International Journal of Thermophysics, Vol. 11, No. 5, 1990

Correlation of High-Pressure Thermal Conductivity, Viscosity, and Diffusion Coefficients for *n*-Alkanes

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Received October 6, 1989

Thermal conductivity, viscosity, and self-diffusion coefficient data for liquid *n*-alkanes are satisfactorily correlated simultaneously by a method based on the hard-sphere theory of transport properties. Universal curves are developed for the reduced transport properties λ^*, η^*, and D^* as a function of the reduced volume. A consistent set of equations is derived for the characteristic volume and for the parameters R_λ, R_η, and R_D, introduced to account for the nonsphericity and roughness of the molecules. The temperature range of the above scheme extends from 110 to 370 K, and the pressure range up to 650 MPa.

KEY WORDS: diffusion; hard-sphere theory; *n*-alkanes; thermal conductivity; viscosity.

1. INTRODUCTION

In recent years, semiempirical schemes based on a consideration of the exact hard-sphere theory of transport properties have been applied for the correlation and prediction of transport properties. These applications have demonstrated [1–5] that the thermal conductivity, viscosity, and self-diffusion coefficients can, separately, be successfully correlated over a wide range of temperatures and pressures. Unfortunately, values which have been reported for the molecular parameter V_0, the volume of close packing, differ significantly between the various authors [6]. For a satisfactory correlation of transport properties of *n*-alkanes using methods based on hard-sphere models, it is essential to establish a consistent set of V_0

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values. This is particularly important when this approach is to be used for calculation of the transport coefficients at other temperatures or for other members of the series where data are, at present, limited. It is also preferable to have an agreed set of V_0 parameters before embarking on the correlation of the transport properties of liquid *n*-alkane mixtures.

In a recent paper, Dymond and Awan [6] produced, for the first time, a successful simultaneous fit of the viscosity and self-diffusion coefficients for liquid *n*-alkanes, and a consistent set of V_0 values was reported. In this paper, this scheme is extended to include the thermal conductivity. Moreover, a consistent set of equations for V_0 is derived which can be used for the prediction of the thermal conductivity, viscosity, and self-diffusion coefficients of the liquid *n*-alkanes.

2. THE CORRELATION METHOD

2.1. Theory

In a dense fluid, the physically realistic Van der Waals description is equivalent to the hard-sphere model for transport properties. For this model, approximate expressions for the coefficients of thermal conductivity, λ, viscosity, η, and self-diffusion, D, are given by the Enskog theory [7], as

$$\lambda_E/\lambda_0 = [1/g(\sigma) + 1.2b/V + 0.755g(\sigma)(b/V)^2] \tag{1}$$

$$\eta_E/\eta_0 = [1/g(\sigma) + 0.8b/V + 0.761g(\sigma)(b/V)^2] \tag{2}$$

$$(nD_E/n_0D_0) = 1/g(\sigma) \tag{3}$$

where $g(\sigma)$ is the radial distribution function at contact given by Carnahan and Starling [8], n is the particle number density, and $b = 2\pi N\sigma^3/3$, where σ is the hard-sphere core diameter. The subscript 0 refers to the low-density hard-sphere coefficients.

Corrections to this theory for correlated molecular motions have been calculated [9, 10] by molecular dynamics studies. In the case of the thermal conductivity and viscosity, however, there are greater uncertainties in the computed corrections associated with the longer computing time necessary for these properties. Corrections to the Enskog theory were therefore determined recently [11] by comparing experimental data for these properties for argon, considered as a smooth hard-sphere system, with predicted values from the Enskog theory and selecting the core sizes that gave the closest agreement with the molecular dynamics corrections.

Calculation of the thermal conductivity, viscosity, and self-diffusion coefficients for any compound at a given temperature and pressure requires just a value for the parameter V_0, the volume of close-packing of spheres, given by $N\sigma^3/2^{1/2}$. This can be derived by the established curve-fitting procedure [2, 4, 12] based on the reduced quantities λ^*, η^*, and D^* defined by the following expressions:

$$\lambda^* = \left[\frac{\lambda_{\mathrm{SHS}}}{\lambda_0}\right]\left[\frac{V}{V_0}\right]^{2/3} \tag{4}$$

$$\eta^* = \left[\frac{\eta_{\mathrm{SHS}}}{\eta_0}\right]\left[\frac{V}{V_0}\right]^{2/3} \tag{5}$$

$$D^* = \left[\frac{nD_{\mathrm{SHS}}}{n_0 D_0}\right]\left[\frac{V}{V_0}\right]^{2/3} \tag{6}$$

where the smooth hard-sphere coefficients are given by the product of the Enskog values and the corrections to the Enskog theory,

$$\lambda_{\mathrm{SHS}} = \lambda_{\mathrm{E}}(\lambda/\lambda_{\mathrm{E}})_{\mathrm{MD}}, \qquad \eta_{\mathrm{SHS}} = \eta_{\mathrm{E}}(\eta/\eta_{\mathrm{E}})_{\mathrm{MD}}, \qquad D_{\mathrm{SHS}} = D_{\mathrm{E}}(D/D_{\mathrm{E}})_{\mathrm{MD}} \tag{7}$$

Values for the reduced quantities λ^*, η^*, and D^* can be calculated for different reduced volumes V/V_0. Values can also be calculated from experiment since on substitution of the hard-sphere expressions:

$$\lambda^* = 1.936 \times 10^7 \left[\frac{M}{RT}\right]^{1/2} \lambda V^{2/3} \tag{8}$$

$$\eta^* = 6.035 \times 10^8 \left[\frac{1}{MRT}\right]^{1/2} \eta V^{2/3} \tag{9}$$

$$D^* = 5.030 \times 10^8 \left[\frac{M}{RT}\right]^{1/2} D V^{-1/3} \tag{10}$$

The determination of V_0 for a given compound from, say, self-diffusion data at a given temperature, can be achieved when a plot of $\log D^*$ from experiment versus $\log V$, where V is the molar volume, is superimposed on the theoretical curve of $\log D^*$ versus $\log(V/V_0)$ by translation along the x axes. Similar results can be obtained using data from the other two properties. It is essential, however, that all curve-fitting should be carried out with respect to the same reference curves.

At high densities the hard-sphere system becomes metastable. In the case of spherical molecules, Chandler [13] has shown that at sufficiently high densities the rough hard-sphere coefficients are proportional to the smooth hard-sphere coefficients:

$$\eta_{\mathrm{RHS}} = C\eta_{\mathrm{SHS}} \tag{11}$$

$$D_{\mathrm{RHS}} = AD_{\mathrm{SHS}} \tag{12}$$

where $C \geqslant 1$ and $A \leqslant 1$. These translational-rotational coupling factors are supposedly density independent and are assumed to have, at most, a very weak temperature dependence.

On the basis of this model and in order to determine absolute values for different *n*-alkanes, Dymond and Awan [6] compared the correlated curves for a given compound with the appropriate smooth hard-sphere curve. To allow for the fact that higher *n*-alkanes are nonspherical, the above ideas were extended to give

$$\eta = R_\eta \eta_{\mathrm{SHS}} \tag{13}$$

$$D = R_{\mathrm{D}} D_{\mathrm{SHS}} \tag{14}$$

where the factors R_η and R_{D} account for nonspherical shape and translational-rotational coupling. This idea made possible horizontal and vertical adjustment of the logarithmic plot, resulting in a range of values of V_0 at the reference temperature.

In extending their work, in this paper a relation similar to Eqs. (13) and (14) has been adopted for the analysis of the thermal conductivity data, as

$$\lambda = R_\lambda \lambda_{\mathrm{SHS}} \tag{15}$$

2.2. Application

In their work, Dymond and Awan [6] proceeded to obtain a successful simultaneous fit of the experimental viscosity and self-diffusion coefficient data. They found from accurate self-diffusion coefficient data for methane [12, 15] and for hexane [14] and from less accurate diffusion coefficients for other *n*-alkanes [16, 17] that, in terms of this model, effects of nonspherical molecular shape and roughness are very small, and indeed, R_{D} may be set equal to unity. As a reference value for V_0 they used the value of $20.825 \times 10^{-6}\ \mathrm{m^3 \cdot mol^{-1}}$ for methane at 140 K. They have therefore accordingly taken R_{D} as 1.0 and determined by curve-fitting the optimum V_0 and R_{n} values that produced the best simultaneous fit to the hard-sphere viscosity and self-diffusion experimental data. The universal curves obtained for the viscosity and self-diffusion coefficients for the *n*-alkanes are [6]

$$\log_{10} \eta^* = \sum_{i=0}^{4} a_{\eta i} (1/V_{\mathrm{r}})^i \qquad \text{with} \qquad \eta_{\exp} = R_\eta \eta \tag{16}$$

and

$$\log_{10} D^* = \sum_{i=0}^{5} a_{\mathrm{D}i} (1/V_{\mathrm{r}})^i \qquad \text{with} \qquad D_{\exp} = R_{\mathrm{D}} D \tag{17}$$

where

$$V_r = V/V_0 \tag{18}$$

The values of the coefficients $a_{\eta i}$ and a_{Di} are shown in Table I. Values were also tabulated for V_0 at different temperatures and for R_η for various *n*-alkanes.

In this work, an attempt was made to express all quantities involved in equation form. However, it proved impossible to fit the characteristic volume V_0 values given by Dymond and Awan [6] for methane, ethane, propane, butane, hexane, octane, dodecane, and hexadecane using a least-squares regression method, based on the Fisher T test, as a function of absolute temperature T and the carbon number C, within the narrow limits necessary to give a satisfactory fit to experimental data. Calculated viscosity and diffusion coefficients are very sensitive to changes in this parameter, varying by up to 20% at the highest densities for a 1% variation in V_0. However, it is often the case that lower members of a homologous series show a somewhat different behavior in their properties from higher members and so the alkanes were split into two groups, methane to butane and pentane to hexadecane. The V_0 values were fitted by the following equations.

CH_4–C_4H_{10},

$$\begin{aligned}10^6 V_0 = {} & -2.574\theta^{-4} + 0.4842C^2\theta^{-3} + 4.311C^{-1}\theta^{-2} \\ & + 3.607\theta^{-1} + 1.982C^{-2} + 14.656C - 0.03418C^3 \\ & - 0.03498C^2\theta^2 + 9.161 \times 10^{-4}C^4\theta^2\end{aligned} \tag{19}$$

C_5H_{12}–$C_{16}H_{34}$,

$$\begin{aligned}10^6 V_0 = {} & 106.677 - 13.655\theta + 1.6266\theta^2 \\ & + (C-6)(18.028 - 1.2\theta)(0.944 + 0.0035C)\end{aligned} \tag{20}$$

Table I. The Coefficients $a_{\lambda i}$, $a_{\eta i}$, and a_{Di}

i	$a_{\lambda i}$	$a_{\eta i}$	a_{Di}
0	1.0655	0.877	3.285
1	−3.538	−3.79208	−31.74261
2	12.121	16.4416	133.0472
3	−12.469	−24.2509	−285.1914
4	4.562	16.3540	298.1413
5	—	—	−125.2472

where

$$\theta = T/100$$

For the higher alkanes, the V_0 values of *n*-hexane were taken as reference values since for this compound there are accurate measurements for both viscosity and self-diffusion coefficients.

In Table II, values for the characteristic volume are given at selected temperatures. Also included are V_0 values calculated from Eq. (20) for other alkanes, including all those with an odd number of carbon atoms, for which accurate viscosity and diffusion data are lacking. These values were used, as described below, for the prediction of thermal conductivities for comparison with experimental measurements.

The quantity R_η was fitted by least-squares regression analysis as a function of *n*-alkane carbon number, giving the expression

$$R_\eta = 0.9858 + 0.0164C + 0.001432C^2 \tag{21}$$

Table II. Typical Values for the Characteristic System Volume V_0 (in $10^{-6}\,m^3 \cdot mol^{-1}$)

T (K)	90	100	110	120	130	140	150	160
CH_4	22.64	22.40	22.01	21.59	21.19	20.82	20.48	20.18
C_2H_6	34.84	34.53	34.14	33.73	33.35	33.00	32.68	32.39
C_3H_8	50.91	49.85	48.96	48.20	47.57	47.02	46.55	46.14
C_4H_{10}						61.20	60.50	59.90
T (K)	200	225	250	275	300	325	350	375
CH_4	19.25	18.83	18.49	18.21	17.96	17.75		
C_2H_6	31.46	31.00	30.60	30.23	29.89	29.56		
C_3H_8	44.85	44.22	43.65	43.11	42.59	42.07		
C_4H_{10}	58.14	57.31	56.57	55.88	55.21	54.54		
C_5H_{12}		69.45	68.26	67.27	66.48	65.90	65.51	65.34
C_6H_{14}		84.19	82.71	81.42	80.35	79.48	78.81	78.34
C_7H_{16}				95.69	94.32	93.16	92.20	91.45
C_8H_{18}				110.06	108.40	106.94	105.69	104.64
C_9H_{20}				124.53	122.57	120.82	119.28	117.93
$C_{10}H_{22}$				139.10	136.85	134.80	132.96	131.32
$C_{11}H_{24}$				153.78	151.23	148.88	146.74	144.80
$C_{12}H_{26}$				168.56	165.71	163.06	160.62	158.37
$C_{13}H_{28}$				183.44	180.27	177.34	174.59	172.05
$C_{14}H_{30}$				198.43	194.97	191.71	188.66	185.81
$C_{15}H_{32}$				213.51	209.75	206.19	202.83	199.67
$C_{16}H_{34}$				228.71	224.63	220.76	217.09	213.62

In the case of the thermal conductivity, the value of R_λ equal to 1.16 for methane was adopted as the reference value for the thermal conductivity curve, as this was obtained using the exact smooth-hard sphere theory [11, 18]. Measurements made above the critical temperature which showed a critical enhancement were not considered since the hard-sphere theory cannot account for this. Consequently, experimental thermal conductivity data for ethane, propane, butane, hexane, octane, dodecane, and tridecane were also taken into account to derive the universal curve, expressed by the equation

$$\log_{10} \lambda^* = \sum_{i=0}^{4} a_{\lambda i}(1/V_r)^i \qquad \text{with} \quad \lambda_{\text{exp}} = R_\lambda \lambda \tag{22}$$

Values for the coefficients $a_{\lambda i}$ are given in Table I. A smooth curve was drawn through the derived values for the factor R_λ against the alkane carbon number and fitted by the equation

$$R_\lambda = 0.1989C + 1.199 - 2.547C^{-1} + 6.404C^{-2} - 4.094C^{-3} \tag{23}$$

The possible variation in R_λ for any given alkane is very small because, in contrast to other transport properties, the calculated thermal conductivity is relatively insensitive to choice of V_0, a change of 1% in this parameter producing a variation of only about 2% at liquid densities. This is a consequence of the significantly smaller effect of increasing pressure on the thermal conductivity at constant temperature. The dependence of R_λ, R_η, and R_D on the size of the alkane molecules is shown in Fig. 1.

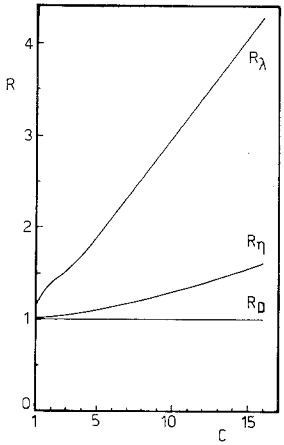

Fig. 1. Variation of the *R* factors with carbon number.

Table III. Comparison of Self-Diffusion Coefficients Calculated by the Present Method with Experimental Values

	No of points			
		Deviations from expt.		
Compound	Total	5–10%	>10%	Ref. No.
CH_4	54	6	—	12, 15
C_2H_6	—	—	—	
C_3H_8	—	—	—	
C_4H_{10}	19	6	9	16, 17
C_5H_{12}	—	—	—	
C_6H_{14}	76	11	6	14, 16, 17
C_7H_{16}	—	—	—	
C_8H_{18}	—	—	—	
C_9H_{20}	—	—	—	
$C_{10}H_{22}$	20	6	3	16, 17
Total	169	29	18	

Table IV. Comparison of Viscosity Coefficients Calculated by the Present Method with Experimental Values

	No of points			
		Deviations from expt.		
Compound	Total	5–10%	>10%	Ref. No.
CH_4	136	—	—	20, 26
C_2H_6	99	—	—	21
C_3H_8	60	1	—	22
C_4H_{10}	79	—	—	23
C_5H_{12}				
C_6H_{14}	43	3	3	19, 24
C_7H_{16}	7	1	—	19
C_8H_{18}	50	15	4	19, 25
C_9H_{20}				
$C_{10}H_{22}$	14	4	—	19, 25
$C_{11}H_{24}$				
$C_{12}H_{26}$	46	11	1	19,25
$C_{13}H_{28}$				
$C_{14}H_{30}$	14	—	—	19
$C_{15}H_{32}$				
$C_{16}H_{34}$	28	—	—	19
Total	576	35	8	

Thus, Eqs. (8)–(10) and (16)–(23) form a consistent set for the correlation of the thermal conductivity, viscosity, and self-diffusion coefficients of the *n*-alkanes. The overall success of this method is demonstrated by the excellence of the fit to the experimental data as shown in Tables III, IV, and V. In the case of self-diffusion, Table III, there is very close agreement with the accurate measurements of Harris [12, 14, 15] and reasonable satisfactory agreement with the data of Bachl and Ludemann [16, 17], for which the reliability is quoted as 10%.

In Table IV, the deviations of the experimental viscosity data from those calculated by this scheme are shown. The agreement is extremely good, with only 8 of nearly 600 points differing by more than 10%. This is particularly satisfactory since *n*-alkane viscosities increase by a factor of about 15 on raising the pressure from 0.1 to 500 MPa. It should also be noted that uncertainties in the density, particularly at high pressures, where the estimated accuracy is often only 0.2%, may well account for such discrepancies.

Table IV also demonstrates the applicability of this scheme for the prediction of transport properties of alkanes. Heptane, decane, and

Table V. Comparison of Thermal Conductivity Coefficients Calculated by the Present Method with Experimental Values

	No. of points			
		Deviations from expt.		
Compound	Total	5–10%	>10%	Ref. No.
CH_4	58	—	—	27
C_2H_6	71	12	—	28
C_3H_8	71	1	—	29
C_4H_{10}	16	—	—	30
C_5H_{12}	68	—	—	31
C_6H_{14}	77	—	—	32, 33
C_7H_{16}	60	—	—	32, 34, 35
C_8H_{18}	81	—	—	33, 36
C_9H_{20}	72	—	—	36, 37
$C_{10}H_{22}$	13	—	—	32
$C_{11}H_{24}$	61	—	—	36, 37
$C_{12}H_{26}$	7	—	—	38
$C_{13}H_{28}$	57	—	—	39
$C_{14}H_{30}$	21	—	—	36
Total	733	13	—	

tetradecane were not included in the original Dymond and Awan analysis [6] and were not used in the determination of Eq. (21) for R_η.

An even more satisfactory situation exists with regard to thermal conductivity, Table V, where less than 2% of the experimental points differed by more than 5% from the present calculated values. Practically all this discrepancy is due to the points on the 110 and 135 K isotherms for ethane. The predictive ability of this scheme is clearly demonstrated for pentane, heptane, nonane, undecane, and tetradecane, which were not used to derive Eq. (23) for R_λ. Experimental measurements for these compounds, with the exception of tetradecane, extend to 650 MPa.

3. CONCLUSIONS

It is shown that a simultaneous fit is possible for thermal conductivity, viscosity, and self-diffusion coefficient data of *n*-alkanes up to 650-MPa pressure, by a correlation method based on consideration of the exact hard-sphere theory of transport properties. Universal curves are developed for the reduced quantities λ^*, η^*, and D^*, by extension of the hard-sphere results. A single equation is given for the characteristic volume V_0 for *n*-alkanes methane to butane as a function of the absolute temperature and the number of carbon atoms in the molecule, with a separate equation for the *n*-alkanes pentane to hexadecane. Equations are also given for the factors R_λ and R_η ($R_D = 1$), which are introduced to account for effects of nonspherical molecular shape and molecular roughness, in terms of carbon number.

The predictive power of this scheme is demonstrated by the very close agreement of calculated viscosity and thermal conductivity coefficients with experimental results for some *n*-alkanes not used in the correlation scheme.

REFERENCES

1. J. H. Dymond, *Chem. Soc. Rev.* **3**:317 (1985).
2. J. H. Dymond and T. A. Brawn, *Proc. 7th Symp. Thermophys. Prop.* (ASME, New York, 1977), p. 660.
3. J. Menashe, M. Mustafa, M. Sage, and W. A. Wakeham, *Proc. 8th Symp. Thermophys. Prop.* (ASME, New York, 1982), p. 254.
4. S. F. Y. Li, G. C. Maitland, and W. A. Wakeham, *High Temp. High Press.* **17**:241 (1985).
5. M. J. Assael, E. Charitidou, and W. A. Wakeham, *Int. J. Thermophys.* **10**:779 (1989).
6. J. H. Dymond and M. A. Awan, *Int. J. Thermophys.* **10**:941 (1989).
7. D. Enskog, *Kungl. Svensks. Vet.-Ak. Handl.* **4**:63 (1922).
8. N. F. Carnahan and K. E. Starling, *J. Chem. Phys.* **51**:635 (1969).
9. B. J. Alder, D. M. Gass, and T. E. Wainwright, *J. Chem. Phys.* **53**:3813 (1970).
10. A. J. Easteal, L. A. Woolf, and D. L. Jolly, *Physica* **121A**:286 (1983).
11. J. H. Dymond, *Physica* **144B**:267 (1987).

12. K. R. Harris and N. J. Trappeniers, *Physica* **104A**:262 (1980).
13. D. Chandler, *J. Chem. Phys.* **62**:1358 (1975).
14. K. R. Harris, *J. Chem. Soc. Faraday Trans. I* **78**:2265 (1982).
15. K. R. Harris, *Physica* **94A**:448 (1978).
16. F. Bachl and H. D. Ludemann, *Physica* **139–140B**:100 (1986).
17. F. Bachl and H. D. Ludemann, Personal communication.
18. J. H. Dymond, *Int. J. Thermophys.* **9**:153 (1988).
19. B. Knapstad, P. A. Skjolsvik, and H. A. Oye, Personal communication (1987).
20. D. E. Diller, *Physica* **104A**:417 (1980).
21. D. E. Diller and J. M. Saber, *Physica* **108A**:143 (1981).
22. D. E. Diller, *J. Chem. Eng. Data* **27**:240 (1982).
23. D. E. Diller and L. J. van Poolen, *Int. J. Thermophys.* **6**:43 (1985).
24. J. H. Dymond, K. J. Young, and J. D. Isdale, *Int. J. Thermophys.* **1**:345 (1980).
25. J. H. Dymond, J. Robertson, and J. Isdale, *Int. J. Thermophys.* **2**:133 (1981).
26. P. S. Van der Gulik, R. Mostert, and H. R. Van der Berg, *Physica* **151A**:153 (1988).
27. U. V. Mardolcar and C. A. Nieto de Castro, *Ber. Bunsenges. Phys. Chem.* **91**:152 (1987).
28. H. M. Roder and C. A. Nieto de Castro, *High Temp. High Press.* **17**:453 (1985).
29. H. M. Roder and C. A. Nieto de Castro, *J. Chem. Eng. Data* **27**:12 (1982).
30. C. A. Nieto de Castro, R. Tufeu, and B. Le Neindre, *Int. J. Thermophys.* **4**:11 (1983).
31. A. M. F. Palavra, W. A. Wakeham, and M. Zalaf, *Int. J. Thermophys.* **8**:305 (1987).
32. M. J. Assael, E. Charitidou, C. A. Nieto de Castro, and W. A. Wakeham, *Int. J. Thermophys.* **8**:663 (1987).
33. S. F. Y. Li, G. C. Maitland, and W. A. Wakeham, *Ber. Bunsenges. Phys. Chem.* **88**:32 (1984).
34. J. Menashe and W. A. Wakeham, *Ber. Bunsenges. Phys. Chem.* **85**:340 (1981).
35. Y. Nagasaka and A. Nagashima, *Ind. Eng. Chem. Fund.* **20**:216 (1981).
36. J. Calado, J. M. N. Fareleira, C. A. Nieto de Castro, and W. A. Wakeham, *Int. J. Thermophys.* **4**:193 (1983).
37. J. Menashe and W. A. Wakeham, *Ber. Bunsenges. Phys. Chem.* **86**:541 (1982).
38. H. Kashiwagi, M. Oishi, Y. Tanaka, H. Kubota, and T. Makita, *Int. J. Thermophys.* **3**:101 (1982).
39. M. Mustafa, M. Sage, and W. A. Wakeham, *Int. J. Thermophys.* **3**:217 (1982).