# Lennard-Jones Force Constants from Viscosity Data: Their Relationship to Critical Properties

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**Lennard-Jones force constants calculated from viscosity values at normal pressures for nearly forty nonpolar organic and inorganic substances have been used to develop relationships for the estimation of these constants from the critical temperature and volume of the substance. The product of the critical temperature and volume $T_c v_c$ was found to correlate linearly with the force constant modulus $\frac{\epsilon}{\kappa}\sigma^3$.**

**When the collision diameter $\sigma$ was plotted against the cube root of the critical volume on log-log coordinates, a straight line of slope 5/4 resulted. The corresponding relationship was found to predict $\sigma$ values with an average deviation of 3.1% when compared with values calculated from viscosity measurements. The temperature force constant $\epsilon/\kappa$ was found to vary as the 5/6 power of the critical temperature, and the resulting relationship produced an average deviation of 10%.**

Current interest in the transport properties of gases at normal pressures is concerned with the calculation of viscosities, thermal conductivities, and self-diffusivities. The force constants for the Lennard-Jones potential $\epsilon/\kappa$ and $\sigma$ represent the basic quantities needed for the calculation of these transport properties for nonpolar gases from the following equations developed by Hirschfelder, Curtiss, and Bird (*8*) for spherical molecules:

$$[\mu]_3 = 266.93 \times 10^{-7} f_\mu^{(3)} \frac{\sqrt{MT}}{\sigma^2\Omega^{(2,2)*}[T_N]} \tag{1}$$

$$[k]_3 = 1989.1 \times 10^{-7} f_k^{(3)} \frac{\sqrt{T/M}}{\sigma^2\Omega^{(2,2)*}[T_N]} \tag{2}$$

$$[D]_2 = 26{,}280 \times 10^{-7} f_D^{(2)} \frac{\sqrt{T^3/M}}{\pi\sigma^2\Omega^{(1,1)*}[T_N]} \tag{3}$$

In Equations (1), (2), and (3) the collision integrals $\Omega^{(1,1)*}[T_N]$ and $\Omega^{(2,2)*}[T_N]$ and the correction factors $f$ are related to the normalized temperature $T_N = T/\frac{\epsilon}{\kappa}$, and their values are available elsewhere (*8*). The subscripts of these transport properties represent the order of the approximation of these values.

Lennard-Jones force constants can be calculated from either experimental viscosity values for gases at atmospheric pressure or from second-virial coefficients. Force constants for a number of substances resulting from both methods are compared by Hirschfelder, Bird, and Spotz (*7*). Although these constants are valuable, they are restricted to specific substances for which experimental viscosities and/or PVT data are available. In order to obtain constants for which such information is not available, Hirschfelder, Curtiss, and Bird (*8*) propose expressions which relate the force constants to the critical values of the substance as follows:

$$\frac{\epsilon}{\kappa} = 0.794\, T_c \tag{4}$$

and

$$\sigma = 0.808\, v_c^{1/3} \tag{5}$$

These equations are based on the assumption conformed to the classical principle of corresponding states. Force constants estimated from these equations are frequently found to vary considerably from those obtained directly from viscosity and/or PVT data. Hirschfelder, Bird, and Spotz (*7*), for example, report for carbon tetrachloride $\frac{\epsilon}{\kappa} = 227$°K. and $\sigma = 5.881$ Å., but Equations (4) and (5) produce values for $\frac{\epsilon}{\kappa} = 417$°K. and $\sigma = 5.406$ Å. from the critical values $T_c = 556$°K. and $v_c = 276$ cc./g.-mole. Therefore this study has attempted to relate the Lennard-Jones force constants of a substance to its critical temperature and volume to produce expressions capable of predicting force constants more accurately.

## LENNARD-JONES CONSTANTS FROM EXPERIMENTAL VISCOSITY DATA

Since the values of the calculated force constants are very sensitive to slight viscosity variations, it was considered necessary to re-examine the consistency of the experimental viscosity data from which $\epsilon/\kappa$ and $\sigma$ could

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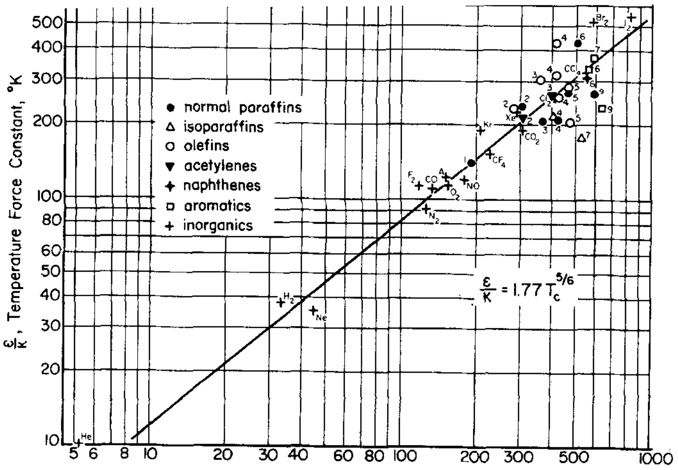

Fig. 1. Relationship of temperature force constant and critical temperature for nonpolar substances.

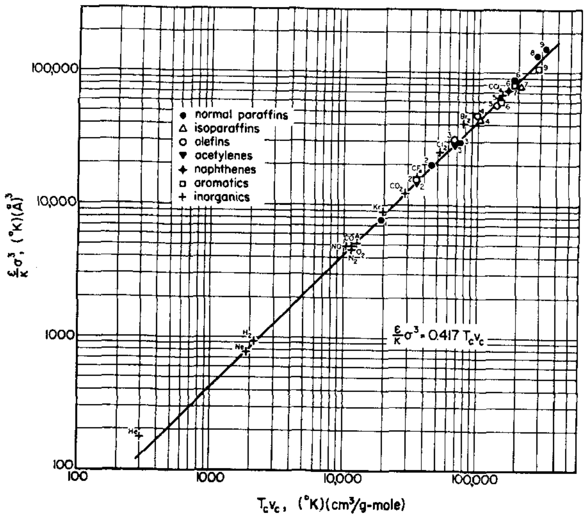

Fig. 3. Relationship between the Lennard-Jones force constant modulus $\epsilon\sigma^3/\kappa$ and the critical constant modulus $T_c v_c$.

be calculated. Consequently a comprehensive survey was undertaken, and viscosity data reported in the literature for twenty-four hydrocarbons, including the normal paraffins up to nonane, several isoparaffins, olefins, acetylenes, naphthenes, and aromatics were compiled. The hydrocarbons considered and the sources of viscosity data are presented in Table 1.

The viscosity data for these hydrocarbons were plotted against absolute temperature on log-log coordinates, from which representative values were selected for the calculation of the force constants. The experimental viscosities from most of the different sources showed good consistency. Viscosity values at two temperature levels can be used with the following expression resulting from Equation (1)

$$\frac{\mu_1}{\mu_2}\sqrt{\frac{T_2}{T_1}} = \frac{\eta_2}{\eta_1} \tag{6}$$

to produce $\epsilon/\kappa$ values by a trial-and-error procedure. In Equation (6) $\eta = \Omega^{(2,2)*}[T_N]/f_\mu^{(3)}[T_N]$ and can be evaluated from $\Omega$ and $f$ values given elsewhere (*8*). The procedure consists of evaluating from experimental viscosity data the left side of Equation (6) and then assuming values of $\epsilon/\kappa$ until the ratio $\eta_2/\eta_1$ became the same. This procedure was used for several pairs of values covering the entire temperature range of the data for each substance. Each calculated $\epsilon/\kappa$ value was used with Equation (1) to produce a corresponding $\sigma$ value. The averaged $\epsilon/\kappa$ and $\sigma$ values for each hydrocarbon are presented in Table 1 and are compared whenever possible with those reported by Hirschfelder, Bird, and Spotz (*7*). Table 1 shows that generally good agreement exists between the values reported by Hirschfelder et al. (*7*) and those obtained in this study. However in several cases a wide variation exists between force constant values. For example Hirschfelder et al. (*7*) report for *n*-butane $\epsilon/\kappa$ = 410°K. based on the viscosity data of Titani (*18*), whereas this study produced a value of $\epsilon/\kappa$ = 208°K. from the combined data of Titani (*18*) and Wobser and Müller (*28*). These differences, although significant, are plausible unless the viscosity data used in the two studies were identical. The establishment of reliable $\epsilon/\kappa$ and $\sigma$ values requires exacting viscosity data covering significant temperature ranges. This is necessary in order to minimize the variations in $\epsilon/\kappa$ values resulting from the sensitivity of the trial-and-error calculations. In order to broaden the range of this investigation to include substances other than hydrocarbons the Lennard-Jones force constants for sixteen nonpolar substances reported by Hirschfelder, Bird, and Spotz (*7*) were included in this study. Consequently correlations have been developed using these values and those obtained for the hydrocarbons.

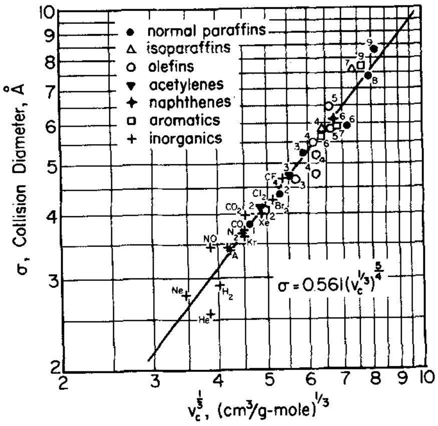

Fig. 2. Relationship of collision diameter and critical volume for nonpolar substances.

### Temperature Force Constant

A dimensional analysis relating the Lennard-Jones force constants $\epsilon/\kappa$ and $\sigma$ with molecular weight and the critical constants $T_c$, $P_c$, and $v_c$ shows that the temperature force constant $\epsilon/\kappa$ should be related to the critical temperature as follows:

$$\frac{\epsilon}{\kappa} = \alpha T_c \tag{7}$$

and that the collision diameter $\sigma$ should depend directly on the cube root of the critical volume:

$$\sigma = \beta v_c^{1/3} \tag{8}$$

Equations (7) and (8) are consistent with Equations (4) and (5) proposed by Hirschfelder, Curtiss, and Bird (*8*), where $\alpha$ = 0.794 and $\beta$ = 0.808.

In order to check the validity of Equation (7) the temperature force constant $\epsilon/\kappa$ was plotted against the critical temperature on log-log coordinates in Figure 1. It is seen from this figure that the hydrocarbon data show considerable scattering. The best relationship appears to be linear and can be expressed analytically as

$$\frac{\epsilon}{\kappa} = 1.77\, T_c^{5/6} \tag{9}$$

Values of $\epsilon/\kappa$ were calculated for the substances examined in this study with Equations (4) and (9). Equation (4) produced an average deviation of 31%, while Equation (9) produced an average deviation of 17%. If the values for helium, bromine, and six hydrocarbons (*n*-hexane, *n*-nonane, isobutylene, pentene-2, 2,2,3-trimethylbutane, and trimethylbenzene) whose force constants show definite inconsistencies are eliminated in these comparisons, these deviations reduce to 23% for

TABLE 1. LENNARD-JONES FORCE CONSTANTS FOR HYDROCARBONS CALCULATED FROM VISCOSITY DATA

|  |  |  | $\epsilon/\kappa$, °K. |  | $\sigma$, Å. |  |  |
|---|---|---|---|---|---|---|---|
|  | $T_c$, °K. | $v_c$, cc./g.-mole | Reference *8* | Present study | Reference *8* | Present study | Viscosity references |
| Normal paraffins |  |  |  |  |  |  |  |
| Methane | 191.1 | 99.0 | 140.5 | 140 | 3.809* | 3.808 | *1, 2, 4, 9, 10, 15, 24, 25, 27, 28* |
| Ethane | 305.5 | 148.1 | 230 | 236 | 4.418 | 4.384 | *1, 5, 9, 17, 18, 24* |
| Propane | 370.0 | 200.4 | 254 | 206 | 5.061 | 5.240 | *1, 2, 17, 18, 22, 24, 28* |
| *n*-Butane | 425.2 | 254.9 | 410 | 208 | 4.997 | 5.869 | *18, 28* |
| *n*-Pentane | 469.8 | 311.0 | 345 | 269 | 5.769 | 6.099 | *19* |
| *n*-Hexane | 547.9 | 368.2 | 413 | 423 | 5.909 | 5.916 | *5, 19* |
| *n*-Heptane | 540.2 | 426.4 |  |  |  |  | *13* |
| *n*-Octane | 569.4 | 490.1 | 320 | 333 | 7.451 | 7.407 | *13* |
| *n*-Nonane | 595.4 | 540 | 240 | 266 | 8.448 | 8.302 | *13* |
| Isoparaffins |  |  |  |  |  |  |  |
| Methylpropane | 408.5 | 263.0 | 313 | 217 | 5.341 | 5.819 | *18* |
| 2,2,3-Trimethylbutane | 531.5 | 394.5 |  | 178 |  | 7.621 | *6* |
| Olefins |  |  |  |  |  |  |  |
| Ethylene | 283.1 | 123.6 | 205 | 230 | 4.232 | 4.066 | *18, 20, 23, 26* |
| Propylene | 365.0 | 180.6 |  | 303 |  | 4.670 | *1, 18, 21, 26* |
| Butene-1 | 419.6 | 239.7 |  | 319 |  | 5.198 | *18* |
| Butene-2 | 430 | 235.7 |  | 259 |  | 5.508 | *18, 21* |
| *i*-Butene | 417.9 | 238.7 |  | 425 |  | 4.776 | *18* |
| *i*-Amylene | 464.8 | 293.0 |  | 283 |  | 5.829 | *18* |
| Pentene-2 | 475.0 | 289.7 |  | 204 |  | 6.476 | *3* |
| Acetylenes |  |  |  |  |  |  |  |
| Ethyne | 309.2 | 112.7 | 185 | 212 | 4.221 | 4.114 | *1, 18, 28* |
| Propyne | 401.2 | 165.7 |  | 261 |  | 4.742 | *18* |
| Naphthenes |  |  |  |  |  |  |  |
| Cyclohexane | 553.2 | 308.3 | 324 | 313 | 6.093 | 6.143 | *5, 14, 19* |
| Aromatics |  |  |  |  |  |  |  |
| Benzene | 562.2 | 260.4 | 440 | 335 | 5.270 | 5.628 | *5, 14, 19* |
| Toluene | 594.0 | 317.7 |  | 377 |  | 5,932 | *14* |
| Trimethylbenzene | 641.2 | 449 |  | 234 |  | 7.706 | *6* |

* Average value.

Equation (4) and 10% for Equation (9)

### Collision Diameter $\sigma$

A plot on log-log coordinates of the collision diameter $\sigma$ vs. the cube root of the critical volume produced a linear relationship of slope 1.25, as shown in Figure 2. The best line through these points can be represented in equation form as

$$\sigma = 0.561 (v_c^{1/3})^{5/4} \qquad (10)$$

With the exception of helium, bromine, and the six hydrocarbons for which meager data exist, Equation (10) represents the relationship between the collision diameter and the critical volume.

Collision diameters have been calculated with Equations (5) and (10). Equation (5) reproduces the values of the collision diameters obtained from viscosity data with an average deviation of 6.3%, while Equation (10) shows an average deviation of 3.1%.

Equations (9) and (10) indicate that the force constants do not follow the relationships predicted by dimensional analysis. Since these equations are dimensionally inconsistent, a dimensionality must be associated with each constant. Despite this dimensional inconsistency the above comparisons indicate that these equations produce more accurate results than Equations (4) and (5), which are dimensionally consistent.

### The Lennard-Jones Force Constant Modulus $\epsilon\sigma^3/\kappa$

Since the variation of $\epsilon/\kappa$ with $T_c$ and that of $\sigma$ with $v_c^{1/3}$ does not follow a direct correspondence as indicated by dimensional analysis, an attempt has been made to consider some combination of the force constants which is dimensionally consistent and capable of providing a better basis for correlation. It can be shown that the product $T_c v_c$ is more directly adaptable to treatment. This deduction follows from the definition of the critical temperature and the critical volume in terms of the van der Waals' constants a and b where $T_c = 8a/27Rb$ and $v_c = 3b$. The product $T_c v_c$ simplifies to the expression $8a/9R$, which requires for its definition only the pressure van der Waals' constant a. The product $T_c v_c$ suggests a direct correspondence to the force constant modulus $\epsilon\sigma^3/\kappa$. A correlation of this modulus with $T_c v_c$ is presented in Figure 3 for all the substances examined in this investigation. An excellent linear relationship between these variables resulted, which can be expressed analytically as follows:

$$\frac{\epsilon}{\kappa} \sigma^3 = 0.417\, T_c v_c \qquad (11)$$

Equation (11) reproduces the product $\epsilon\sigma^3/\kappa$ for all the substances with an average deviation of 6.7% from the corresponding values resulting from viscosity measurements. When helium, bromine, and the six hydrocarbons are excluded, this deviation reduces to 4.9%.

When Equation (10) is combined with Equation (11), the temperature force constant is found to be

$$\frac{\epsilon}{\kappa} = 2.36 \frac{T_c}{v_c^{1/4}} \qquad (12)$$

while a combination of Equations (9) and (11) produces the following relationship for the collision diameter:

$$\sigma = 0.618\, v_c^{1/3} T_c^{1/18} \qquad (13)$$

Equation (12) shows that the temperature force constant $\epsilon/\kappa$ is somewhat dependent upon the critical volume, while the collision diameter in Equation (13) is essentially independent of the critical temperature. Equations (12) and (13) produce for all substances considered except helium, bromine, and the six hydrocarbons average deviations of 10.8% and 3.0%, respectively. From a comparison of these average deviations it can be concluded that Equations (9) and (12) and Equations (10) and (13) can be used to estimate force constants with the same degree of confidence.

## NOTATION

$a$ = pressure van der Waals' constant, (cc./g.-mole)$^2$ atm.
$b$ = volume van der Waals' constant, cc./g.mole
$D$ = self-diffusivity, sq. cm./sec.
$f$ = approximation coefficient
$k$ = thermal conductivity, cal./sec. cm. °K.
$M$ = molecular weight
$T$ = absolute temperature, °K.
$T_c$ = critical temperature, °K.
$T_N$ = normalized temperature, $T/\frac{\epsilon}{\kappa}$
$v_c$ = critical volume, cc./g.-mole

### Greek Letters

$\alpha$ = constant, Equation (7)
$\beta$ = constant, Equation (8)
$\epsilon$ = maximum energy of attraction for Lennard-Jones potential, ergs
$\eta$ = ratio, $\Omega^{(2,2)*}[T_N]/f_\mu^{(3)}[T_N]$
$\kappa$ = Boltzmann constant, 1.3805 × $10^{-16}$ ergs/°K.
$\mu$ = viscosity, g./sec. cm.
$\pi$ = pressure, atm.
$\sigma$ = collision diameter for Lennard-Jones potential, Å.
$\Omega^{(1,1)*}[T_N]$ = collision integral function
$\Omega^{(2,2)*}[T_N]$ = collision integral function

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# Six-Stage Vapor-Liquid Equilibrium Unit

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Accurate vapor-liquid equilibrium data are of great importance in the design of pilot plant and industrial fractional-distillation equipment. Today particularly, when compounds of high purity are required for the petrochemical and many other industries, it is necessary to know the factors that affect the efficient separation of the compounds in multicomponent systems.

Single-plate vapor-liquid equilibrium units have been utilized for many years in the study of binary systems and relatively simple multicomponent mixtures. Myers (*1*) developed a two-plate equilibrium unit patterned after the Othmer design (*2*) to more accurately determine equilibrium data on binary systems. The unit consisted of two glass stills equipped with condensers and lines to connect the two stills.

But for mixtures in which the relative volatilities approach unity or for mixtures which cannot be analyzed accurately, the single- or two-plate equilibrium units are inadequate for the determination of accurate equilibrium data. A versatile multiplate vapor-liquid equilibrium unit is needed.

Herring (*3*) developed a six-plate vapor-liquid equilibrium unit which contained six helix-packed sections of Pyrex glass through which vapor and liquid flowed concurrently on each stage but countercurrently between the stages.

The unit described in the present work is a versatile six-stage unit which can be operated at pressures ranging from atmospheric to 400 lb./sq. in. abs., and at temperatures of 25° to 400°F. Each stage consists of a still equipped with a condenser, a heater, and a mechanical mixer. Auxiliary lines connect the stages, so the terminal samples represent a six-plate separation. Samples of vapor and liquid can be removed from each of the stages so that any number of the stages may be utilized to determine equilibrium relationships. For equilibrium data on binary or multicomponent mixtures that are difficult to determine accurately in a single stage, this unit provides as many as six stages. If the change in composition over the stages is small or if the relative volatility is not affected