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ON THE CALCULATION OF PROPERTIES OF GASES AT ELEVATED TEMPERATURES

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Abstract

The role of the potential of intermolecular force in determining properties of gases at elevated temperatures is discussed, and the following points are emphasized.

a. The calculation of accurate values of such properties requires potential parameters which are valid at interaction distances which are important at the temperatures in question.

b. Extrapolation of potentials obtained from low temperature properties for calculation of high temperature properties is, in general, not justified, and leads to values of transport coefficients and second virial coefficients which differ considerably from those calculated from potentials based on the elastic scattering of high energy molecular beams.

c. The high temperature range in which such beam potentials are useful, is not determined by the kinetic energy of the beam particles, but by the small fraction of this energy which is converted into potential energy in the scattering process.

For purposes of illustration, coefficients of viscosity and self-diffusion, isotopic reduced thermal diffusion ratios, and second virial coefficients for helium, argon and nitrogen at 1000°, 5000° and 15000°K have been calculated from extrapolated potentials, Lennard-Jones (12-6) and modified Buckingham (exp-6), and from beam potentials.

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The prediction of equilibrium and non-equilibrium macroscopic properties of matter from appropriate statistical mechanical theories and sufficient information of the molecular constituents (intermolecular forces, spectroscopic constants, etc.) has attracted much attention in the past decade.[1] a In particular, attempts have been made to obtain thermodynamic and transport properties at temperatures and densities which, for the most part, are not readily accessible to experiment, for instance, properties of gases at extremely high temperatures.

It is the purpose of this article to comment on the choice of intermolecular forces for such computations, and the influence of this choice on the numerical results. The illustrations given, limited to several transport coefficients and the second virial coefficients for non-polar gases, may serve as indications of the reliability of past and future calculations in this field. Although available statistical mechanical theories which relate the molecular properties of a system to measurable quantities have distinct regions of applicability which may be, and indeed have been, exceeded, the effects of such misapplications are not discussed here.

Potentials of intermolecular force between atoms or molecules may be determined by three methods: (1) á priori calculations based upon solutions of the Schrödinger equation;[1] (2) interpretation of molecular scattering experiments;[2] and (3) deduction from macroscopic measurements with the aid of a statistical mechanical theory.[1] a The determination of the intermolecular potential by the first two methods requires only the laws of quantum mechanics or classical mechanics.[3] This theoretical simplicity, unfortunately, is difficult to exploit in practice. Except for a few very simple atomic systems exact á priori calculations of

intermolecular potentials are beyond the capacity of the most advanced electronic computers, and molecular scattering experiments, although done, are extremely complex.

The third method has been used extensively despite the fact that many macroscopic properties are not particularly sensitive to the choice of intermolecular potentials. The determination of intermolecular potentials follows this procedure: (1) a transport or equilibrium property is determined as a function of temperature in a given, finite temperature range; (2) an analytic form is assumed for the intermolecular potential and the property under consideration is evaluated á priori with the parameters in the potential function as required by a statistical mechanical theory; (3) the best parameters are chosen on comparison with the experimental results. In Appendix I expressions are given for some properties to which this procedure may be applied: the coefficients of viscosity and self-diffusion, the isotopic reduced thermal diffusion ratio, and the second virial coefficient.

The conditions to be met by a generally valid intermolecular potential for a given system are clear. In principle, all thermodynamic and transport quantities should be determined by such a potential (together with other molecular properties, if necessary) at all temperatures and densities, with a single set of parameters in the potential function. To realize this it is essential to have extensive knowledge of the proper analytical form of the potential. Although the quantum theory provides a reasonably adequate answer to this problem for the interaction leading to attraction between molecules (London dispersion forces) equivalent information has not been obtained for repulsive forces. The inadequacy of simple forms of the intermolecular potential

such as the Lennard-Jones potential may be illustrated as follows. Suppose an estimate of the parameters of the Lennard-Jones potential (Appendix II) is obtained for a given system from data on the second virial coefficient in a temperature range $T_2 - T_1$. If this range is not too large[4] a single set of parameters will suffice to reproduce the measured values to within experimental error (generally of the order of 1%.) If, however, the temperature range is extended it becomes necessary to ascribe an apparent temperature dependence to the potential parameters, namely, more than one set is necessary to reproduce properly the original measurements. Furthermore, the prediction of other macroscopic properties, for instance, self-diffusion coefficients, is not as satisfactory as with potential parameters which were originally determined from self-diffusion measurements.

The conclusions are evident: Information on molecular properties gleaned from measurements of transport or second virial coefficients should be viewed as intermolecular potentials of a very restricted kind which may be used with some confidence as interpolation devices for predicting the property from which they were derived. They may be used as an interpolation device for predicting other properties with varying degrees of success depending on the analytical form of the potential, the number of parameters, and the specific properties involved.

The equations listed in Appendix I appear to show that all portions of the potential function contribute to the calculation of the transport and thermodynamic coefficients at all temperatures. This

is literally true, but it is apparent on closer inspection that a coefficient at a given temperature is determined essentially by a limited region of the potential. Although there is no direct correspondence between a temperature and an intermolecular distance, at low temperatures the potential of forces of attraction contributes to the macroscopic behavior, whereas at sufficiently high temperatures this region of the potential is completely unimportant. Conversely, measurements of macroscopic properties at low temperatures yield information about potentials of forces of attraction, whereas measurements at high temperatures can be interpreted by a well defined potential of repulsive forces combined, in some cases, with a variety of potentials of attractive forces. This shows that if potential functions have been determined from measurements in one temperature interval, their use for predicting properties outside this temperature interval will lead to errors, except for rare, fortuitious coincidences. Stated in other terms, the use of the intermolecular potential as an extrapolation device will lead to unreliable results.

To support the above contentions, the coefficients of viscosity and self-diffusion, isotopic reduced thermal diffusion ratios, and second virial coefficients for helium, argon and nitrogen (Tables I - III) have been calculated as a function of temperature. Three potential energy functions have been used: (1) a Lennard-Jones (12-6) potential evaluated from measured transport properties in a temperature interval near room temperature; (2) a modified Buckingham (exp - 6) potential evaluated from various bulk properties below 1000°K; and (3) a potential derived from the interpretation of experiments on the scattering of molecular beams. The analytic forms and the parameters of the potentials

are given in Appendix II; the three potentials for the argon system are shown graphically in Fig. I, and numerical values at selected separation distances are given in Table V.

Of the three potentials, that derived from scattering experiments requires further comment. The description of a molecular beam apparatus for the study of scattering of neutral atoms and molecules, the measurements of total collission cross-sections as a function of velocity, and the intermolecular potential deduced from these experiments have been reported in a series of articles.[2] A potential function representing repulsion invariably accounts adequately for the observed scattering cross-sections. The range of applicability of the potential as an interpolation device can be inferred approximately from a simple rule, as shown in Appendix III. The accuracy of these potentials is of the order of 20% as estimated from internal consistency and comparison with quantum mechanical calculations,[1]d as well as with potentials derived from measurements of thermodynamic functions at high temperatures.

Some pertinent conclusions may be deduced from the calculations presented here. Fig. I and the entries in Table 1A show that appropriate potential functions may differ significantly from "extrapolated" potential functions. (An "extrapolated" potential function is one determined from properties in one temperature interval corresponding approximately to a given range of intermolecular distance, which has been extrapolated to another range of distance corresponding to a widely different temperature interval.) For example, the Lennard-Jones potential for argon determined from the temperature dependence of the viscosity as a function of temperature from 80°K to 300°K, differs

from the potential derived from molecular beam experiments in its appropriate range (2.18 Å $\leq$ r $\leq$ 2.69 A) by as much as a factor of seven.

Errors of this order of magnitude in intermolecular potentials are not reflected directly as errors of equal order in the same macroscopic properties. For instance, comparison of viscosities of argon evaluated from the two potentials cited, Table II, shows a maximum deviation of only 27%. The calculation of quantities such as vibrational relaxation times,[5] reaction rate constants, and barriers to intramolecular rotation,[6] may be more sensitive to the choice of intermolecular potential.

As suggested in the introductory paragraphs, the present discussion has been in the nature of a guide for those interested in calculating properties of gases at high temperatures, or in assessing the usefulness of such calculations made by others. No attempt has been made to present a complete review of the very extensive literature associated with topics mentioned in the discussion, or to repeat derivations of fundamental relations which can be readily found elsewhere.

Tables I - III. High temperature gas properties

Temp °K	$10^4[\eta]_1$ g cm^{-1} sec^{-1}			$10^4\rho[D_{11}]_1$ g cm^{-1} sec^{-1}			$[k_T^*]_1$			B(T) cc mole^{-1}		
	12-6	exp-6	beam	12-6	exp-6	beam	12-6	exp-6	beam	12-6	exp-6	beam
					I. Helium							
1000	4.3	4.4	4.4	5.9	6.6	6.4	0.57	0.42	0.33	10.0	9.1	17.0
5000	12.3	---*	16.3	16.9	---*	24.4	0.54	----*	0.33	8.0	---*	7.6
15000	25.6	---*	41.0	35.2	---*	61.5	0.54	----*	0.33	6.0	---	4.3
					II. Argon							
1000	5.4	5.4	5.6	7.1	7.3	8.1	0.56	0.51	0.41	20.9	21.2	48.6
5000	15.2	15.6	18.6	20.6	21.7	26.6	0.57	0.50	0.41	26.1	24.6	27.2
15000	30.7	33.2	42.0	42.0	47.4	60.1	0.57	0.50	0.41	22.8	20.3	18.3
					III. Nitrogen							
1000	4.0	4.0	3.8	5.4	5.3	5.5	0.57	0.58	0.35	29.4	31.3	70.1
5000	11.5	11.2	13.2	15.6	15.1	19.1	0.57	0.60	0.35	31.7	32.1	36.1
15000	23.1	----*	30.9	31.7	----*	44.8	0.57	----*	0.35	27.1	----*	22.9

Values of collision integrals and reduced second virial coefficients have not been tabulated for values of T as large as those required for these entries.

Table V. Magnitudes of various potentials for the argon system

Lennard-Jones (12-6)		Modified Buckingham (exp-6)		Beam K/r^s	
r, Å	$\phi(r)\times10^{15}$, ergs	r, Å	$\phi(r)\times10^{15}$, ergs	r, Å	$\phi(r)\times10^{15}$, ergs
(2.18)	(14110)	(2.18)	(4819)	2.18	2058
(2.60)	(1473)	(2.60)	(935)	2.30	1317
(3.10)	(98.2)	3.10	93.6	2.43	833
3.60	-13.4	3.60	-12.0	2.55	558
3.837	-17.1	3.866	-17.0	2.69	357
4.30	-12.9	4.30	-13.1		
4.80	- 7.76	4.80	- 7.69		
		5.30	- 4.41		

Values in parentheses have been extrapolated beyond the estimated range of validity of the parameters listed in Table IV.

Appendix I

A. The expressions, to the first approximation, for the coefficient of viscosity, $[\eta]_1$, the coefficient of self-diffusion, $[D_{11}]_1$, and the isotopic reduced thermal diffusion ratio, $[k_T^*]_1$, as obtained from solutions of the Maxwell Boltzmann equation of transport for dilute gases, are as follows:

$$[\eta]_1 = \frac{5}{16N}\left(\frac{MRT}{\pi}\right)^{1/2} \frac{1}{r_m^2 \Omega^{(2,2)*}(T^*)}$$

$$[D_{11}]_1 = \frac{3}{8N}\left(\frac{MRT}{\pi}\right)^{1/2} \frac{1}{\rho\, r_m^2 \Omega^{(1,1)*}(T^*)}$$

$$[k_T^*]_1 = \frac{15}{16}\,\frac{(6C^* - 5)}{A^*}$$

where

$$\Omega^{(\ell,n)*}(T^*) = \frac{2}{(n+1)!\; T^{*n+2}} \int_0^\infty e^{-g^{*2}/T^*}\, g^{*2n+3}\, Q^{(\ell)*}\, g^*\, dg^*$$

$$Q^{(\ell)*} = \frac{2}{\left[1 - \frac{1 + (-1)^\ell}{2(1+\ell)}\right]} \int_0^\infty (1 - \cos^\ell \chi)\, b^*\, db^*$$

$$\chi(g^*, b^*) = \pi - 2b^* \int_{r_o^*}^\infty \left[1 - b^{*2}/r^{*2} - \phi^*(r^*)/g^{*2}\right]^{-1/2} dr^*/r^{*2} =$$

relative angle through which initial relative velocity is turned by collision

$$A^* = \Omega^{(2,2)*}(T^*)/\Omega^{(1,1)*}(T^*)$$

$$C^* = \Omega^{(1,2)*}(T^*)/\Omega^{(1,1)*}(T^*)$$

$T^* = kT/\epsilon$ = reduced temperature

$-\epsilon$ = minimum value of intermolecular potential

$g^{*2} = 1/2\ \mu g^2/\epsilon$ (g = initial relative speed and μ = reduced mass of colliding particles)

$b^* = b/r_m$ = reduced impact parameter

r_m = separation distance at which intermolecular potential is a minimum

$\phi^*(r^*) = \phi(r)/\epsilon$ = reduced intermolecular potential

r_o^* = reduced distance of closest approach = smallest positive root of $[1 - \phi^*(r_o^*)/g^{*2}]r_o^{*2} = b^{*2}$

N = Avagadro's number

M = molecular weight

T = absolute temperature

R = gas constant per mole

k = gas constant per molecule

ρ = mass density of molecules

B. The second virial coefficient is related to the potential of intermolecular force by the equation

$$B^*(T^*) = -\frac{1}{T^*}\int_0^\infty r^{*3}\,\frac{d\,\phi^*(r^*)}{dr^*}\,e^{-\phi^*(r^*)/T^*}\,dr^*$$

$$= -3\int_0^\infty r^{*2}\,[e^{-\phi^*(r^*)/T^*} - 1]\,dr^*$$

where

$$B^*(T^*) = \frac{B(T)}{2/3\ \pi N r_m^3} = \text{reduced second virial coefficient}$$

Appendix II

The Lennard-Jone (12-6) potential has the analytical form

$$\phi(r) = \epsilon[(r_m/r)^{12} - 2(r_m/r)^6]$$

and the modified Buckingham (exp-6) potential has the form

$$\phi(r) = \frac{\epsilon}{1 - 6/\alpha}\left\{6/\alpha \exp[(1 - r/r_m)] - (r_m/r)^6\right\} \qquad r \geqslant r_{max}$$

$$\phi(r) = \infty \qquad r \leqslant r_{max}$$

where ϵ and r_m are parameters which specify the magnitude and position of the minimum potential energy, α is a parameter which permits variation of the steepness of the repulsive portion of the potential, and r_{max} is the value of r where $\phi(r)$ has a (spurious) maximum. The potentials derived from scattering experiments are represented by

$$\phi(r) = K/r^s$$

where K and s are parameters. The values of the parameters used in the calculation of $[\eta]_1$, $[D_{11}]_1$, $[k_T^*]_1$, and B(T) are given in the following table.

Table IV. Numerical values of potential parameters

System	ϵ/k °K	r_m Å	α	K/k °K-Å^s	s	Source
Helium	10.22	2.891				(1)a
	9.16	3.135	12.4			(7)a
				5.471×10^4	5.94	
Argon	124	3.837				(1)a
	123.2	3.866	14.0			(7)b
				9.855×10^6	8.33	(2)c
Nitrogen	91.5	4.132				(1)a
	101.2	4.011	17.0			(7)b
				6.911×10^6	7.27	(2)d

The very limited region of the intermolecular potential which influences properties of gases at given temperatures can readily be inferred from the following analysis based on material previously published by LeFevre.[8]

It will be assumed that at very high temperatures the potential of intermolecular force may be represented by $\phi(r) = K/r^s = \epsilon(r_m/r)^s$ where ϵ and r_m are now to be regarded merely as energy and distance parameters which, together with s, characterize the potential. For a potential of this form the reduced collision integral $\Omega^{(2,2)*}(T^*)$ may be written

$$\Omega^{(2,2)*}(T^*) = W_o(s)/T^{*2/s} \qquad (1)$$

so that

$$W_o(s) = 1/T^{*4+2/s} \int_0^\infty e^{-g^{*2}/T^*} g^{*2n+3} \left[\int_0^\infty \sin^2\chi\, b^*\, db^*\right] dg^*. \qquad (2)$$

Le Fevre and others[9] have evaluated $W_o(s)$ for selected values of s from 2 where $W_o(2) = 1.0557$ to ∞ where $W_o(\infty) = 1$, so that for the present purpose $W_o(s)$ may be set equal to unity for all values of s. In addition, for <u>hard spheres</u> for which $s = \infty$, $T^{*2/s} = 1$ so that $\Omega^{(2,2)*}(T^*) = 1$. If, therefore, for <u>any</u> value of T^* we set

$$R^2 = \Omega^{(2,2)*}(T^*) \qquad (3)$$

by definition it follows that Rr_m is the equivalent hard sphere diameter, σ_o, which, at a given temperature, gives the same value of the viscosity as the actual inverse power potential. From Eqs. (2) and (3) it follows directly that

$$T^* = kT/\epsilon = \left[\sqrt{W_o(s)}\,/\,R\right]^s = (1/R)^s = (r_m/\sigma_o)^s \qquad (4)$$

or, since $\phi(r) = \epsilon(r_m/r)^s$,

$$kT = \phi(\sigma_o) \quad . \tag{5}$$

Equation (5) states that, to the extent that $W_o(s)$ may be set equal to unity, for $\phi(r) = K/r^s$, at sufficiently high temperatures, it is effectively the single value of the potential energy corresponding to $\phi(r)$ at $r = \sigma_o$ that determines the magnitude of the coefficient of viscosity at the temperature T. Thus, at 1000°K, a potential energy of about 0.1 ev determines the magnitude of the viscosity, and at 10,000°K, a potential energy of about 1 ev. In experiments on the scattering of high velocity neutral particles, it is the range of the derived potential energy, not the kinetic energy of the beam particles, which fixes the range of temperature for which gas properties may be calculated justifiably. For example, if beam particles with kinetic energies in the range 100 ev to 1000 ev are elastically scattered through a relative angle of the order of 10^{-3} radians, the deduced interaction potentials for the distance of closest approach will be in the range of 0.1 ev to 1 ev. The appropriate temperature range corresponding to this range of potential energy will be 1000°K to 10,000°K, and not temperatures (which would be about 1000 times larger) incorrectly associated with the beam energies.

The relations based on an inverse power potential and applied to the coefficient of viscosity, are very nearly the same for other potential forms applied to viscosity and other gas properties at elevated temperatures.

References and Footnotes

(1) a. Hirschfelder, Curtiss, and Bird, "Molecular Theory of Gases and Liquids" (John Wiley and Sons, Inc., New York, 1954); b. H. J. James and A. S. Coolidge, J. Chem. Phys. 1, 825 (1933); c. P. Rosen, J. Chem. Phys. 18, 1182 (1950); d. Mason, Ross, and Schatz, J. Chem. Phys. 25, 626 (1926).

(2) a. Amdur, Glick, and Pearlman, Proc. Am. Acad. Arts. Sci. 76, 101 (1948); b. Amdur and Harkness, J. Chem. Phys. 22, 664 (1954); c. Amdur and Mason, J. Chem. Phys. 22, 670 (1954); d. Amdur, Mason and Jordan, J. Chem. Phys. 27, 527 (1957). A number of other publications have appeared in J. Chem. Phys. which deal with derivation of potential energy information from the scattering of molecular beams.

(3) Under some circumstances scattering experiments may be interpreted according to classical mechanics.

(4) The temperature range must, of course, not be too small. It is not possible to derive information concerning the form and magnitude of the intermolecular potential from measurements at a single temperature. This can be verified from the equations given in Appendix I.

(5) Schwartz, Slawsky, and Herzfeld, J. Chem. Phys. 20, 1591 (1952); R. N. Schwartz and K. F. Herzfeld, J. Chem. Phys. 22, 767 (1954).

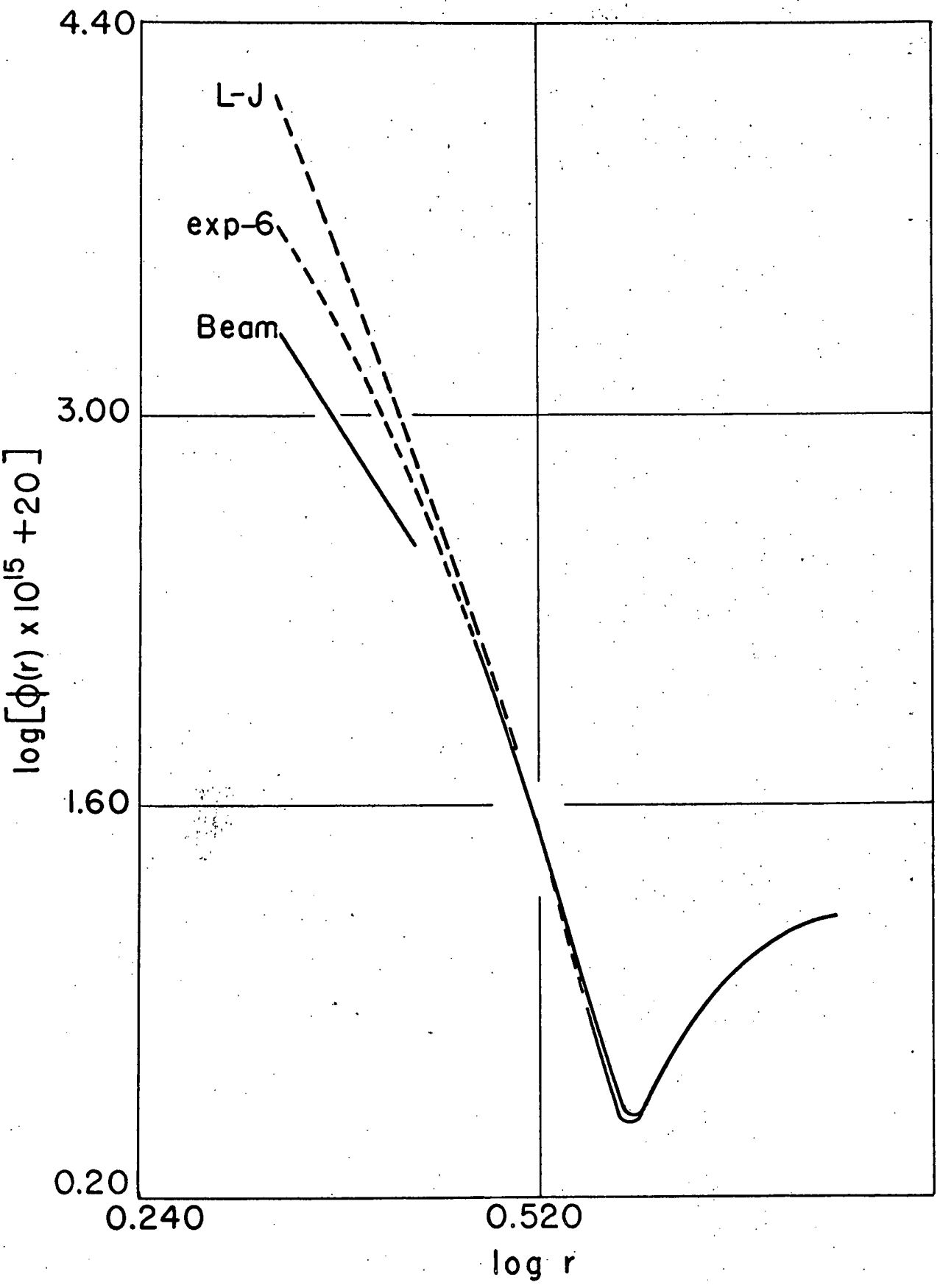
(6) E. A. Mason and M. M. Kreevoy, J. A. C. S. 77, 5808 (1955); M. M. Kreevoy and E. A. Mason, J. A. C. S. 79, 4851 (1957).

(7) a. Mason and Rice, J. Chem. Phys. 22, 522 (1954); b. J. Chem. Phys. 22, 843 (1954).

(8) E. J. LeFevre, "The Classical Viscosity of Gases at Extreme Temperatures", Paper 3, Section 3 in "Conference on Thermodyanmics and the Transport Properties of Fluids" (Institution of Mechanical Engineers, London, 1957).

(9) See reference (8) for a bibliography on this topic.

Fig. 1. Various intermolecular potentials for the argon system. Dashed portions of the curves represent extrapolations corresponding to parenthetical values in Table V.


4.40
3.00
1.60
0.20
L-J
exp-6
Beam
log[φ(r) x 10^15 +20]
0.240
0.520
log r