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Intermolecular Energies and Excluded Volume Force of Cohesion and Internal Energy in the Condensed Phase

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The force of cohesion and a new equation of internal energy in the condensed phase are exploited to obtain the intermolecular energies of different fluids in the gaseous and liquid states for polar and nonpolar molecules. The attractive energies of dispersion, orientation, and induction are expressed in the form of a unique and general relationship taking into account only the polarizability α, the dipole moment μ, and the excluded volume V_τ of the molecule under consideration. It thus becomes possible to calculate the critical temperature on the basis of these three molecular parameters.

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1. Introduction

Intermolecular forces are responsible for most of the physical and chemical properties of materials. This explains the number of works devoted to such studies. The first attempt to explain intermolecular forces was made by Keesom (1912) based on the interaction between permanent dipoles. Debye in 1920 extended the dipole theory to take into account the induction effect in which a permanent dipole induces a dipole in another molecule and a mutual attraction results. This interaction depends on the polarizability α and on the dipole moment μ of the molecule. The cause of the attractive forces between neutral molecules is the dispersion interaction: the quantum mechanical treatment of this interaction was given by London in 1930. These different works furnished much very interesting information, were based on the potential energies of the Lennard−Jones type, and were very often limited to isolated molecules.

It has since become necessary to propose new formulations to better describe the interaction energies. One important development was via quantum mechanical calculations which call upon complex considerations. In this case, the interactions are described in terms of a multidimensional potential energy which describes the energy as a function of the configuration of the separated molecules, their relative orientations, and the intermolecular distances. Very little information concerns the interactions of diatomic and polyatomic molecules, and the potential energies were always of the types developed by Lennard−Jones, Morse, Buckingham, Stockmeyer, and Kihara. Another development exploited the reaction field technique which considers that the dispersion forces are linked to the frequency-dependent polarizabilities by averaging over the fluctuating instantaneous dipole-induced dipole interaction. In this approach both quantum mechanical and statistical mechanical fluctuations are simultaneously averaged. For many practical problems it is necessary to understand forces between molecules in liquids. This is a very difficult problem since it involves the detailed packing of the molecules in a liquid as well as the many-body forces between neighboring molecules. A complete and well-documented development can be found in refs 1 and 2 for the interested reader. To go further in our understanding of molecular interactions, much recent research calls upon molecular dynamics simulations.[3–5] The computational methods are used in molecular modeling to compute the energy of an assembly of molecules and to perform a molecular simulation. These simulations are carried out using Lennard−Jones or Buckingham potentials and require taking into account a very large number of atomic and molecular parameters, the estimation of which may be delicate.

This paper exploits a new equation of state developed previously[6] which allows proposing a new expression for the cohesive forces and internal energy. On the basis of this expression, it becomes easy to obtain the interaction energy of polar and nonpolar molecules under various pressures and temperatures in the gaseous and liquid states by simply following the variation of excluded volume according to the physical conditions to which the considered fluid is subjected. This excluded volume V_τ appears as the average volume occupied by the considered molecule which in the liquid forbids the presence of any other molecule. The molecule in perpetual translational, rotational, and vibrational movement undergoes a countless number of shocks with its neighbors and as a result remains confined within a volume which on the average over time can be considered as a sphere whatever the molecule under consideration. This volume thus represents the fictive volume of the molecule which will become its true volume under very high pressure. If the temperature is increased, the intermolecular movements are more rapid, the collisions more frequent, and the distances between successive collisions lower, and thus the excluded volume diminishes. So both increased pressure and temperature lead to the same result.

2. Forces of Cohesion in Condensed Phase. Internal Energy

In gaseous phases, cohesion due to the molecular structure is manifested inside the fluid through the presence of the internal pressure P_{int} according to the relation established in the previous study:[6]

$$\frac{P_{\text{int}}}{RT_c} = \left(\frac{1}{m} + \frac{T_c}{T}\right)\exp\left(m\frac{T_c}{T}\right)\frac{V_\tau}{V^2} - E\frac{T_c}{T}\frac{V_\tau}{(V - V_\tau)^2} \quad (1)$$

In this expression, m, introduced in the attractive term of the potential energy, is a constant equal to 0.175 for all of the bodies

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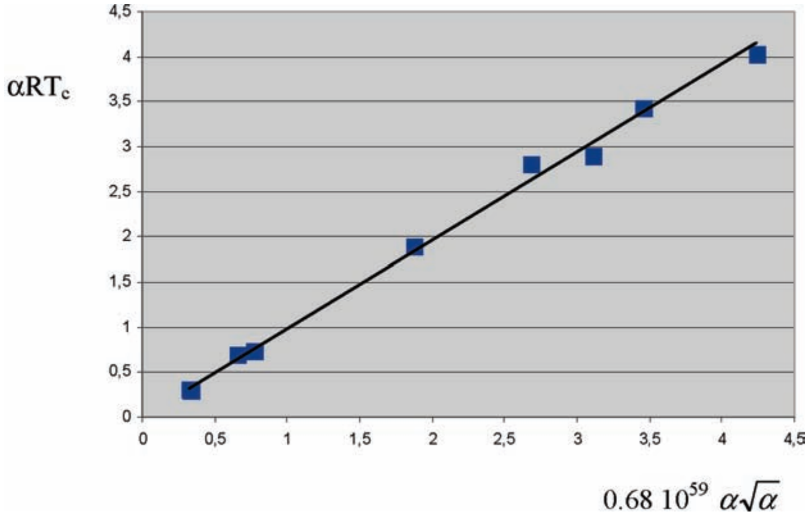
Table 1. Internal Energy and Intermolecular Energy of Nonpolar Molecules[a]



	T_c (K)	V_c ($m^3 \cdot 10^6$)	$\alpha \cdot 10^{40}$	γ	aRT_c	$0.68 \cdot 10^{59}\ \alpha(\alpha)^{1/2}$
K_r	209.4	92	2.76	0	0.33	0.31
CH_4	190.55	98.8	2.88	0	0.32	0.32
C_2H_6	305.5	141.8	4.92	0.16	0.77	0.74
C_2H_4	282.3	131	4.73	0.12	0.65	0.7
2-methyl propene	428.6	239	9.22	0.32	1.87	1.90
cyclohexane	553	308	12.24	0.33	3.11	2.91
benzene	562.1	259	11.95	0.39	2.68	2.81
toluene	591.8	316	13.68	0.39	3.45	3.44
heptane	540	416	15.24	0.54	4.24	4.04

[a] Parity plot shows the values of the second to last column versus those of the right-most column.

studied except for neon and helium for which $m = 0.162$ and 0.13, respectively. E, introduced in the repulsive term of the internal energy, is equal to 0.36 for rare gases and small molecules. It diminishes when the molecular volume increases.

One can therefore calculate the energy of molecular interaction by calculating the internal work done by the internal pressure from the infinite volume to the volume V. This gives

$$\frac{W}{RT_c} = \int_\infty^V P_{\text{int}}\,\mathrm{d}V = -\left(\frac{1}{m} + \frac{T_c}{T}\right)\exp\left(m\frac{T_c}{T}\right)\frac{V_\tau}{V} + E\frac{T_c}{T}\frac{V_\tau}{(V - V_\tau)} \qquad (2)$$

It can be seen that this work corresponds exactly to the energy of internal interaction $(U - U_{id})/(RT_c)$ which was previously established.[6]

As indicated above, the parameter E in eq 2 is equal to 0.36 for small molecules, decreases gradually as the molecular volume increases, and may become negative. Because of this, we have supposed that the constant involved in the repulsive term is a positive constant for the different bodies. We have therefore empirically added the supplementary term $\gamma(T_c/T)(V_\tau/(V - V_\tau))$ to the repulsive term and naturally the same negative component to the attractive term. Equation 3 is thus generalized for all molecules with $(E + \gamma) = 0.36$

$$\frac{U - U_{id}}{RT_c} = \left[-\left(\frac{1}{m} + \frac{T_c}{T}\right)\exp\left(m\frac{T_c}{T}\right)\frac{V_\tau}{V} - \gamma\frac{T_c}{T}\frac{V_\tau}{(V - V_\tau)}\right] + 0.36\frac{T_c}{T}\frac{V_\tau}{(V - V_\tau)} \qquad (3)$$

In this new expression, a negative term appears which can be attributed to the energy of a molecular attraction and a positive term which is the energy of molecular repulsion.

Calculations of the internal energy in the following paragraphs require knowledge of the excluded volume. We recall here the formula given previously[6]

$$V_\tau = \frac{a_o}{\left[\exp 3\left(\frac{V_c}{V}\frac{T}{T_c}\right) + 1\right]} + b_o$$

where b_o represents the excluded volume V_τ for a very small molar volume which is very close to the real volume derived from the solid state volume at 0 K.

A study of different molecules has shown that a_o is related to b_o by the general relationship $a_o = 4.1 \cdot 10^{-3} \exp(25b_o)$ and furthermore, at the critical point, $V_\tau/V_c = 0.26$ for molecules of different sizes and forms. Furthermore, m is constant for all of the molecules studied and equal to 0.175.

3. Study of Nonpolar Molecules

In the case of nonpolar molecules, the energy of attraction corresponds to the potential energy of the system made of molecules occupying a volume V at a temperature T. This energy, generally referring to the dispersion energy due to electronic oscillators, is obtained by equating this new expression to the attractive part of the internal molecular energy obtained above, and the general relation obtained is

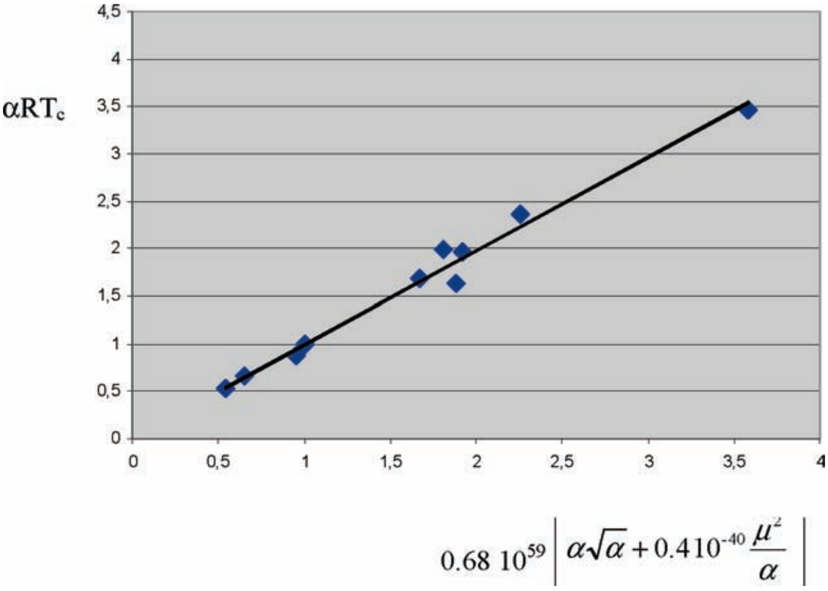
$$RT_c a = \frac{0.6810^{59}}{V}\alpha\sqrt{\alpha}$$

in SI units with

$$a = \left[\left(\frac{1}{m} + \frac{T_c}{T}\right)\exp\left(m\frac{T_c}{T}\right)\frac{V_\tau}{V} + \gamma\frac{T_c}{T}\frac{V_\tau}{(V - V_\tau)}\right] \qquad (4)$$

This dispersion energy has thus the same representation for different molecules irrespective of their volume for $T = T_c$.

Table 2. Internal Energy and Intermolecular Energy of Polar Molecules[a]



	T_c (K)	V_c ($m^3 \cdot 10^6$)	$\alpha \cdot 10^{40}$	$\mu \cdot 10^{30}$	γ	aRT_c	$0.68 \cdot 10^{59}[\alpha\sqrt{\alpha} + 0.4 \cdot 10^{-40}\mu^2 / \alpha]$
SH_2	373	99	4.206	3.67	0.14	0.65	0.67
$CHCl_3$	536.4	239	10.57	3.47	0.1	2.26	2.36
NH_3	405	72	2.51	4.90	0.46	0.54	0.53
SO_2	430	122	4.76	5.33	0.30	0.95	0.87
C_6H_5Cl	632	308	13.57	5.67	0.39	3.58	3.46
CH_3Cl	416.2	139	5.07	6.33	0	1.0	0.99
C_2H_5Br	503.9	215	8.95	6.77	0.16	1.92	1.96
acetone	508.1	209	7.03	9.67	0.16	1.88	1.63
CH_3NO_2	588	173	8.20	11.47	0.16	1.81	1.99
CH_3CN	545.5	173	4.89	13.21	0.16	1.67	1.68

[a] Parity plot shows values of second-last column versus those of right-most column.

Table 1 compares the two terms of eq 4 for nonpolar molecules of different sizes and shapes. This last relation allows calculating T_c, and consequently, the study of a new molecule is reduced to knowledge of b_0 and α for nonpolar molecules. The critical temperature thus appears as the temperature communicating to the molecules an attractive molecular energy equal to the energy of dispersion.

The independent variables involved in the term, *a*, above (eq 4) are *m*, *E*, and V_τ. Each of these variables has been defined elsewhere[6] with $(E + \gamma) = 0.36$. The value of V_τ is obtained from the general expression $(V_\tau/V_c) = 0.26$. The constants T_c, V_c, α, and μ are taken from the CRC Handbook of Chemistry and Physics.

As an example, the calculation of the two terms of expression 4 is carried out for methane for $T = T_c$.

$$T_c = 190.55\ \text{K} \qquad V_c = 98.8 \cdot 10^{-6}\ \text{m}^3$$

$$\alpha = 2.8 \cdot 10^{-40}\ \text{S.I.} \qquad \gamma = 0$$

$$V_\tau = 0.26 \cdot (98.8 \cdot 10^{-6}) = 25.64 \cdot 10^{-6}\ \text{m}^3$$

$$R = 8.314\ \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$a = \left(\frac{1}{0.175} + 1\right)\exp(0.175)\frac{V_\tau}{V} = \frac{205}{V} \cdot 10^{-6}$$

$$aRT_c = \frac{205}{V} \cdot 8.314 \cdot (190.55 \cdot 10^{-6}) = \frac{0.32}{V}\ \text{J} \cdot \text{mol}^{-1}$$

The term corresponding to the dispersion energy

$$0.68 \cdot 10^{59}\frac{\alpha\sqrt{\alpha}}{V} = \frac{4.6 \cdot 10^{-60}}{V}0.68 \cdot 10^{59} = \frac{0.32}{V}\ \text{J} \cdot \text{mol}^{-1}$$

This thus verifies the equality of these two terms as can be confirmed for all of the nonpolar and polar molecules studied.

4. Study of Polar Molecules

In the case of polar molecules, the molecular interaction energy must also take into account the energy of orientation because of the dipoles and the energy of mutual induction. In our case, the two energies have the general form $(k'/V)(\mu^2/\alpha)$. Consequently, for $T = T_c$ the total energy becomes the following.

$$RT_c a = \frac{0.68 \cdot 10^{59}}{V}\left(\alpha\sqrt{\alpha} + 0.410^{-40}\frac{\mu^2}{\alpha}\right) \tag{7}$$

Table 2 presents the experimental results which are in satisfactory agreement for the polar molecules and thus confirm the validity of the new expression for the intermolecular energies of molecules of very different shapes and sizes.

5. Variation of the Intermolecular Energy with the Temperature

The preceding expressions can be generalized to different temperatures by introducing the term $\exp[0.35((T_c/T) - 1)]$. The general expression then becomes

$$RT_c a = \frac{0.68 \cdot 10^{59}}{V}\left(\alpha\sqrt{\alpha} + 0.4 \cdot 10^{-40}\frac{\mu^2}{\alpha}\right)\exp\left(0.35\left(\frac{T_c}{T} - 1\right)\right) \tag{6}$$

This equation allows determining the critical temperature T_c of a body if one knows α, μ, and b_0.

The calculations were done for a series of polar and nonpolar molecules, and the results in Tables 3 and 4 agree well with the experimental values. So, the critical temperature is that at which the attraction energy of the molecules is equal

Table 3. Determination of the Critical Temperature of Nonpolar Molecules at Different Temperatures

Krypton ($T_c = 209.4$, $V_c = 0.092$, $\alpha = 2.76$)			
(T_c/T)	1	0.5	0.2
$T_{c(calc)}$	195	193	192
Methane ($T_c = 190.5$, $V_c = 0.099$, $\alpha = 2.88$)			
(T_c/T)	1	0.5	0.2
$T_{c(calc)}$	193	191	190
Ethane ($T_c = 305.5$, $V_c = 0.1417$, $\alpha = 4.92$)			
(T_c/T)	1	0.5	0.2
$T_{c(calc)}$	294	300	300
Toluene ($T_c = 591.8$, $V_c = 0.32$, $\alpha = 13.68$)			
(T_c/T)	1	0.5	0.2
$T_{c(calc)}$	591	606	613
Cyclohexane ($T_c = 553.5$, $V_c = 0.309$, $\alpha = 12.24$)			
(T_c/T)	1	0.5	0.2
$T_{c(calc)}$	568	528	533

Table 4. Determination of the Critical Temperature of Polar Molecules at Different Temperatures

CH_3Cl ($T_c = 416.2$, $V_c = 0.139$, $\alpha = 5.07$, $\mu = 6.33$)			
(T_c/T)	1	0.5	0.2
$T_{c(calc)}$	412	408	407
$CHCl_3$ ($T_c = 536.4$, $V_c = 0.239$, $\alpha = 10.57$, $\mu = 3.47$)			
(T_c/T)	1	0.5	0.2
$T_{c(calc)}$	561	560	561
C_2H_5Br ($T_c = 503.9$, $V_c = 0.215$, $\alpha = 8.95$, $\mu = 6.77$)			
(T_c/T)	1	0.5	0.2
$T_{c(calc)}$	512	514	517
CH_3CN ($T_c = 545.5$, $V_c = 0.173$, $\alpha = 4.89$, $\mu = 13.21$)			
(T_c/T)	1	0.5	0.2
$T_{c(calc)}$	549	548	533
C_6H_5Cl ($T_c = 632$, $V_c = 0.308$, $\alpha = 13.57$, $\mu = 5.67$)			
(T_c/T)	1	0.5	0.2
$T_{c(calc)}$	610	625	631

to the attractive intermolecular energy, whatever the fluid temperature.

6. Discussion

Internal Energy and Excluded Volume. The calculations developed for the determination of the internal energy of a fluid generalize the pair potential to an assembly of molecules by a pairwise additive potential. This allows its application to a small ensemble of molecules or even to a cluster but does not allow the study of the gaseous or liquid states.

The calculations are carried out using Lennard–Jones, Morse, Buckingham, or Kihara pair potentials. It should be noted that these potentials represent a first approximation to a more complex phenomenon.

These calculations take into consideration the different relative orientations of the molecules with respect to each other but suppose that they are always situated at a distance r from each other. In reality, the molecules constantly change their orientation after each collision with each other, and because of this, the distance between neighboring molecules is also constantly being modified. This difficulty in studying the phenomenon is not taken into account in most calculations.

The excluded volume concept seems to solve this difficulty. Indeed, the molecules in perpetual translational, rotational, and vibrational movement undergo a countless number of shocks with neighbors. As a result, any given molecule remains confined within its excluded volume, and the ensuing intermolecular distance is therefore a constant.

It would be of interest to propose a pair potential which would yield as a result the internal energy for a fluid. It would then be possible to theoretically calculate the value of the excluded volume to confirm the variation obtained in this work.

Theoretical Molecular Determination of the Critical Temperature. The first determination of T_c made use of the van der Waals relationship. The critical temperature is related to the constants a and b by the well-known formula $T_c = 8a/27bR$. This relationship yields values in poor agreement with those found experimentally. Furthermore, the term RT_c/P_cV_c, which from an experimental viewpoint should be equal to 3.70, is found equal to $8/3 = 2.67$. This underlines the very incomplete character of the van der Waals relation. Another estimation of T_c is linked to the Gulberg constant; this author noted that the ratio of the normal boiling point to the critical temperature is relatively constant and approximately equal to 2/3. Other estimations of T_c can be obtained from low-temperature surface tension data or from liquid density data.

This work thus allows a theoretical determination of T_c based on the equation of state. It suffices to write that this temperature is attained when $(\partial P/\partial V)$ and $(\partial^2 P/\partial V^2) = 0$. Such calculations are difficult to perform, and we have preferred using the two relations defining the internal energy based on molecular parameters. The first equation takes into account the excluded volume of the molecule within the fluid to define the attractive and repulsive potentials. The second relation defines the attractive energy expressed as a function of the polarizability α and the dipole moment μ; this is therefore relative to the forces of dispersion, orientation, and induction. The equality between the attractive forces in these two relations yields very simply T_c, which is expressed for the first time as a function of the parameters specific to the molecule being studied, that is, α, μ, and V_τ.

7. Conclusions

This work has allowed proposing a general formula for intermolecular energies by exploiting our new internal energy relation. This new relation, valid for gaseous and liquid fluids for all temperatures and pressures, is expressed simply as a function of the polarizability α and the dipole moment μ of the molecule considered. The dispersion, orientation, and induction energies are thus expressed in a unique form which exploits in priority the concept of excluded volume. It is thus possible to calculate the critical temperature based uniquely on the parameters α, μ, and V_τ.

Note Added after ASAP Publication: This paper was published ASAP on March 1, 2010. The third paragraph of the Introduction was updated. The revised paper was reposted on March 16, 2010.

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