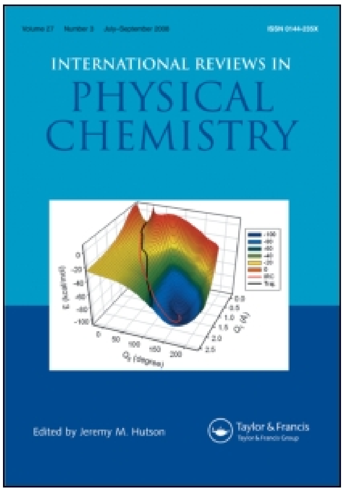

International Reviews in Physical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713724383

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To cite this Article Cuadros, F. , Mulero, A. , Cachadiña, J. and Ahumada, W.(1995) 'A new procedure for determining Lennard-Jones interaction parameters', International Reviews in Physical Chemistry, 14: 2, 205 — 213
To link to this Article: DOI: 10.1080/01442359509353309
URL: http://dx.doi.org/10.1080/01442359509353309

INTERNATIONAL REVIEWS IN PHYSICAL CHEMISTRY, 1995, VOL. 14, NO. 2, 205–213

A new procedure for determining Lennard-Jones interaction parameters

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Because the connection factors between theoretical and experimental results of thermodynamic quantities are given through the molecular interaction parameters, for chemical engineering applications it is necessary to use exact values of these parameters for a determined molecular interaction model. Because the results of computer simulation may be considered 'exact' for a determined intermolecular potential, it makes an excellent tool for investigating this connection. The purpose of the present work is to propose a procedure for determining interaction parameters for fluids by forcing agreement between the values of pressure obtained from empirical Equations of state in phase space regions where we are sure they are most exact and those obtained from computer simulation.

1. Introduction

Knowledge of intermolecular interactions is obtained both from experimental observations and from theoretical considerations. Theory suggests the functional form of the interaction potential, and experimental data are used to determine empirically the adjustable parameters in the potential functions (Hirschfelder *et al.* 1964, Maitland *et al.* 1987). However neither procedure, that of determining the functional form or that of determining the parameters of the potential, is exact because of the theoretical simplifications and experimental errors.

One of the most frequently used molecular interaction models for simple fluids is that due to Lennard-Jones (LJ) (12–6), which is given by

$$U_{\mathrm{LJ}}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right], \tag{1}$$

where ϵ is the depth of the potential energy well, and σ is the distance at which the potential is zero. For systems composed of non-spherical molecules, the microscopic behaviour can be modelled using the LJ parameters ϵ and σ and the acentric factor, ω, introduced by Pitzer (Walas 1985). This factor gives a measure of the deviation of the real intermolecular potential from that of simple spherical molecules (Lewis and Randall 1961). Normally the LJ parameters are obtained by analysis of the experimental data for the second virial coefficients, the viscosity, and the self-diffusion and Joule–Thompson coefficients (Hirschfelder *et al.* 1964). Rough estimates may be obtained from the constants characteristic of the critical, melting, or boiling points. The values which result depend on which property is analysed, and, even using the same property, different authors report different values, the reason for this being the experimental errors and theoretical simplifications. Once a pair of parameters is assumed, the connection between theoretical and experimental thermodynamical properties is made straightforwardly by using the appropriate units conversion factor. This factor, however, is not constant but depends on the pair of LJ parameters chosen. So the comparison between theoretical and experimental results may be questioned because of this parameter dependence of the conversion factor. Recently (Cuadros *et al.* 1993) we faced this problem when we proposed a modification of the Soave equation of state (EOS) (Soave 1972). There, we incorporated a new multiplicative factor linear in the molar volume ($A + Bv$), on the attractive pressure of the Soave EOS for the methane system at high densities where the Soave EOS gives poor results. We observed that the values of A and B were different if one used different values of the intermolecular potential parameters (ϵ and σ) as reported in the literature. Thus, the modification of an EOS depends on the choice of LJ parameters. What are the appropriate values of the LJ parameters? What is the best pair? The goal of this paper is to respond to this question. By forcing agreement between computer simulation results for a LJ gas and the values obtained via empirical EOS's at low density, we have been able to elaborate an efficient, reliable and straightforward procedure to determine the potential parameters. Once the valid parameters are obtained, it is possible to make modifications of a determined empirical EOS or to propose new EOS's in other phase space regions where its validity is questioned (i.e. liquid-vapour equilibria, liquid region, etc.).

2. A new procedure for evaluating LJ parameters

As is well known, computer simulation techniques can be used for comparison with both theoretical and experimental results. Normally, computer simulation results for thermodynamical properties are expressed in reduced units using the molecular version of the principle of corresponding states (PCS), i.e. using the parameters of the intermolecular potential. Moreover, these computer simulation results may be considered as 'exact' for a given model of the intermolecular interaction. According to the PCS, the reduced values of thermodynamic properties are equal for substances modelled by the same potential function. No conversion of units is needed to compare the computer simulation results with theoretical predictions: the test can be made directly in reduced units. But, if one wants to compare computer and/or theoretical results with experiment, it is necessary to convert from PCS reduced units to physical units. The conversion factors may be expressed in powers of the intermolecular interaction parameters. For the thermodynamic variables involved in an EOS, P, ρ, T, their expressions in reduced LJ units are

$$\left.\begin{aligned} P^* &= P\frac{\sigma^3}{\epsilon}, \\ \rho^* &= \rho\sigma^3 = \sigma^3\frac{N}{V}, \\ T^* &= \frac{T}{\left(\frac{\epsilon}{k}\right)}, \end{aligned}\right\} \tag{2}$$

where σ and ϵ/k are the LJ parameters, ρ the number density ($\rho = N/V$), and k the Boltzmann constant. To convert these reduced properties to the units normally used in an EOS, we must use the following expressions

$$\left.\begin{aligned} P^* &= P\frac{\left(\frac{\epsilon}{k}\right)R}{N_a\sigma^3} && \text{(atm.)}, \\ V &= \frac{1}{\rho} = \frac{N_a\sigma^3}{\rho^*} && (\text{cm}^3\,\text{mol}^{-1}), \\ T &= T^*\left(\frac{\epsilon}{k}\right) && \text{(K)}, \end{aligned}\right\} \tag{3}$$

where $R = 82{\cdot}06$ atm cm^3 mol^{-1} K^{-1}, ϵ/k is in Kelvin, σ in centimetres, and N_a is Avogadro's number ($6{\cdot}023 \times 10^{23}$ mol^{-1}). It is easy to see that different pairs of LJ parameters give different values for the EOS properties. To further complicate the problem, there is much LJ data reported in the literature. For example for Ar, Kr, CH_4 and N_2 table 1 lists their LJ values obtained from measurements of the second virial

Table 1. Values of LJ parameters for Ar, Kr, CH_4 and N_2 from the second virial coefficient (*a*) and from the viscosity (*b*) taken from the literature and percentage deviations relative to the minimum between the maximum and the minimum values of these parameters (equation (4)).

System	σ (Å)	ϵ/k (K)		$D(\sigma)$ (%)	$D(\epsilon/k)$ (%)
Ar	3·504	117·7	(*a*)		
	3·336	141·2	(*a*)		
	3·400	122·0	(*a*)		
	3·405	119·8	(*a*)	6·17	51·34
	3·465	116·0	(*b*)		
	3·418	124·0	(*b*)		
	3·542	93·3	(*b*)		
Kr	3·827	164·0	(*a*)		
	3·575	191·4	(*a*)		
	3·597	158·0	(*a*)	7·05	21·14
	3·600	171·0	(*a*)		
	3·610	190·0	(*b*)		
	3·655	178·9	(*b*)		
CH_4	4·010	142·8	(*a*)		
	3·783	148·9	(*a*)		
	3·706	159·7	(*a*)		
	3·817	148·2	(*a*)	8·20	16·57
	3·822	137·0	(*b*)		
	3·797	144·0	(*b*)		
	3·758	148·6	(*b*)		
N_2	3·698	95·0	(*a*)		
	3·710	95·9	(*a*)		
	3·745	95·2	(*a*)		
	3·613	103·0	(*a*)	11·51	60·53
	3·362	128·1	(*a*)		
	3·681	91·5	(*b*)		
	3·749	79·8	(*b*)		

coefficient and viscosity (Walas 1985, Prausnitz *et al.* 1986, Reid *et al* 1987). One can see that there is a deal of divergence among the values.

Moreover in table 1, we have extracted the maximum and minimum values of the LJ parameters for the systems considered above, as given by the different authors, and their relative percentage deviation defined as

$$D(x) = \frac{X_{\max} - X_{\min}}{X_{\min}} \times 100. \qquad (4)$$

It is clear that a meaningful comparison between the theoretical and the experimental values for a particular thermodynamic property is not possible because of the large variation of the LJ parameters. The connection between theoretical and experimental results is thus far from being a resolved problem, and the experimental test of a determined molecular theory is unclear because within the range of LJ values, one can choose those that are most appropriate for a better connection. It may be that, of two theories, one is more exact than the other, but both are accepted and considered useful because of the ability of the investigator to choose the appropriate values of the LJ parameters.

In order to establish a suitable pair of LJ parameters by forcing the empirical and computer simulation results to be equal, as argued above, we have performed computer simulations using the Molecular Dynamics (MD) method for a LJ. The total of states simulated was 312, and we chose three regions of the phase diagram at low, moderate and high density. At low densities, we used 127 points of state ($\rho^* = 0{\cdot}025$–$0{\cdot}300$), at moderate densities 48 points of state ($\rho^* = 0{\cdot}350$–$0{\cdot}500$) and at high densities 99 points of state ($\rho^* = 0{\cdot}650$–$0{\cdot}844 = \rho^*_{\text{triple point}}$). For each state, the radial distribution function (RDF), internal energy, and pressure were obtained as averages of the corresponding values each 1000 time-steps. The total computational time for all states was 5000 time-steps and we followed the same computational procedure as we have used in 3D (Rull *et al.* 1984, 1987) and in 2D (Cuadros and Mulero 1991, 1992, 1993). By way of example, we list in table 2 the average values of pressure, P^*, number of neighbours per particle, *NN*, and number of interactions per particle, *NI*, for a determined temperature, $T^* = 1{\cdot}7$ and for four values each of low, moderate and high densities. Given in parentheses are the root-mean-square deviations with respect to the time averages of these quantities.

As can be seen, the relative deviations of the pressure; that is, the root-mean-squares of the pressure over their corresponding pressure values in all regions, are less than 10%—excluding the state $T^* = 1{\cdot}7$, $\rho^*_{\text{triple point}} = 0{\cdot}844$, where the relative deviation is around 11%. Nevertheless, the lowest relative deviations ($< 5\%$) are for low densities, so that this region will be used to do the fitting between computer simulation and empirical EOS results. It can also be seen that both *NN* and *NI* have a linear dependence on density—as one would expect. The average number of nearest neighbours, *NN*, and the average number of interactions, *NI*, at low densities is less than at moderate and high densities. However they are high enough for the statistics of the computer simulation results to be considered good at these low densities too. Moreover the relative deviation defined as the root-mean-square of *NN* and *NI* over the *NN* and *NI* values is very low: $< 3\%$ for *NN* and $< 5\%$ for *NI*.

Therefore, because all EOS's give good results at low densities (dilute gases)—hardly surprising because, in the low-density region of the phase plane, even the ideal gas EOS works well!—and because our computer simulation results are good

Table 2. Average MD values of the pressure in reduced LJ units, P^*, number of neighbours per particle, *NN*, and number of interactions per particle, *NI*, and in parentheses their corresponding root-mean-square deviations at low, moderate and high densities for reduced temperature $T^* = 1{\cdot}7$.

T^*	ρ^*	$\langle P^* \rangle$	(σ_P)	$\langle NN \rangle$	(σ_{NN})	$\langle NI \rangle$	(σ_{NI})
1·7	0·075	0·112	(0·002)	3·30	(0·10)	2·47	(0·13)
1·7	0·100	0·141	(0·003)	4·41	(0·06)	3·32	(0·07)
1·7	0·125	0·171	(0·006)	5·57	(0·10)	4·19	(0·03)
1·7	0·150	0·196	(0·009)	6·64	(0·13)	5·00	(0·09)
1·7	0·350	0·379	(0·03)	15·09	(0·06)	11·30	(0·06)
1·7	0·400	0·445	(0·03)	17·21	(0·05)	12·84	(0·12)
1·7	0·450	0·534	(0·02)	19·34	(0·05)	14·49	(0·07)
1·7	0·500	0·725	(0·08)	21·46	(0·01)	16·11	(0·03)
1·7	0·750	2·999	(0·223)	31·98	(0·01)	24·27	(0·02)
1·7	0·800	4·103	(0·400)	34·04	(0·02)	25·87	(0·01)
1·7	0·825	4·809	(0·480)	35·05	(0·03)	26·65	(0·03)
1·7	0·844	5·416	(0·590)	35·84	(0·02)	27·23	(0·02)

Table 3. MD pressure in reduced LJ units at low densities and for $T^* = 1{\cdot}1$–$2{\cdot}6$.

	ρ^*								
T^*	0·025	0·050	0·075	0·100	0·125	0·150	0·200	0·250	0·300
1·1	0·025								
1·2	0·028	0·051	0·069						
1·3	0·030	0·057	0·077	0·094	0·108	0·117			
1·4	0·033	0·062	0·086	0·105	0·125	0·137	0·153	0·164	0·165
1·5	0·036	0·067	0·095	0·120	0·139	0·156	0·188	0·203	0·225
1·6	0·038	0·072	0·103	0·130	0·157	0·177	0·219	0·243	0·285
1·7	0·041	0·078	0·112	0·141	0·171	0·196	0·244	0·285	0·330
1·8	0·043	0·083	0·120	0·155	0·188	0·214	0·274	0·328	0·382
1·9	0·046	0·089	0·130	0·167	0·205	0·239	0·301	0·364	0·433
2·0	0·049	0·095	0·138	0·180	0·216	0·256	0·331	0·406	0·489
2·1	0·051	0·100	0·146	0·191	0·235	0·275	0·366	0·446	0·540
2·2	0·054	0·106	0·154	0·204	0·252	0·298	0·387	0·486	0·594
2·3	0·056	0·111	0·164	0·214	0·263	0·316	0·418	0·526	0·644
2·4	0·059	0·117	0·172	0·227	0·282	0·332	0·449	0·570	0·682
2·5	0·062	0·121	0·180	0·238	0·295	0·354	0·474	0·595	0·747
2·6	0·064	0·127	0·190	0·250	0·312	0·374	0·510	0·642	0·782

in this region too, the comparison and the connection between the two appear as the best alternative with respect to other regions of the phase plane.

Table 3 lists the computer MD data for the pressure, P^*, in reduced LJ units, for the different points of state at low densities. As was stated above, the total number of states is 127—high enough for the fit to be reliable.

3. Results and conclusions

For the EOS, we used three empirical equations: Redlich–Kwong (RK) (Redlich and Kwong 1949), Soave (1972), and Peng–Robinson (PR) (Peng and Robinson 1976).

The RK EOS has the advantage of combining simplicity with reasonable accuracy. It has the form

$$P = \frac{RT}{v-b} - \frac{a}{T^{1/2}[v(v+b)]}, \tag{5}$$

where $a = \Omega_a R^2 T_c^{2\cdot5}/P_c$ and $b = \Omega_b R T_c/P_c$ with $\Omega_a = 0\cdot42748$ and $\Omega_b = 0\cdot08664$. Usually the fit of data to the RK equation is improved by allowing the coefficients Ω_a and Ω_b to vary from substance to substance (Walas 1985). The RK equation is not at all satisfactory for the liquid phase, so it cannot be used by itself for calculating vapour–liquid equilibria. However, it gives good results for gases at low densities and high temperatures.

A modification of the RK EOS was proposed by Soave, replacing the temperature dependence term $a/\sqrt{T}$ by a function $\alpha(T, \omega)$ involving the temperature and the acentric factor ω of a determined system. The Soave equation has the form

$$P = \frac{RT}{v-b} - \frac{a_c\alpha(T,\omega)}{v(v+b)}, \tag{6}$$

where $a_c = \Omega_a R^2 T_c^2/P_c$ and $b = \Omega_b R T_c/P_c$, with Ω_a and Ω_b equal to those of the RK equation, and $\alpha(T, \omega)$ given by

$$\alpha(T,\omega) = \left\{1 + (0\cdot48 + 1\cdot574\omega - 0\cdot176\omega^2)\left[1 - \left(\frac{T}{T_c}\right)^{1/2}\right]\right\}^2. \tag{7}$$

The other empirical EOS that we used is the PR equation

$$P = \frac{RT}{v-b} - \frac{a_c\alpha(T,\omega)}{v(v+b) + b(v-b)}, \tag{8}$$

where $a_c = 0\cdot45724 R^2 T_c^2/P_c$, $b = 0\cdot0778 R T_c/P_c$ and

$$\alpha(T,\omega) = \left\{1 + (0\cdot37464 + 1\cdot54226\omega - 0\cdot26992\omega^2)\left[1 - \left(\frac{T}{T_c}\right)^{1/2}\right]\right\}^2. \tag{9}$$

The data of critical temperature, T_c, critical pressure, P_c, and the acentric factor, ω, for Ar, Kr, CH_4 and N_2 were taken from the literature (DIPPD 1993) and are listed in table 4.

By nonlinear least-squares fitting the empirical EOS data of pressure at low density to the computer simulation results at low density too given in table 3, we were able to determine LJ parameters for the four systems of the study. The results and errors are given in table 5. It is easy to see that the values obtained by forcing agreement between an empirical EOS and the computer simulation data are similar whichever EOS is used, and that the dispersion of the LJ parameters obtained from the three EOS's is smaller than the corresponding values obtained from the second virial and viscosity coefficients reported in the literature (table 1).

Since, for all four systems studied here, the lowest percentage mean deviation of the fit corresponds to the Soave EOS, we can conclude that the Soave EOS is the best macroscopic representation of the molecular LJ interaction. Taking this into account, the LJ parameters we propose are the ones obtained via the Soave EOS: $\sigma = 3\cdot623 \pm 0\cdot035$ Å, $\epsilon/k = 111\cdot84 \pm 0\cdot87$ K for argon; $\sigma = 3\cdot895 \pm 0\cdot037$ Å, $\epsilon/k = 154\cdot87 \pm 1\cdot21$ K for krypton; $\sigma = 4\cdot015 \pm 0\cdot039$ Å, $\epsilon/k = 140\cdot42 \pm 1\cdot11$ K for methane; and $\sigma = 3\cdot919 \pm 0\cdot039$ Å, $\epsilon/k = 91\cdot85 \pm 0\cdot75$ K for nitrogen.

To ensure that the values of the LJ parameters are exact, we tested our results

Table 4. Experimental critical constants and acentric factors for Ar, Kr, CH_4 and N_2.

System	T_c(K)	P_c(Atm.)	Acentric factor (ω)
Ar	150·8	48·34	0·000
Kr	209·4	54·28	0·005
CH_4	190·4	45·40	0·011
N_2	126·2	33·46	0·039

Table 5. LJ parameters obtained by fitting the pressures from the EOS's to the MD pressure results for low density.

System	EOS	σ(Å)	(ϵ/k) (K)	Percentage mean deviation (%)
Ar	Redlich–Kwong	3·572 ± 0·035	113·51 ± 0·88	0·96
	Soave	3·623 ± 0·035	111·84 ± 0·87	0·59
	Peng–Robinson	3·540 ± 0·036	117·52 ± 0·94	1·52
Kr	Redlich–Kwong	3·834 ± 0·037	157·55 ± 1·22	0·96
	Soave	3·895 ± 0·037	154·87 ± 1·21	0·56
	Peng–Robinson	3·805 ± 0·038	162·98 ± 1·31	1·14
CH_4	Redlich–Kwong	3·942 ± 0·039	143·26 ± 1·11	0·96
	Soave	4·015 ± 0·039	140·42 ± 1·11	0·53
	Peng–Robinson	3·920 ± 0·040	147·52 ± 1·19	1·46
N_2	Redlich–Kwong	3·805 ± 0·037	94·95 ± 0·74	0·96
	Soave	3·919 ± 0·039	91·85 ± 0·75	0·38
	Peng–Robinson	3·819 ± 0·040	96·47 ± 0·80	1·13

Table 6. Coexistence properties for the LJ fluid in reduced LJ units (Panagiotopoulos *et al.* 1988).

T	ρ^G	P^G	ρ^L	P^L
1·30	0·21 ± 0·01	0·121 ± 0·006	0·46 ± 0·03	0·126 ± 0·012
1·25	0·152 ± 0·015	0·101 ± 0·006	0·526 ± 0·015	0·108 ± 0·020
1·15	0·072 ± 0·009	0·059 ± 0·003	0·605 ± 0·009	0·059 ± 0·017
1·00	0·0291 ± 0·0006	0·0246 ± 0·0012	0·702 ± 0·006	0·024 ± 0·027
0·90	0·0151 ± 0·0003	0·0123 ± 0·0006	0·758 ± 0·009	0·014 ± 0·037
0·75	0·0031 ± 0·0003	0·0023 ± 0·0003	0·819 ± 0·003	0·019 ± 0·036

with those obtained from other non-traditional procedures. First, we used computer simulation results for the liquid–vapour coexistence curve of a LJ system (Panagiotopoulos *et al.* 1988) and, by fitting to the experimental results (DIPPD 1993) we were able to determine the values of the LJ parameters. The liquid–vapour curve data listed in table 6 were obtained by Panagiotopoulos *et al.* using the Monte Carlo (MC) method. Unfortunately, the number of data is so low (only six) because we only used the results of Panagiotopoulos *et al.* referring to the gas region and not corresponding to the liquid region as well, because the errors in the latter are larger than in the gas (see table 6).

For temperatures between 83·78 K and 150·86 K, the DIPPD experimental results for the liquid–vapour curve of argon can be represented by the expression

$$VP = \exp(A + B/T + C\ln T + DT^{E}), \tag{10}$$

where VP is the vapour pressure in Pa, T the absolute temperature in K, and A, B, C, D and E are coefficients whose values are 42·127, $-1\,093{\cdot}1$, $-4{\cdot}143$, $5{\cdot}72\times10^{-5}$ and 2, respectively.

Making the same nonlinear least-square fit to equation (10) and the MC results for the liquid–vapour coexistence line (table 6), the results obtained for argon system are: $\sigma = 3{\cdot}318$ Å and $\epsilon/k = 119{\cdot}26$ K. The disagreements between these values and those we provided for Ar are 8·42% for σ and 5·74% for ϵ/k, practically the same as the error in the pressure for this region of phase space (table 2).

Also; fitting between computer simulation results for two-dimensional LJ systems (Mulero 1994) and experimental results for krypton adsorpted onto non-porous graphite (Putman and Fort 1975) gives a LJ parameter estimate of $\sigma = 3{\cdot}573$ Å and $\epsilon/k = 142{\cdot}8$ K for the mentioned system. These values again are in good agreement with those we proposed, and their deviations with respect to our data are 8·27% and 7·8% for σ and ϵ/k, respectively.

Therefore, we then tested our LJ data for Ar and Kr by means of another procedure—MC computer simulation of the liquid–vapour coexistence curve and adsorption isotherms—the first being a 3D and the second a 2D quantity. The results are concordant—within the experimental error of the MD computer simulation results (table 2)—with those proposed in the present work.

The new procedure consisting of fitting MD computer simulation results of the pressure at low densities and empirical EOS data is at present the most straightforward, reliable and accurate method of determining LJ parameters for a determined system. To have accurate LJ parameters is the key for a good connection between theoretical LJ and experimental results, and therefore for chemical engineering applications of the LJ model. In the near future, we will determine values of the LJ parameters of other substances of chemical engineering interest.

Acknowledgments

We are grateful to Dr A. Santos for helpful suggestions and to F. Fernández for processing the manuscript. W. A. thanks the Universidad Católica del Norte for its support through a grant. We would like to express our gratitude to the European Union for financial support through the European Network 'Dynamics of Multiphase Flows across Interfaces', contract HCM ERB CHRCT 940481.

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