. (8) is computed. For that purpose, 61 values of r are chosen between 0 and 30σ. For each value of r the orientational average is performed by using Conroy's integration method[30] with 577 relative orientations. Once the orientational average has been performed for the 61 values of r, the integrand of Eq. (8) is computed using Simpson's rule so that B_{ij} is determined. This is repeated for the 100 pair of conformers chosen in step (ii).

(iv) The arithmetic average of the 100 values of B_{ij} determined in step (iii) is the computed value of B_2. In other words to obtain B_2 we add the 100 obtained values of B_{ij} and divided by 100.

We checked our code by comparison with the results previously obtained[15,16] with a different algorithm. Good agreement was found. For a given temperature and n-alkane, intermolecular energies are computed approximately 4×10^6 times $(61\times577\times100)$. The standard deviation between the different B_{ij} gives us some estimate of the uncertainty of our calculations.

Our algorithm for the second virial coefficient evaluation also allows the evaluation of the effective interaction potential between n-alkanes. This effective potential will be denoted as $u_e(r)$ and is defined as:

$$\exp[-u_e(r)/kT]=\int\sum_i\sum_j x_i x_j \times\exp(-U_{\text{inter}}/kT)\,d\omega_i\,d\omega_j. \tag{10}$$

In Eq. (10) the integrand is evaluated for a fixed value of r. The Boltzmann factor of the spherical $u_e(r)$ has the same value as the average of the Boltzmann factor of U_{inter} over all the relative orientations and over all pairs of conformers. The effective potential $u_e(r)$ is easily obtained from our algorithm described by steps (i)–(iv).

Since our algorithm for the determination of B_2 requires a Monte Carlo of an isolated chain, some properties defining the geometry of the n-alkane can also be calculated. In particular the mean square radius of gyration $\langle s^2\rangle$ (defined as the mean squared distance from the carbons of the molecule to the center of mass) and the mean square end-to-end distance $\langle r^2\rangle$ (defined as the mean squared distance between the first and last carbon of the n-alkane) have also been evaluated. Particular attention has been paid to the scaling laws of $\langle r^2\rangle$ and $\langle s^2\rangle$ so that

$$\langle r^2\rangle=P_r(n_c-1)^{v_r}, \tag{11}$$

$$\langle s^2\rangle=P_s(n_c-1)^{v_s}, \tag{12}$$

where for long chains it is assumed that $v_r=v_s$. The scaling coefficient v_r depends on temperature so that it is assumed that at high temperature (good solvent conditions) $v_r=1.176$ (see Ref. 31), at the θ temperature $v_r=1$ and for low temperatures (bad solvent) $v_r=2/3$ (see Ref. 32).

III. RESULTS

The second virial coefficient has been computed for temperatures in the range of 1000 K$<T<$2000 K. We computed B_2 for n_c=8, 12, 16, 30, 50, 100, and 200. For n_c=200 the

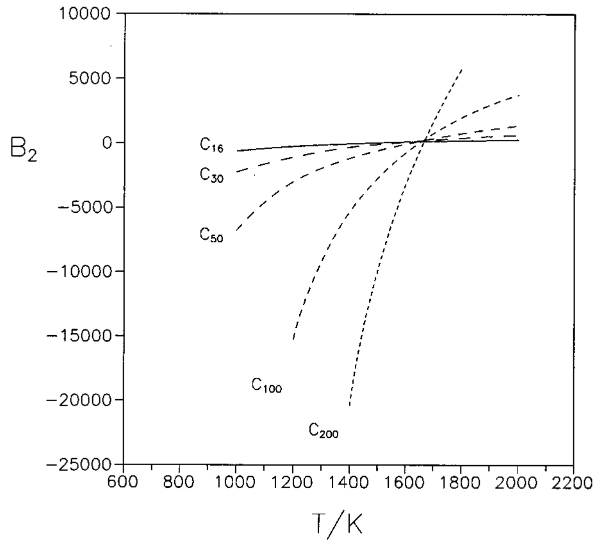

FIG. 1. Second virial coefficient, B_2, vs temperature T (in kelvin) for the M1 model of n-alkanes (see Table I) as obtained in this work. C_{16}, solid lines; C_{30} long dashed line; C_{50}, dashed line; C_{100} short dashed line; C_{200}, dotted line. B_2 is given in cm^3/mol units.

determination of B_2 for a given temperature required 24 h of CPU time in an Alpha 3000/700 workstation. A full description of the model requires values for E_1, E_2, $\epsilon_{CH_3-CH_3}$, and $\epsilon_{CH_2-CH_2}$. The models used in this work are described in Table I. The first model (M1) corresponds to the set of parameters determined in our previous work.[16] This set of parameters (M1) accurately describes the second virial coefficient of *n*-alkanes from *n*-butane up to *n*-octane for temperatures between 300 and 600 K. In Table II the values of the second virial coefficient for the M1 model are presented. The estimated errors of our determination of B_2 for the M1 model are shown in the last column of Table II. These errors correspond to three times the standard deviation of the *average* of the B_{ij} values computed from Eq. (8). In a few cases several independent calculations of B_2 for a given temperature were performed and the obtained values were always within the interval given by the last column of Table II. In Fig. 1 the results of B_2 of the M1 model are shown. As can be seen, the Boyle temperature T_B increases with the length of the chain for short chains (i.e., $n_c<100$). For long chains (i.e., $n_c>100$) T_B is almost independent of the chain length and this is in agreement with the predictions of the Flory–Krigbaum theory for diluted polymer solutions. This is more clearly seen in Table III where the Boyle temperatures obtained for the M1 model are presented. For infinitely long chains T_B is estimated to be $T_B=1660$ K. According to the Flory theory the Boyle temperature of infinitely chains is also the critical temperature of the infinitely long chain. Therefore the set of parameters of our previous work leads to an estimate of the critical temperature of polymethylene of $T=1660$ K.

It is interesting to mention that the variation of the Boyle temperature with the length of the chain depends on the kind of potential used for describing the intermolecular interaction. In lattice systems it has been found that T_B decreases with the length of the chain. For the nonlattice pearl-necklace model, Wichert and Hall[21] have found that when the square well potential (SW) is used for describing the intermolecular interaction then T_B decreases with the length of the chain if $\lambda<0.5$, whereas it increases with the length of the chain if $\lambda>0.5$. Therefore, the variation with the length of the chain of T_B of the more realistic LJ potential is similar to that of the SW model with $\lambda>0.5$. The kind of intermolecular interaction therefore affects the variations of T_B with the length of the chain.

TABLE II. Second virial coefficients (in cm^3/mol) obtained in this work for the M1, M2, and M3 models of *n*-alkanes (see Table I). The number of carbons of the *n*-alkane is denoted as n_c. The results labeled with an asterisk correspond to the M4 model. In the last column the estimated error for the second virial coefficients of the M1 model are shown. Errors for the M2 and M3 models are similar and therefore are not shown.

n_c	T/K	B_2(M1)	B_2(M2)	B_2(M3)	Error
8	1000	−131	−112	−112	±4
8	1200	−35	−21	−21	±3
8	1400	30	42	39	±3
8	1600	75	83	82	±2
8	1800	106	117	115	±2
8	2000	134	140	138	±4
12	1000	−330	−289	−285	±11
12	1200	−127	−91	−92	±6
12	1400	2	25	28	±6
12	1600	88	113	110	±7
12	1800	154	168	168	±6
12	2000	205	216	217	±6
16	1000	−630	−529	−523	±20
16	1200	−257	−201	−208	±16
16	1400	−56	−4	1	±12
16	1600	104	125	129	±12
16	1800	203	233	226	±9
16	2000	279	307	299	±13
30	1000	−2 246	−1 965	−1 974	±78
30	1200	−1 088	−842	−896	±59
30	1400	−316	−235	−238	±36
30	1600	89	207	202	±32
30	1800	411	497	500	±32
30	2000	620	680	673	±35
50	1000	−6 796	−5 766	−5 608	±317
50	1200	−2 977	−2 577	−2 519	±160
50	1400	−1 165	−830	−879	±111
50	1600	−60	235	231	±98
50	1800	759	992	926	±81
50	2000	1353	1519	1425	±91
100	1000	−33 062	−24 913	−23 679	±3 068
100	1200	−13 026	−10 642	−9 999	±727
100	1400	−5 270	−3 511	−3 574	±457
100	1600	−733	518	295	±343
100	1800	2 003	3 214	3 058	±262
100	2000	3 756	4 751	4 720	±253
200	1000	−177 108	−122 603	−124 260	±50 043
200	1200	−57 970	−45 806	−44 173	±8 076
200	1400	−20 400	−13 846	−14 593	±1 955
200	1600	−3 179	1 266	907	±1 335
200	1800	5 817	9 918	9 474	±1 021
200	2000	13 647	15 829	15 931	±799
200	400	−6 062*			
200	410	−4 172*			
200	430	1 124*			

The parameters described by the model M1 were obtained to fit experimental values of B_2 at low temperatures (300–600 K). For the temperature $T=600$ K the second virial coefficient of the M1 model of *n*-octane is smaller than the experimental value. In fact, for *n*-octane at $T=580$ K the experimental value[33,34] is $B_2=-638$ cm^3/mol whereas the calculated value with the M1 model is $B_2=-681$ cm^3/mol. In this work we are interested in the behavior of B_2 at high temperatures. Because of that we decided to adjust the parameters of the M1 model slightly so that the experimental value of *n*-octane at $T=580$ K is reproduced. We decided to keep the values of the M1 model for E_1, E_2, and $\epsilon_{CH_3-CH_3}$ and to reduce slightly the value for $\epsilon_{CH_2-CH_2}$ so that the experimental value of *n*-octane at $T=580$ K is matched. The new model will be denoted as M2 and is presented in Table I. It should be pointed out that the M2 model is similar to the model used by Smit *et al.*[12] for describing the vapor–liquid equilibria of *n*-alkanes (although differences for $\epsilon_{CH_3-CH_3}$ between these models are significant).

In Table II the values of B_2 obtained for the M2 model are presented. In Table III the Boyle temperatures of *n*-alkanes as obtained from the calculations of this work for

TABLE III. Boyle temperatures in kelvin for the M1, M2, M3, and M4 models of Table I.

n_c	T_B (M1)	T_B (M2)	T_B (M3)	T_B (M4)
8	1298	1257	1263	
12	1397	1349	1346	
16	1463	1408	1400	
30	1543	1498	1499	
50	1613	1549	1552	
100	1645	1569	1582	
200	1660	1578	1584	415

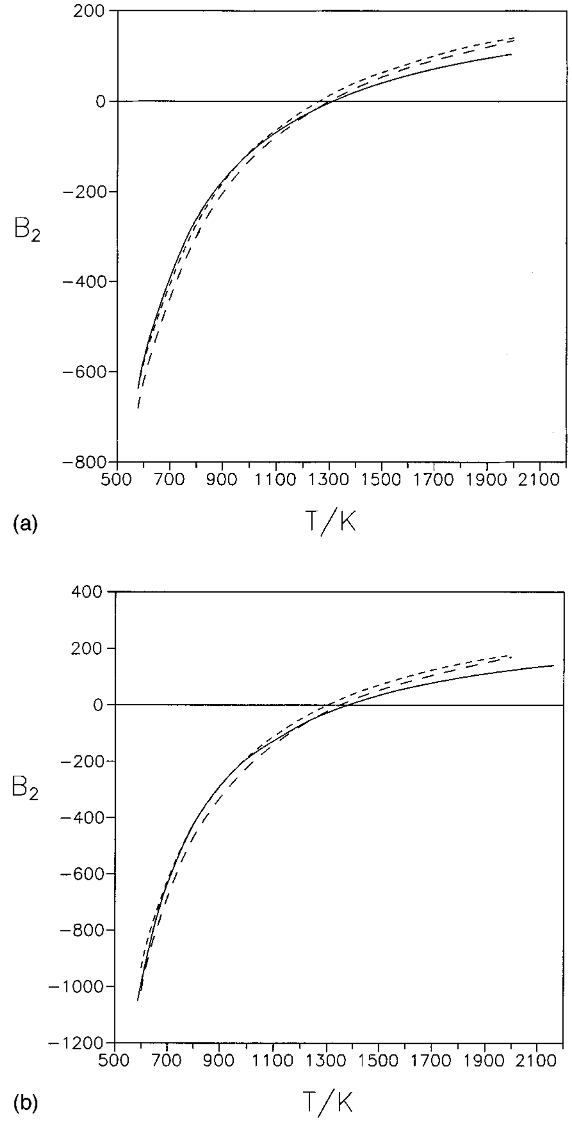

FIG. 2. The second virial coefficient (in cm^3/mol) of *n*-octane and *n*-decane as obtained from experiment (Ref. 35) (solid line), from this work for the M1 (dashed line) and M2 models (short dashed line). (a) Results for *n*-octane. (b) Results for *n*-decane.

the M2 model are presented. T_B increases with n_c and reaches an asymptotic value for long chains which is located at $T_B=1580$ K. In order to analyze the effect of E_1 (the energy of the *gauche* configuration relative to the *trans*) a new parameter set denoted as M3 has been proposed. The M3 model is presented in Table I. The M3 is identical to the M2 model except that E_1 is reduced to 500 cal/mol. Results for B_2 of the M3 model are also presented in Table II. By comparing the results of the M2 and M3 models presented in Table II it can be concluded that the parameter E_1 has little effect on the computed value of B_2. Boyle temperatures for the M3 model are almost identical to those of the M2 model. In any case the differences are very small and they fall within the uncertainty of the calculations.

In order to analyze in further detail which model, M1 or M2 (the M3 model is almost identical to the M2 model), provides a better description of the second virial coefficient of *n*-alkanes we present in Fig. 2 the second virial coefficient of *n*-octane and of *n*-decane in a broad range of temperatures as obtained from experiments[35] and from our calculations for the M1 and M2 models. It can be seen from Fig. 2 that the M1 model provides a better description of B_2 for *n*-octane and *n*-decane at high temperatures whereas the M2 model provides a better description at low temperatures. Both models, M1 and M2, fit the experimental data reasonably well and it is hard to decide which model should be adopted. The experimental Boyle temperature of *n*-octane is situated at $T_B=1309$ K, which is closer to the estimate of the M1 model. For *n*-decane the experimental Boyle temperature is of $T_B=1381$ K which again is closer to the estimate of the M1 model. Since there is no experimental data for longer *n*-alkanes at high temperatures a definitive choice among the M1 and M2 models cannot be made. On the basis of existing information we can regard both the M1 and M2 models as reasonable models for the description of the second virial coefficient of *n*-alkanes at high temperatures. Differences between them represent approximately the uncertainty, due to our approximate knowledge of the intermolecular forces in *n*-alkanes, of our estimates for the second virial coefficient and Boyle temperature of these compounds.

We have fitted the values of B_2 for the M2 model in the range (1000–2000 K) to the following empirical function:

$$B_2/(\mathrm{cm}^3/\mathrm{mol})=y\{1-q[\exp(l/T)-1]\}. \tag{13}$$

Equation (13) has the same form as the analytical expression of B_2 for the SW potential of a spherical molecule. Recently it has been shown[36] that Eq. (13) reproduces quite well experimental data of B_2 for *n*-alkanes. The parameters of the fit are presented in Table IV for the *n*-alkanes considered in this work.

TABLE IV. Coefficients of the fit of Eq. (13) for the second virial coefficient of *n*-alkanes as estimated from the calculations of this work for the M2 model.

n_c	y	q	l
8	332.037 1	1.7928	557.5339
12	526.561 1	0.9630	958.3204
16	823.739 9	1.0401	946.7219
30	1 952.278 7	0.5868	1485.7495
50	4 469.346 5	0.4530	1800.6588
100	13 115.101 8	0.2424	2562.3475
200	35 426.860 4	0.0923	3898.8884

One of the main results of this work is an estimate of the critical temperature of infinitely long n-alkanes, which is denoted as the θ temperature. The two models of this work for B_2 at high temperatures are the M1 and M2 models, which predict that for n-alkanes $\theta=1660$ K and $\theta=1580$ K, respectively. The difference between θ for both models represents approximately the uncertainty of our estimate of the θ temperature of polymethylene. The origin of this uncertainty is our ignorance on the true intermolecular forces in n-alkanes. Since there is not definitive arguments to state the superiority of any among these two models we shall simply adopt the arithmetic average as the estimate of the θ temperature of n-alkanes. Therefore, this work suggests $\theta=1620\pm80$ K as the estimate of the critical temperature of polymethylene. Is this estimate of the critical temperature of very long n-alkanes in agreement with the most recent experimental and simulation data for n-alkanes? To check this point we shall use first the critical temperature of n-alkanes as determined from the computer simulations of Smit *et al.*[12] According to the Flory–Huggins theory the critical temperature of a long chain molecule is given by[24,25]

$$1/T_c=1/\theta+1/(\theta\psi_1)[1/n_c^{0.5}+1/(2n_c)], \tag{14}$$

where ψ_1 is an adimensional parameter[19] characterizing the entropy of dilution of polymer with solvent (vacuum for pure n-alkanes). According to Eq. (14) a representation of $1/T_c$ vs $1/(n_c)^{0.5}+1/(2n_c)$ (which is usually denoted as a Shultz–Flory plot[37]) should be linear and the value of θ can be obtained from the ordinate in the origin. Equation (14) holds very well for many polymer–solvent systems provided that the chains are sufficiently long. Some recent simulation data indicates that Eq. (14) holds relatively well for fully flexible chains of about 100 monomer units.[22,38] We decided to analyze the critical data of n-alkanes by using Eq. (14), although it must be recognized that the n-alkanes of this work are probably too short for Eq. (14) to be strictly valid. In Fig. 3 a Shultz–Flory plot of the computer simulation data of Smit *et al.*[12] is presented. By fitting the results of Smit *et al.* for n-alkanes with carbon atoms in the range of 10–48 we found $\theta_{\mathrm{MC}}=1507$ K. In Fig. 3 a Shultz–Flory plot of the experimental results of the critical temperature of n-alkanes is presented. From this plot and using the experimental critical temperatures of n-alkanes with carbon atoms in the range of 8–24 we obtain $\theta_{\mathrm{expt}}=1576$ K. If we use the experimental data with carbon atoms in the range of 5–16 we obtain $\theta_{\mathrm{expt}}=1687$ K (the same result was found in Ref. 9 by using data of n-alkanes with up to 16 carbon atoms). As can be seen the critical temperature of polymethylene obtained from a Shultz–Flory plot of experimental data of short n-alkanes is quite sensitive to the choice of the data used. Further theoretical work to analyze the minimum chain length that could be used in a Shultz–Flory plot to obtain reliable estimates of the critical temperature of infinitely long chains is clearly needed. Therefore, our use of the Shultz–Flory plot for short chains should be regarded with caution. However, it is encouraging that our estimate of the critical temperature of polymethylene seems to be close to that obtained from a Shultz–Flory plot of the experimental data. At this point it is interesting to mention that other estimates of the θ temperature for polymethylene are[10,8] $\theta=1072$ K and $\theta=960$ K. The results of this work along with those of Ref. 12 strongly suggest that these previous estimates are too low.

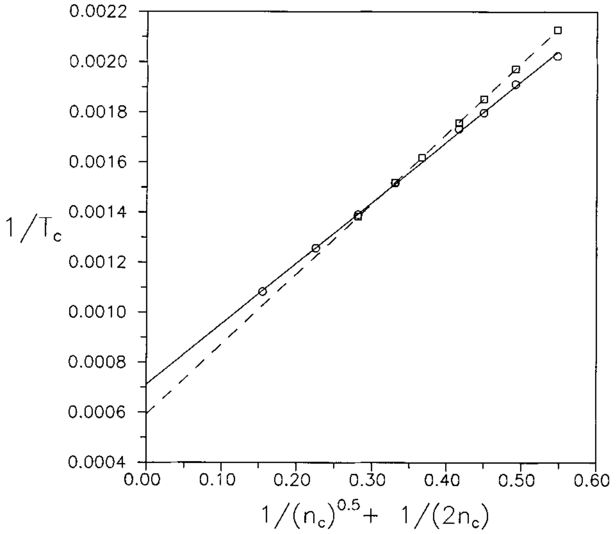

FIG. 3. Shultz–Flory plot of the critical temperature of n-alkanes. Solid line and open circles: Gibbs ensemble data of T_c are from Ref. 12. Dashed line and open squares: experimental data as reported in Refs. 7 and 9.

Before continuing let us discuss briefly the meaning of the θ temperature of polymethylene. We shall recall that $\theta=1620$ K refers to the estimate of the critical temperature of polymethylene with no solvent present and assuming that chemical decomposition does not take place. Another different issue is the θ temperature of polymethylene when dissolved in a given solvent. In this case we have a binary system (solvent/polymethylene) and the θ temperature is the upper critical solution temperature (UCST) of the system. For instance θ temperatures of polymethylene in common solvents (dodecanol-, diphenylmethane, α-Cl-naphthalene) are around $\theta=413$ K. According to the McMillan and Mayer theory[39] when treating the solvent/polymer systems the solvent can be ignored if the potential of mean force is used instead of the true pair potential between polymer molecules. We shall propose now a model for the potential of mean force of polymethylene in common solvents which approximately reproduces the θ temperature found in experimental studies. This model is shown in Table I and is denoted as M4. For the M4 model B_2 becomes zero for long chains for a temperature very close to $T=413$ K. Therefore the M4 model can be used as an approximation to the potential of mean force of polymethylene in common solvents.

The results presented so far were mainly focused on the Boyle temperature of polymethylene. However, the results obtained can be useful for considering some issues currently discussed in polymer science. We should emphasize that the second virial coefficient of continuous chain models are rather scarce although it seems that there is a growing interest in that field.[14–17,20–23] Let us start by discussing the behavior of the osmotic second virial coefficient. When study-

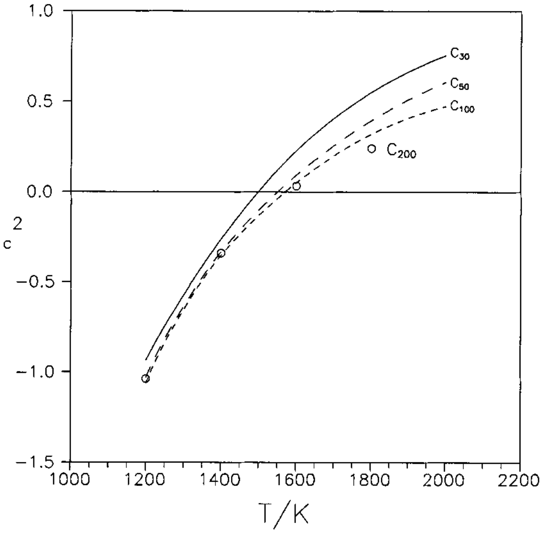

FIG. 4. B_2/n_c^2 vs T plot for the M2 model. Results are for C_{30} (solid line) C_{50} (dashed line), C_{100} (short dashed line), and C_{200} (open circles). B_2 is given in cm^3/mol units.

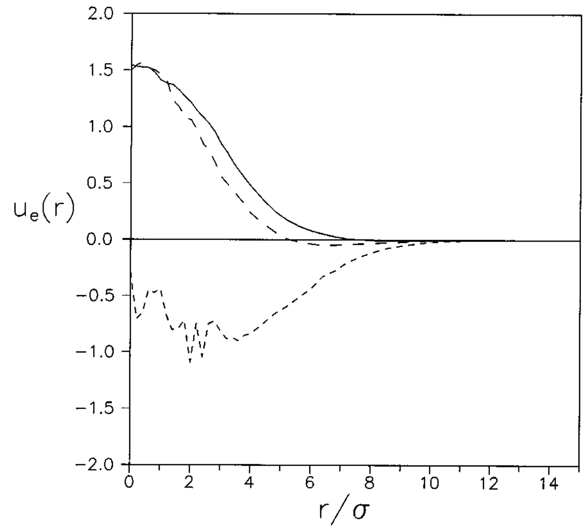

FIG. 5. The effective pair potential u_e (in kT units) for the M2 model of C_{100} at several temperatures. Solid line $T=2000$ K, dashed line $T=1600$ K, short dashed line $T=1200$ K.

ing polymers dissolved in solution the osmotic pressure is usually expanded in power of the polymer concentration c as

$$\Pi/(cRT)=1/M+A_2c+\cdots\ , \tag{15}$$

where Π is the osmotic pressure, c is the polymer concentration expressed in units of mass per volume, and M is the molecular weight. This is to be compared with the virial expansion of the pressure which is usually written as

$$p/(c'RT)=1+B_2c'+\cdots\ , \tag{16}$$

where c' is the concentration in mole per volume. The similarity between Eq. (15) and Eq. (16) is due to the fact, as first shown by McMillan and Mayer,[39] that the osmotic pressure can be expanded in the same way as the virial pressure if the potential of mean force is used instead of the pair potential. By identifying p with Π then it is found that

$$A_2=B_2/(M)^2\propto B_2/(n_c)^2. \tag{17}$$

In polymer science some theories have been developed for A_2. Therefore, we shall now present our B_2 data for n-alkanes reduced by the square of n_c. This is done in Fig. 4 for the M2 model. The choice of this model is just performed for convenience since we have already discussed that there is no clear evidence to prefer the M2 over the M1 model for describing n-alkanes. All of our conclusions hold equally well for the M1 model. At low temperatures (where B_2 is negative) the value of $A_2\propto B_2/(n_c)^2$ is hardly affected by the length of the chain. This is in agreement with recent experimental data for A_2 of several polymer–solvent systems below the θ temperature.[40–42] For high temperatures where B_2 is positive, the function $B_2/(n_c)^2$ decreases when n_c increases at a given temperature. This is in agreement with the Flory–Krigbaum theory of dilute polymer solutions. The results of Fig. 4 can be summarized by saying that A_2 is almost independent of the molecular weight for temperatures where it is negative and depends strongly on n_c for temperatures where it is positive, decreasing as the molecular weight increases. By fitting our results of A_2 for the M2 model with $n_c=50$, 100, and 200 at $T=2000$ K we found $A_2\propto n_c^{-\delta}$ with $\delta=0.31\pm0.03$. For $T=1800$ K and using the results for $n_c=50$, 100, and 200 we found $\delta=0.34\pm0.02$. Experimental values for δ in good solvent conditions[40] are usually in the range $\delta=0.2$–0.3. Our somewhat higher value is probably due to the fact that our chains are too short in order to the scaling law to be valid.

The effective pair potential u_e defined by Eq. (10) is plotted in Fig. 5 for several temperatures and lengths of the chain. For long chains it has a finite value when $r=0$ (positive for high temperatures and negative for low temperatures). This is in agreement with the results of Harismiadis and Szleifer[23] and from Dautenhahn and Hall.[20]

Let us now analyze the behavior of $\langle r^2\rangle$ and $\langle s^2\rangle$. In Table V values of $\langle r^2\rangle$ and $\langle s^2\rangle$ for the M2 model are presented. For short n-alkanes $\langle r^2\rangle$ decreases as the temperature increases. For long n-alkanes the opposite is true. This is due to the opposite effect of the temperature on the short- and long-range intramolecular forces. The increase of the temperature favors the presence of *gauche* configurations (short-range interaction) which makes the molecules more spherical and therefore reduces the value of $\langle r^2\rangle$. On the other hand the increase of the temperatures (long-range interaction) makes the attractive interaction between different units of the chain weaker so that the value of $\langle r^2\rangle$ increases. Therefore the effect of temperature on short- and long-range intramolecular forces is different. For short chains, short-range intramolecular forces are dominant so that the chain becomes less expanded as T increases. For long chains, the long-range intramolecular forces are dominant so that the chain becomes more expanded as T increases. For C_{30} both effects cancel out approximately so that $\langle r^2\rangle$ does not change much with temperature. The dimensions of the chain without long-range

TABLE V. Values of $\langle r^2\rangle$ and $\langle s^2\rangle$ for the M2 model. Dimensions of the chain without long-range interactions $\langle r^2\rangle_0$ and $\langle s^2\rangle_0$ for the M2 model are also evaluated. Dimensions of the unperturbed chains were obtained by using Eq. (1) for defining the short-range intramolecular interactions. Results of the last rows (labeled with asterisks) were obtained for the M4 model. In this case the dimension of the unperturbed chain were obtained by using only the first two terms on the right-hand side of Eq. (1). The results are given in σ^2 units.

n_c	T/K	$\langle r^2\rangle$	$\langle s^2\rangle$	$\langle r^2\rangle_0$	$\langle s^2\rangle_0$
16	1200	8.79	1.17	9.16	1.20
16	1600	8.59	1.15	8.83	1.17
16	2000	8.54	1.14	8.50	1.14
30	1200	19.42	2.78	20.96	2.92
30	1600	19.89	2.80	19.98	2.82
30	2000	19.65	2.77	19.05	2.71
50	1200	35.23	5.29	38.05	5.60
50	1600	36.66	5.40	36.16	5.36
50	2000	36.68	5.40	34.28	5.13
100	1200	72.33	11.49	80.65	12.60
100	1600	80.13	12.40	75.40	11.84
100	2000	82.67	12.69	72.13	11.35
200	1200	143.17	23.70	166.06	26.67
200	1600	170.84	27.21	156.86	25.25
200	2000	180.58	28.56	148.65	24.01
400	1200	268.34	45.35	337.42	55.15
400	1600	355.08	57.69	314.31	51.72
400	2000	395.55	63.44	301.37	49.42
600	1200	370.42	63.97	505.03	83.25
600	1600	546.33	89.16	476.62	78.45
600	2000	621.35	99.66	451.89	74.55
200	400	225.37*	35.32*	228.88*	36.29*
200	410	225.52*	35.53*	228.55*	36.19*
200	430	224.40*	35.30*	222.36*	35.18*

TABLE VI. Scaling coefficients ν_r and ν_s [see Eqs. (11) and (12)] obtained for the M2 model with the data of Table V. The temperature is denoted as T. In the column labeled as n_c the length of the n-alkanes used in the fit are presented. For instance 100–200 means that n-alkanes with a number of carbon atoms between 100 and 200 were used. We also determined the scaling coefficients ν_r^0 and ν_s^0 for an unperturbed chain (a chain with short range interactions only) from the data of Table V for $\langle r^2\rangle_0$ and $\langle s^2\rangle_0$.

T/K	n_c	ν_r	ν_s	ν_r^0	ν_s^0
1200	100–200	0.98	1.04	1.03	1.07
1200	200–400	0.90	0.93	1.02	1.04
1200	400–600	0.79	0.85	0.99	1.01
1600	100–200	1.08	1.13	1.05	1.09
1600	200–400	1.05	1.08	1.00	1.03
1600	400–600	1.06	1.07	1.03	1.03
2000	100–200	1.12	1.16	1.04	1.07
2000	200–400	1.13	1.15	1.02	1.04
2000	400–600	1.11	1.11	1.00	1.01

interactions, $\langle r^2\rangle_0$ and $\langle s^2\rangle_0$ have also been calculated for the M2 model. A Monte Carlo run was performed and long-range interactions were not considered. Results are presented in Table V. As expected $\langle r^2\rangle_0$ and $\langle s^2\rangle_0$ decreases with the temperature. Expansion factors defined as $\alpha_r^2=\langle r^2\rangle/\langle r^2\rangle_0$ and $\alpha_s^2=\langle s^2\rangle/\langle s^2\rangle_0$ were also evaluated. In general α_r is larger than α_s, which is in agreement with the results of Ref. 43. Although they will not be presented here values of $\langle r^2\rangle$ and $\langle s^2\rangle$ for the M3 are somewhat smaller than those of the M2 model. The chain becomes somewhat more expanded when the energy of the *gauche* configuration is large (M2 model).

The scaling behavior [Eqs. (11) and (12)] of $\langle r^2\rangle$ and $\langle s^2\rangle$ for the M2 model has been analyzed. In Table VI the obtained values of ν_r and ν_s for the M2 model are presented. In general values of ν_r are smaller than those of ν_s. For $T=1200$ K, a temperature well below the θ temperature we obtain $\nu_r=0.79$; for $T=1600$ K, a temperature close to the θ temperature we obtain $\nu_r=1.06$, and for $T=2000$ K, a temperature higher than the θ temperature we obtain $\nu_r=1.11$. The expected value of ν_r for the θ temperature is unity. Clearly for $T=1600$ K our value $\nu_r=1.06$ is somewhat high. This discrepancy is due to the fact that the scaling law [Eq. (11)] has not been achieved for the chains considered in this work (i.e., $n_c<600$). Evidence of that is obtained in two different ways. First ν_r decreases significantly when the length of the chains is increased (see Table VI). Second, even unperturbed chains (chains with short-range interactions only) do not yield a value of one for ν_r^0 as they should be (see Table VI) but a somewhat higher value. This point was further tested by analyzing the results of Ref. 43 for unperturbed n-alkane models. Again we found a value of ν_r^0 larger than one from the results of this previous work. The conclusion of this digression is that it is necessary to go to longer chains for obtaining accurate estimates of ν_r. In view of this we decided to fit our results for $\langle r^2\rangle$ and $\langle s^2\rangle$ to a new expression which includes logarithmic corrections[44] in the way predicted by the renormalization group theory.[45] For instance, for $\langle r^2\rangle$ one obtains

$$\langle r^2\rangle=a(n_c-1)^{\nu}r[1-c/\ln(n_c-1)], \tag{18}$$

and a similar expression can be written for $\langle s^2\rangle$. When the $\langle r^2\rangle$ data of Table V for $T=1600$ K and $n_c\geqslant 50$ are fitted to Eq. (18) one obtains $a=0.97\pm0.18$, $\upsilon_r=1.02\pm0.02$ and $c=1.08\pm0.37$. When the same fitting is done for the $\langle s^2\rangle$ data one obtains $a=0.21\pm0.02$ $\upsilon_s=1.00\pm0.01$, and $c=1.82$ ±0.11. Logarithmic corrections in Eq. (18) are of about 20% for chains with $n_c=600$, confirming our previous suggestions that chains with $n_c=600$ are too short for Eqs. (11) and (12) to be applicable. Once these corrections are taken into account the results of $\langle r^2\rangle$ and $\langle s^2\rangle$ for $T=1600$ K are consistent (within the numerical uncertainty) with $\upsilon_r=1.00$ and $\upsilon_s=1.00$. Therefore our results support the idea that the Boyle temperature of the infinitely long chain (in our case $T_B=1580$ K for the M2 model) is also the temperature where the scaling law given by Eqs. (11) and (12) satisfied with $\upsilon_r=\upsilon_s=1$ (note that we are assuming that the values of υ_r and υ_s for $T=1600$ K should be quite similar to their values at $T=1580$ K since the difference in temperature is small). To gain further evidence in support of the fact that for $T=1600$ K $\upsilon_r=\upsilon_s=1$ we have plotted in Fig. 6 the ratio $\langle s^2\rangle/\langle s^2\rangle_0$ versus the inverse of the temperature (in Kelvin) for several values of n_c for the M2 model. This kind of plot was first suggested by Bruns.[46] If results for all chains intersect at a single point then, for the temperature of this intersection point $\langle s^2\rangle$ scales with (n_c-1) (note that $\langle s^2\rangle_0$ scales with n_c-1 for long chains). It is seen that for the chains

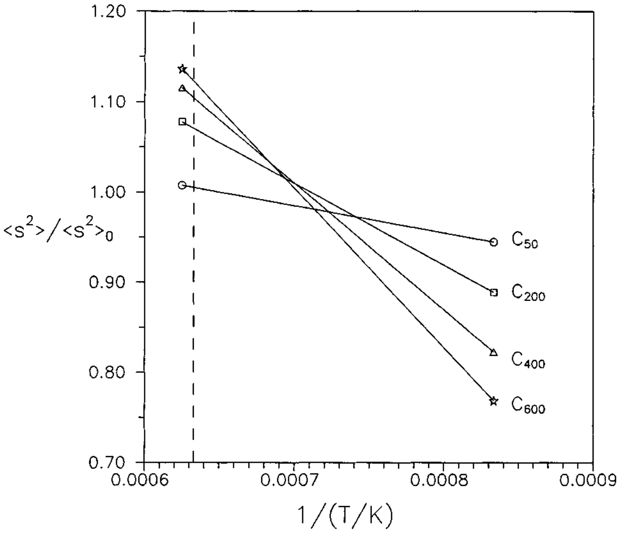

FIG. 6. Plot of $\langle s^2\rangle/\langle s^2\rangle_0$ vs $1/(T/\mathrm{K})$ for the M2 model. We used the data of Table V for $T=1200$ K and $T=1600$ K and linear behavior was assumed for intermediate temperatures. Results are for $n_c=50$ (circles), $n_c=200$ (squares), $n_c=400$ (triangles), and $n_c=600$ (starts). The dashed line stands for 1/1580, the Boyle temperature of long chains in the M2 model.

considered in this work there is not a single intersection point. The intersection point between two consecutive chains moves to higher temperatures (i.e., lower values of $1/T$) as the chains become longer. A tentative extrapolation of the intersection point for infinitely long chains yields a temperature close to the temperature where the second virial coefficient vanishes. This gives further evidence that at the Boyle temperature of long chains, the scaling law for $\langle r^2\rangle$ and $\langle s^2\rangle$ is $\upsilon_r=\upsilon_s=1$. We should mention that in a recent study Sheng *et al.*[22] have proved for a simple model that the Boyle temperature of long chains is coincident (within the uncertainty of the calculations) with the temperature where $\upsilon_r=\upsilon_s=1$. The same result has been obtained for lattice models.[46,47] In this work we obtain further evidence of this point for a more realistic *n*-alkane model.

Our choice for the definition of short-range interactions described by Eq. (1) may appear somewhat unusual. Let us recall that the choice of the short-range interactions is somewhat arbitrary. The only requirement is that dimensions of the chain at the θ temperature are close to that determined from the unperturbed chain (the chain with short-range interactions only). It was found for the M1, M2, and M3 models that only when the LJ interaction between carbons separated by five bonds was included dimensions of the unperturbed chain becomes close (although not identical) to that of a real chain at the θ temperature. For the M4 model it is not necessary to include the LJ interaction between carbons separated by five bonds into the short-range potential in order to have comparable values of $\langle r^2\rangle$ and $\langle r^2\rangle_0$ at the θ point. Summarizing, if one imposes the condition that dimensions of the real and unperturbed chain be similar at the θ temperature then LJ interactions should be included in the short-range potential for the M1, M2, and M3 models of *n*-alkanes whereas it is not necessary to do so for the M4 model. The origin of that is the wild difference in the θ temperatures of the M1, M2, and M3 models (which is of about 1600 K) and that of the M4 model (close to 400 K). At low temperatures (the M4 model) the occurrence of sequences with several consecutive *gauche* bonds are scarce. However at high temperatures (M1, M2, and M3 models) it is more frequent and unless steric hindrance is introduced for this sequence (through the LJ interaction) some sequences of *gauche* bonds will present higher probability than they should. That was somehow anticipated by Flory[27] who stated that for usual temperature interactions between carbon separated by four bonds are sufficient to describe the dimension of the chain at the θ point but that for other conditions more interactions should be included within the short-range interactions. This is indeed the case for long *n*-alkanes at the critical point. We stress again that even at the θ temperature dimensions of real and unperturbed chain are not identical. Although at the θ temperature, real and unperturbed chain dimensions scale with $\upsilon_r=\upsilon_s=1$, the coefficients P_r and P_s in Eqs. (11) and (12) are not the same for these two models.

In addition to the scaling laws for $\langle r^2\rangle$ and $\langle s^2\rangle$ an interesting issue is that concerning the shape of the *n*-alkane. It has been well known for a long time that the instantaneous shape of a random walk is rather elongated.[48,49] The same has been found for lattice models with long-range interactions.[50] To analyze the shape of long *n*-alkanes we proceeded as follows. A Monte Carlo run of an isolated chain has been performed. Every five time steps the three principal moments of inertia of the molecule were calculated by computing the eigenvalues of the inertia tensor. Since we are interested in the shape of the molecule rather than in its mass distribution the mass of each interaction site (CH_3 or CH_2) was uniformly distributed within a sphere of radius σ. Therefore, the inertia tensor for a distribution of compact hard spheres of diameter σ is computed (see Ref. 51 for further details). The mass of the CH_3 and CH_2 groups was set to the arbitrary value μ (the small difference in mass between CH_3 and CH_2 groups was neglected). The smallest principal moment of inertia was labeled as I_1^c, the medium one as I_2^c, and the largest one as I_3^c. The averages values of $\langle I_1^c/I_3^c\rangle$ and $\langle I_2^c/I_3^c\rangle$ were computed and they are presented in Table VII. It is clear that the average values of $\langle I_1^c/I_3^c\rangle$ and $\langle I_2^c/I_3^c\rangle$ are quite different than one (the expected value for a spherical distribution of sites) indicating that the instantaneous configurations of the *n*-alkane are rather anisotropic. In order to get more information concerning the shape of *n*-alkanes, we assign to every configuration of the *n*-alkane an equivalent parallelepiped (of uniform mass density) with the same principal moments of inertia than the considered configuration. The lengths of the sides of the parallelepiped a, b, and c (with $a<b<c$) are obtained from the solution of the following equations:[51]

$$I_1^c=M/12(a^2+b^2), \tag{19}$$

$$I_2^c=M/12(a^2+c^2), \tag{20}$$

$$I_3^c=M/12(b^2+c^2), \tag{21}$$

TABLE VII. Averages values of I_1^c, I_2^c, and I_3^c for the M2 model. The dimensions of the equivalent parallelepiped, a, b, and c are given in σ units.

n_c	T/K	$\langle I_1^c/I_3^c\rangle$	$\langle I_2^c/I_3^c\rangle$	$\langle a\rangle$	$\langle b\rangle$	$\langle c\rangle$	$\langle b\rangle/\langle a\rangle$	$\langle c\rangle\langle a\rangle$
100	1200	0.29	0.87	2.83	4.80	10.02	1.69	3.54
100	1600	0.28	0.87	2.83	4.88	10.50	1.72	3.71
100	2000	0.27	0.87	2.82	4.93	10.65	1.75	3.78
200	1200	0.30	0.87	4.20	6.93	14.20	1.65	3.38
200	1600	0.29	0.87	4.29	7.28	15.37	1.70	3.58
200	2000	0.28	0.87	4.32	7.40	15.83	1.71	3.66

where M is the total mass of the parallelepiped which is given by $n_c\mu$ (i.e., the same total mass is assigned to the parallelepiped and to the *n*-alkane). In Table VII values for $\langle a\rangle$,$\langle b\rangle$,$\langle c\rangle$ and $\langle c\rangle/\langle a\rangle$ and $\langle b\rangle/\langle a\rangle$ are presented. As can be seen the values of $\langle c\rangle/\langle a\rangle$ and $\langle b\rangle/\langle a\rangle$ differ significantly from one showing the anisotropy of the chains. At lower temperatures chains are slightly more spherical than at high temperatures (for instance for C_{200} the value of $\langle c\rangle/\langle a\rangle$ changes from 3.38 to 3.66 when increasing the temperature from $T=1200$ K to $T=2000$ K). In any case the effect of the temperature on the anisotropy of the chain is small. For a temperature close to the θ point (see $T=1600$ K) the principal moments of inertia of the chain are the same as those of a parallelepiped with a ratio of a:b:c of 1:1.7:3.6. Although the chain with $n_c=200$ is slightly more spherical than the one with $n_c=100$, the differences are small so that the ratio 1:1.7:3.6 seems to be close to the anisotropy of the infinitely long polymethylene chain. This ratio is in agreement with previous calculations of Solc[49] for self-avoiding walks. We conclude that *n*-alkanes present a considerable anisotropy at the θ temperature and for higher and lower temperatures. To further illustrate this point in Fig. 7 an instantaneous configurations of the *n*-alkane is plotted. A simple visual inspection reveals the anisotropy of *n*-alkanes. The strong anisotropy of long chains was also suggested by previous studies concerning the second virial coefficient of hard *n*-alkane models.[51,52] Although we cannot speak on the shape of a long *n*-alkane since each configuration presents a different shape, it can be stated however that the instantaneous configurations of a *n*-alkane resemble more an elongated body (parallelepiped, ellipsoid) than a sphere.

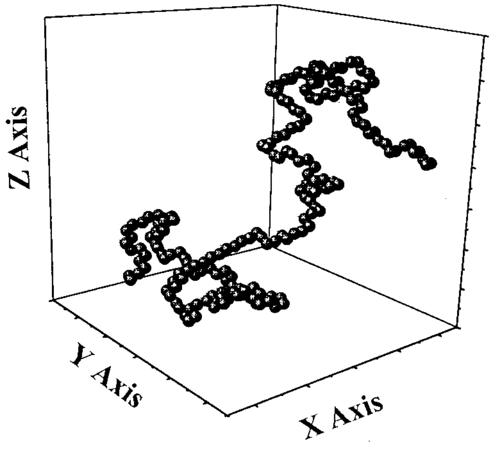

FIG. 7. A representative configuration of the *n*-alkane C_{200} obtained at $T=1600$ K for the M2 model.

IV. CONCLUSIONS

In this work the second virial coefficient of *n*-alkanes has been calculated. The model used is quite similar to that proposed in a previous work.[15,16] It is shown that the Boyle temperature of *n*-alkanes is fairly insensitive to the length of the chain for chains with $n_c>100$. This is in agreement with the prediction of the Flory–Krigbaum theory. Since according to the Flory–Huggins theory the temperature at which the second virial (osmotic) coefficient vanishes is also the critical temperature of the infinitely long chain, the Boyle temperature of infinitely long chains provides an estimate of the critical temperature of polymethylene. The results of this work suggest $\theta=1620$ K. This result is in reasonable agreement with the critical temperature of polymethylene estimated from Shultz–Flory plots of the computer simulations of Smit *et al.*[12] and from the available critical temperatures of short chains. Therefore we believe that $\theta=1620\pm80$ K is a reasonable estimate of the critical temperature of polymethylene. This is much higher than previous estimates[8,10] which are located around $\theta=1000$ K.

It is shown that A_2 (i.e., B_2/n_c^2) is independent of the length of the chain for temperatures below the θ temperature and it scales as $n_c^{-\delta}$ with δ close to 0.30 for temperatures above the θ temperature. This is in agreement with some recent experimental data.[40–42]

The scaling laws for $\langle r^2\rangle$ and $\langle s^2\rangle$ at $T=0$ and for other different temperatures were analyzed. At the θ temperature the exponent v_R took the value $v_R=1.06$. This exponent was obtained from the rather short chains considered in this work. For *n*-alkanes it seems necessary to go to longer chains in order to obtain the correct scaling behavior. In fact when logarithmic corrections are properly taken into account we obtain at the θ temperature that $v_r=v_s=1$, giving further evidence that at the temperature where the second virial coefficient of the infinitely long chain vanishes, the square of the radius of gyration and the square of the end-to-end distance scale with (n_c-1).

The shape of polymethylene has been analyzed. It is found that the average values of the three principal moments of inertia of polymethylene are identical to that of a parallelepiped with a length of the sides in the ratio 1:1.7:3.6.

Recently it has been suggested that the vapor–liquid equilibria of chain molecules can be approximated by that of a representative conformer[53] or even by that of a body of simple geometry[54–56] (spherocylinder, ellipsoid). The importance of this simplification is that it reduces the difficult problem of calculating the vapor–liquid equilibria of a chain molecule to the simpler one of computing the vapor–liquid equilibria of a rigid model with a fixed shape. Perturbation theories are now available for anisotropic pure fluids.[55,57] The results of this work suggest that this representative body should be rather anisotropic if the ''average'' shape of the *n*-alkane should be described. For instance Boublik *et al.*[54,55] have recently described successfully the vapor–liquid equilibria of *n*-alkanes up to *n*-hexadecane by taking the *n*-alkane as a spherocylinder with a relatively large length to breath ratio. This work provides support for this approach and similar ones since after all, chains are rather anisotropic.

ACKNOWLEDGMENT

This project has been financially supported at the University Complutense by Project No. PB94-0285 of the DGICYT of Spain.

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