Calculation of the Mean Force Constants
of the Rare Gases and the Rectilinear
Law of Mean Force.*

MASTER

Myung W. Lee and Jacob Bigeleisen

Department of Chemistry

University of Rochester

Rochester, New York 14627

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

*Research supported in part by Contract No. EY-76-S-02-3498
with the U.S. Energy Research and Development Administration.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED 88

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Abstract

The mean energies, $\langle U \rangle$, and the mean force constants, $\langle \nabla^2 U \rangle$, have been calculated for liquid argon and liquid krypton using the WCA perturbation theory, and for gaseous argon and krypton along the coexistence line by solution of the PY equation for the radial distribution function. Calculations have been made for the Lennard-Jones, Barker-Henderson and Maitland-Smith potentials. There is little difference in the values of $\langle U \rangle$ and $\langle \nabla^2 U \rangle$ calculated for the three potentials. The calculated values are in good agreement with experimental data. Correlation of the calculated values of $\langle \nabla^2 U \rangle$ for the liquid and gas leads to an empirical relationship between $\langle \nabla^2 U \rangle$ and the density of the phase along the coexistence line. When the latter is combined with the law of rectilinear diameters of the density, one obtains the rectilinear law of mean force, which is in good agreement with experimental data on argon. It is shown that the scaling exponent for the mean force constant, $\langle \nabla^2 U \rangle_l - \langle \nabla^2 U \rangle_g$, is larger than the scaling exponent of the density below the critical temperature and becomes equal to it at the critical temperature. The rationale for the rectilinear law of mean force is provided by an expansion of the radial distribution function of the liquid in powers of the density and the use of the WCA approximation to the radial distribution function.

Introduction

The logarithm of the ratio of the vapor pressures of the isotopes of any of the rare gases, other than helium, or the liquid-vapor isotope separation factor is of the order of 10^{-2} to 10^{-3} at the triple point of the substance. Improvements in recent years in the measurement of differential vapor pressures and isotope ratios have led to quantitative data on the vapor pressure isotope effect for neon,¹⁻⁵ argon⁶⁻⁸ and krypton⁹ as a function of temperature. The most extensive data exist for argon where the measurements cover the range from the low temperature solid (63°K)⁷ to the critical temperature (150°K).⁸ The isotope separation factor, α , can be related to the isotopic vapor pressure ratio through small corrections associated with the equations of state of the liquid and vapor phases.^{3,10} The liquid-vapor isotope fractionation factor for a near classical fluid is directly related to the difference in the means of the Laplacian of the potential energy in the liquid and vapor phases respectively.^{11,12}

$$\ln \alpha = \frac{1}{24} (h/kT)^2 \left(\frac{1}{m'} - \frac{1}{m} \right) [\langle \nabla^2 U \rangle_c - \langle \nabla^2 U \rangle_g] \quad (1)$$

where m' and m are the masses of the light and heavy isotopes respectively. For a spherically symmetric potential, $U = U(r_1, r_2, \dots, r_N)$, which is approximated as a sum of pair potentials, $U_{ij} = U(r_{ij})$, the mean potential energy, $\langle U \rangle$, and mean force constant, $\langle \nabla^2 U \rangle_i$ are respectively

$$\langle U \rangle = 2\pi\rho \int g_{ij}(r) r^2 U_{ij} dr \quad (2)$$

$$\langle \nabla^2 U \rangle_i = 4\pi\rho \int g_{ij}(r) r^2 \nabla^2 U_{ij} dr \quad (3)$$

where ρ is the number density and g_{ij} is the radial distribution function.

Excellent agreement has been obtained between theory and experiment for both the mean potential energy and mean force constant for liquid argon by molecular dynamics calculations with the L-J (12-6) potential.¹³ Mandel¹⁴ has shown the Weeks-Chandler-Anderson perturbation theory also yields excellent results over the entire temperature range of liquid argon with the L-J potential. Calculations on krypton are not as satisfactory.¹⁵ The major contribution of the integral in Eq. (3) comes from the area under the first peak in the radial distribution curve and the repulsive part of the pair potential.¹⁶ Mandel found an inverse 18.5 power law for the effective repulsive potential in liquid krypton. Recently several effective two body potentials have been proposed for liquid argon and krypton and argon-krypton pairs.¹⁷⁻¹⁹ These potentials have been constructed from a variety of experimental data including molecular scattering, vibrational states of the dimer, and thermodynamic data related to $\langle U \rangle$ and $\langle \partial U / \partial r \rangle$. These recent potentials have repulsive potentials with power laws between 12 and 14 for $\sigma < r < r_{\min}$, contrary to Mandel's findings. In addition, the steepness of the repulsive branch of the potential falls as r decreases.

We have, therefore, calculated mean force constants, $\langle \nabla^2 U \rangle$, for argon and krypton for the recent LHB¹⁷ and MS¹⁸⁻¹⁹ potentials and compare them with experiment in this paper. Simultaneously we make a comparison of $\langle U \rangle$ and $\langle \nabla^2 U \rangle$ calculated by these potentials with the L-J potential.

In our work on the rare gases we have found that $\langle v^2 U \rangle$ is rather insensitive to the temperature coefficient of the integral in Eq. (3). Thus $\langle v^2 U \rangle$ is to a very good approximation proportional to the density of the fluid. We have now found a more general dependence of $\langle v^2 U \rangle$ on the density which is applicable to both liquid and vapor states along the coexistence line. It is related to the law of rectilinear diameters for the density and may be called the rectilinear law of mean force. We shall show that the WCA perturbation theory for the liquid does in fact suggest the empirical dependence of $\langle v^2 U \rangle$ on density.

Calculation of $\langle U \rangle$ and $\langle \nabla^2 U \rangle$

The Weeks-Chandler-Anderson theory approximates the repulsive part of the potential by

$$U_0(r) = U(r) + \epsilon \quad r \leq r_m \quad (4)$$

$$= 0 \quad r > r_m \quad (5)$$

The repulsive part of the potential dominates the liquid structures at moderate to high number densities. In Eqs.(4) and (5) $U(r)$ is any reference potential, e.g. L-J, L-H-B,¹⁷ M-S,¹⁸ etc., and ϵ is the well depth. The radial distribution function $g(r)$ is calculated from the relation

$$g(r) = Y_d(r) \exp (-U_0(r)/kT) \quad (6)$$

where Y_d is an analytical solution of the Percus-Yevick²⁰ equation for hard spheres.^{21,22}

The results of the calculations of $\langle U \rangle$ and $\langle \nabla^2 U \rangle$ for liquid argon and liquid krypton are given in Tables I and II respectively where comparisons are made with experimental data. There is little difference in the values of $\langle U \rangle$ and $\langle \nabla^2 U \rangle$ for the liquid calculated respectively from the Lee-Henderson-Barker and Maitland-Smith potentials for both argon and krypton. The Percus-Yevick equation is used to calculate $g(r)$, the radial distribution function in the gas, directly and then $\langle U \rangle$ and $\langle \nabla^2 U \rangle$ through Eqs.(2) and (3). We can compare either calculated values of $\langle U \rangle_l - \langle U \rangle_g$ with experiment or $\langle U \rangle_l$ calculated with an experimental value of $\langle U \rangle_l$ derived from an observed value of $\langle U \rangle_l - \langle U \rangle_g$ and either experimental or calculated values of $\langle U \rangle_g$. From the

values of $\langle v^2 U \rangle_c$ and $\langle v^2 U \rangle_g$ we calculate $T^2 \ln \alpha$ for Ar and Kr and compare them with experiments in Figs. 1 and 2. The calculated values of $\langle U \rangle_g$ for argon and krypton given in Tables I and II respectively are in good agreement with experiment. In the case of argon the L-H-B and M-S potentials agree with the isotopic separation factors as well as Mandel's calculation with the L-J potential. Our calculations for krypton show little difference between these three potentials for the isotope separation factor. The experimental data cover the narrow temperature range 116-130°K. Over this temperature range the calculated separation factor for $^{80}\text{Kr}/^{84}\text{Kr}$ deviates at most (M-S potential) from experiment by ten per cent. The L-J does somewhat better.

Density Dependence of $\langle v^2 U \rangle$

Lee, Fuks and Bigeleisen⁷ found $\langle v^2 U \rangle_c / \rho_c$ to be independent of temperature in the range $0.7 < T^* = (kT/\epsilon) < 0.84$ for liquid argon. Phillips, Linderstrom-Lang and Bigeleisen⁸ found the quantity $(\langle v^2 U \rangle_c - \langle v^2 U \rangle_g) / (\rho_c - \rho_g)$ constant in the range $0.55 < T^* = T/T_{cr} < 0.8$.

We have correlated our data for $\langle v^2 U \rangle_c$ and $\langle v^2 U \rangle_g$, calculated respectively by the NCA and PY radial distribution functions for the L-J, L-H-B and M-S potentials, for argon and krypton with the density along the coexistence line. We shall use reduced units, $v^* = v/v_{cr}$, $U^* = U/RT_{cr}$, and $\rho^* = \rho/\rho_{cr}$. The data for argon and krypton in Table III show that $\langle v^2 U^* \rangle / [\rho^* (1 + \rho^*)]$ is the same along the coexistence line for argon and krypton liquid and vapor. It is a universal constant. In Fig. 3 we plot $\ln [\langle v^2 U^* \rangle / \rho^*]$ vs. $\ln (1 + \rho^*)$ and obtain a linear relationship over the entire range of the coexistence curve.

Along the coexistence line the densities of liquid and vapor obey the following functional form^{23,24}

$$\rho_l^* = 1 + 3/4 (1 - T^*) + 7/4 (1 - T^*)^{1/3} \quad (7a)$$

$$\rho_g^* = 1 + 3/4 (1 - T^*) - 7/4 (1 - T^*)^{1/3} \quad (7b)$$

Substitution of Eqs. (7a) and (7b) into the quantity $\langle v^2 U^* \rangle / \rho^* (1 + \rho^*)$ gives

$$\frac{\langle v^2 U \rangle_l - \langle v^2 U \rangle_g}{(\rho_l - \rho_g)} = \frac{3}{2} (1.72 \times 10^{-6}) RT_{cr} \rho_{cr}^{1/3} (3 - T^*) \quad (8)$$

The quantity 1.72×10^{-6} in Eq. (8) is obtained from the intercept

of the line in Fig. 3. Eq.(8) predicts an 18% decrease in $\langle v^2 U \rangle_L - \langle v^2 U \rangle_g / (\rho_L - \rho_g)$ from the triple point to the critical temperature. The experimental data show a 17% decrease over that temperature range. A comparison of the predictions of Eq.(8) with the experimental data of Phillips, Linderstrom-Lang and Bigeleisen⁸ and Lee, Fuks, and Bigeleisen⁷ is given in Fig. 4. Equation (8) involves no empirical constants related to $\langle v^2 U \rangle$. It utilizes a reasonable potential, perturbation theory and the law of rectilinear diameters. Equation (8) is consistent with the experimentally determined temperature dependence of the isotope fractionation factor, $\ln \alpha$. The theoretical line is systematically higher than the experimental values of $T^2 \ln \alpha / (\rho_L - \rho_g)$ by six per cent. If one disregards the four points closest to T_c , the slopes are the same within experimental error.

Equation (8) provides a basis for the comparison of the scaling law exponent for $\langle v^2 U \rangle_L - \langle v^2 U \rangle_g$ with that for $\rho_L - \rho_g$. Let

$$\langle v^2 U \rangle_L - \langle v^2 U \rangle_g = a(1 - T^*)^\alpha \quad (9)$$

and

$$\rho_L - \rho_g = b(1 - T^*)^\beta \quad (10)$$

Then

$$(\alpha - \beta) \ln(1 - T^*) = \ln C + \ln(3 - T^*) \quad (11)$$

where C is a constant related to a , b , and the coefficient of $(3 - T^*)$ in Eq.(8). From which it follows

$$\alpha - \beta = (1 - T^*) / (3 - T^*) \quad (12)$$

At $T^* = 1$, $\alpha = \beta$ and the scaling exponent for $\langle \nabla^2 U \rangle$ is the same as the density exponent β . As one moves away from the critical temperature, e.g. $(1 - T^*) = 0.125$, Eq. (12) predicts $\alpha > \beta$ and $\alpha - \beta = 0.04$ in good agreement with the experimental value for argon which has been found to be²³ 0.06 ± 0.02 . Farther away from the critical temperature, Eqs. (9) and (10) fail.

We will now show that the empirical result shown in Fig. 3

$$\langle \nabla^2 U^* \rangle = C \rho^* (1 + \rho^*), \quad (13)$$

where C is an empirical constant equal to 1.72×10^{-6} , can be rationalized in terms of the WCA perturbation theory. We expand Y_d , the unweighted hard sphere radial distribution function, in powers of the density. Then $Y_d(r) = 1 + \rho \beta(\rho, r)$ (14)

The mean force constant, $\langle \nabla^2 U \rangle$, is then

$$\langle \nabla^2 U \rangle = 4\pi \rho \int_0^\infty (1 + \rho \beta(\rho, r)) (\nabla^2 U) e^{-U_0(r)/kT} r^2 dr \quad (15)$$

$$\langle \nabla^2 U \rangle = A \rho^* [1 + \rho^* B/A] \quad (16)$$

where

$$A \equiv 4\pi \rho_{cr} \int_0^\infty e^{-U_0/kT} (\nabla^2 U) r^2 dr \quad (17)$$

$$\text{and } B \equiv 4\pi \rho_{cr}^2 \int_0^\infty \beta e^{-U_0/kT} (\nabla^2 U) r^2 dr \quad (18)$$

The leading term A has been calculated as a function of temperature along the coexistence line for argon and krypton using the L-J potential for $U(r)$. The results are given in Table IV. The calculated values of $A^* = A/RT_{cr} \rho_{cr}^{2/3}$ are compared with experimental and calculated values of $\langle \nabla^2 U^* \rangle / \rho^* (1 + \rho^*)$ for the rare gases in Fig. 5. A^* increases linearly with temperature in the range $0.55 < T^* < 1$, and is equal to $\langle \nabla^2 U^* \rangle / \rho^* (1 + \rho^*)$ mid range at

$T^* = 0.74$. It is low by 18% at $T^* = 0.55$ and high by 23% at the critical point. The leading term A^* calculated by the WCA method is quite close to $\langle v^2 U^* \rangle / \rho^* (1 + \rho^*)$ over the entire temperature range. This is not true of other types of perturbation theories.

In Fig.(5) we also give calculations of $\langle v^2 U^* \rangle / [\rho^* (1 + \rho^*)]$ for liquid argon and krypton and argon and krypton vapor along the coexistence line. The liquid curves are calculated by the WCA method; the vapor curves are from solution of the PY equation. Finally we give experimental values of the function for liquid neon, argon, and krypton. The comparison of the WCA calculations of $\langle v^2 U \rangle$ for argon and krypton with experiment have already been discussed. We note that the experimental values of $\langle v^2 U^* \rangle / [\rho^* (1 + \rho^*)]$ for liquid neon are significantly below the lines calculated for liquid argon and neon, particularly near the triple point. With increasing temperature the experimental data for neon approach the reduced lines for liquid argon and liquid krypton. This behaviour is consistent with the low melting point of neon and the low density of the liquid at the triple point--both a consequence of the large zero point energies of the solid and liquid.

We have also calculated A using $U_0 = U(r)$, the L-J potential, and $U_0 = U_{BH}$, where U_{BH} is the Barker-Henderson cut of an LJ potential. The Barker-Henderson cut is

$$\begin{aligned} U_0 &= U(r) & r &\leq \sigma \\ &= 0 & r &> \sigma \end{aligned} \tag{19}$$

The values of A calculated by the WCA cut, the Barker-Henderson cut, and the complete L-J potential are intercompared

with one another and $\langle \nabla^2 U \rangle / \rho (1 + \rho)$ in Fig. 6. Clearly the WCA perturbation theory gives the best first order approximation, A, to $\langle \nabla^2 U \rangle / \rho$.

Intercomparison of calculated values of A and $\langle \nabla^2 U \rangle$ suggests that B is related to A through the relations

$$B = A_0 - \alpha_A T^* / \rho^* \quad (20)$$

where A_0 and α_A are defined by

$$A = A_0 + \alpha_A T^* \quad (21)$$

Table I

Mean Force Constant (in erg cm^{-2}) and Average Potential Energy (in Kcal/mole) of Liquid Argon Along the Coexistence Line.

T°K	ρ (mole/l)	$-\langle U \rangle_{\text{obs}}$	$-\langle U \rangle_{\text{LHB}}^a$	$-\langle U \rangle_{\text{M-S}}^b$	$\langle \nabla^2 U \rangle_{\text{obs}}$	$\langle \nabla^2 U \rangle_{\text{LHB}}$	$\langle \nabla^2 U \rangle_{\text{M-S}}$
84	35.399		1.487	1.484	11,000	11,709	11,794
90	33.634		1.432	1.428	10,600	11,162	11,250
100	32.763	1.306	1.341	1.337	10,000	10,280	10,371
110	31.014		1.249	1.245	8,900	9,376	9,467
120	29.045		1.149	1.145	8,100	8,386	8,475
130	26.679	1.012	1.035	1.030	7,200	7,247	7,329
140	23.557		0.890	0.886	6,000	5,855	5,926
150	17.048		0.609	0.606	3,600	3,427	3,473

^aLee, Henderson, and Barker⁴ Potential

$$U/\epsilon = \left\{ \sum_{i=0}^5 A_i \left(\frac{r}{r_m} - 1 \right)^i \right\} e^{-12.5(1-r/r_m)} - \sum_{j=0}^2 \frac{C_{2j} + 6}{0.01 + (r/r_m)^{2j+6}}$$

$$\epsilon/k = 142.10^\circ\text{K}, r_m = 3.7612 \text{ \AA}, A_0 = 0.27783, A_1 = -4.50431,$$

$$A_2 = -8.33122, A_3 = -25.2696, A_4 = -102.0195, A_5 = -113.25,$$

$$C_6 = 1.10727, C_8 = 0.16971, C_{10} = 0.01361$$

^bMS-potential

$$U/\epsilon = \frac{6}{n(r)-6} \left(\frac{r}{r_m} \right)^{-n(r)} - \frac{n(r)}{n(r)-6} \left(\frac{r}{r_m} \right)^{-6}$$

$$n(r) = -3.310 \left(\frac{r}{r_m} \right)^2 + 20.571 \left(r/r_m \right) - 2.657$$

$$\epsilon/k = 142.5^\circ\text{K}, r_m = 3.75 \text{ \AA}$$

Tab. II

Mean Force Constant (in erg cm^{-2}) and Average Potential Energy (in Kcal/mole) of Liquid Krypton along the Coexistence Line

T°K	ρ (mole/l)	$-\langle U \rangle_{\text{obs}}$	$-\langle U \rangle_{\text{LHB}}^a$	$-\langle U \rangle_{\text{M-S}}^b$	$-\langle U \rangle_{\text{L-J}}^c$	$\langle \nabla^2 U \rangle_{\text{obs}}$	$\langle \nabla^2 U \rangle_{\text{LHB}}$	$\langle \nabla^2 U \rangle_{\text{M-S}}$	$\langle \nabla^2 U \rangle_{\text{L-J}}$
120	28.581	1.925	2.016	2.052	1.983	14900	13825	13350	14310
130	27.639		1.926	1.961	1.901	14200	13093	12636	13565
140	26.665		1.834	1.868	1.818		12329	11894	12783
150	25.597		1.740	1.773	1.731		11530	11119	11961
160	24.465		1.641	1.673	1.640		10688	10305	11092
170	23.226		1.536	1.567	1.542		9792	9438	10162
180	21.827	1.418	1.421	1.450	1.433		8816	8496	9146
190	20.162		1.289	1.317	1.307		7710	7429	7991
200	17.929		1.119	1.144	1.143		6330	6099	6547
150	30.542*	2.067	2.097	2.131	2.036		18008	17331	19007
180	31.602*	2.118	2.097	2.129	2.017		21220	20367	22732
200	18.704*	1.171	1.175	1.201	1.197		6850	6598	7096
200	32.765*	2.121	2.112	2.143	2.011		24425	23393	26459

*These data are not on the coexistence line.

a) See Table I for potential form.

$\epsilon/k = 201.31^\circ\text{K}$, $r_m = 4.0078 \text{ \AA}$, $A_0 = 0.23526$, $A_1 = -4.78686$, $A_2 = -9.2$, $A_3 = -20.0$,
 $A_4 = -60.0$, $A_5 = -114.$, $C_6 = 1.06324$, $C_8 = 0.17012$, $C_{10} = 0.01425$

b) See Table I for potential form

$n(r) = 10(r/r_m) + 3$, $\epsilon/k = 199.2^\circ\text{K}$, $r_m = 4.02 \text{ \AA}$

c) $U/\epsilon = (\frac{r}{r_m})^{-12} - 2(\frac{r}{r_m})^{-6}$, $\epsilon/k = 165.20^\circ\text{K}$, $r_m = 4.108 \text{ \AA}$

Table III

$$\frac{10^6 \times \langle v^2 \rangle_U}{(RT_{cr} \rho_{cr})^{2/3}} / [(\rho/\rho_{cr})(1 + \rho/\rho_{cr})]^{1/2}$$

T°K	Argon (l)			Argon (g)			
	obs	LHB	M-S	LHB	M-S		
84	(1.72) ²						
	1.60	1.706	1.72				
90	(1.70) ²						
	1.68	1.78	1.77				
100	(1.67) ²						
	1.66	1.71	1.72				
110	1.62	1.71	1.73	1.64	1.67		
120	1.66	1.71	1.73	1.70	1.72		
130	1.71	1.71	1.73	1.74	1.77		
140	1.74	1.69	1.71	1.74	1.77		
150	1.75	1.66	1.69	1.69	1.71		
T°K	Krypton (l)				Krypton (g)		
	obs	LHB	MS	LJ	LHB	MS	LJ
120	(1.81) ²	1.68	1.62	1.74			
130	(1.83) ²	1.68	1.63	1.75			
140		1.69	1.63	1.75			
150		1.69	1.63	1.75	1.63	1.58	1.62
160		1.69	1.63	1.76	1.68	1.62	1.67
170		1.69	1.63	1.76	1.71	1.65	1.71
180		1.69	1.63	1.76	1.74	1.68	1.74
190		1.69	1.63	1.75	1.75	1.69	1.76
200		1.68	1.62	1.74	1.74	1.69	1.76

¹ $\begin{cases} T_{cr} = 150.86^\circ\text{K}, \rho_{cr} = 0.013294 \text{ mole/cc for Ar} \\ T_{cr} = 209.35^\circ\text{K}, \rho_{cr} = 0.010764 \text{ mole/cc for Kr} \end{cases}$

² Vapor pressure measurement

Captions

Figure 1. $T^2 \ln \alpha(\text{Ar})$ vs $T^\circ\text{K}$

⊙ Vapor pressure measurement; — . — fractionation factor measurement; —, WCA calculation for LEB potential; -----, WCA calculation for MS potential.

Figure 2. $T^2 \ln \alpha(\text{Kr})$ vs. $T^\circ\text{K}$

⊙ Vapor pressure measurement; —, WCA calculation for L-J(n,6); — — —, WCA calculations for LHB potential; — — — — —, WCA calculation for MS potential.

Figure 3. $\ln[\langle \nabla^2 U \rangle^* / \rho^*]$ vs. $\ln[1 + \rho^*]$

⊙ for Ar; Δ for Krypton.

Figure 4. Law of rectilinear diameters plot of the isotope fractionation factor, α , for the isotopes of argon.

• vapor pressure data⁸, o isotope fractionation data⁹, and — Eq. (8).

Figure 5. $10^6 \langle \nabla^2 U \rangle / [(RT_{cr} \rho_{cr}^{2/3}) (\rho / \rho_{cr}) (1 + \rho / \rho_{cr})]$ vs. (T / T_{cr})

Δ Vapor pressure measurement of neon; ⊙ fractionation measurement of Ar, ⊕ vapor pressure measurement of Ar; □ vapor pressure measurement of krypton; — . — . —, WCA calculation of argon liquid; — .. — .. —, WCA calculation of krypton liquid; — — — — —, PY calculation of argon vapor; -----, PY calculation of krypton vapor; — — — — —, A values of argon and krypton calculated by Eq. (9).

Figure 6. $\int_0^\infty e^{-u/kT} (v^2 u/\epsilon) x^2 dx$

_____, L-J (12,6); _____._____, Barker-Henderson cut;

_____ .. _____ .. _____, WCA cut; ----- experimental value

for liquid

$$C = (4\pi\rho_{cr} r_m^2/\epsilon)^{-1}$$

References

1. E. Roth and J. Bigeleisen, J. Chem. Phys. 32, 612 (1960).
2. G. Boato, G. Casanova, and M. E. Vallauri, Nuovo Cimento 16, 505 (1960).
3. J. Bigeleisen and E. Roth, J. Chem. Phys. 35, 68 (1961).
4. G. T. Furukawa, Metrologia 8, 11 (1972).
5. G. T. McConville, J. Low Temp. Phys. 15, 647 (1974).
6. K. Clusius, K. Schleich and M. Vogelmann, Helv. Chem. Acta. 46, 1705 (1963).
7. M. W. Lee, S. Fuks and J. Bigeleisen, J. Chem. Phys. 53, 4066 (1970).
8. J. T. Phillips, C. U. Linderstrom-Lang and J. Bigeleisen, J. Chem. Phys. 56, 5053 (1972).
9. M. W. Lee, D. M. Eshelman and J. Bigeleisen, J. Chem. Phys. 56, 4585 (1972).
10. J. Bigeleisen, J. Chem. Phys. 38, 769 (1963).
11. K. F. Herzfeld and E. Teller, Phys. Rev. 54, 912 (1938).
12. J. Bigeleisen, J. Chem. Phys. 34, 1485 (1961).
13. G. Casanova, A. Levi and N. Terzi, Physica 30, 937 (1964).
14. F. Mandel, J. Chem. Phys. 57, 3929 (1972).
15. F. Mandel, J. Chem. Phys. 62, 2261 (1975).
16. J. Bigeleisen, M. W. Lee, and F. Mandel, Accounts of Chem. Res. 8, 179 (1975).
17. J. K. Lee, D. Henderson and J. A. Barker, Mol. Phys. 29, 429 (1975).
18. G. C. Maitland and E. B. Smith, Mol. Phys. 22, 861 (1971).
19. D. W. Gough, E. B. Smith and G. C. Maitland, Mol. Phys. 27, 867 (1974).
20. J. K. Percus and G. J. Yevick, Phys. Rev. 110, 1 (1958).
21. M. S. Wertheim, Phys. Rev. Letter 10, 321 (1963).

22. E. Thiele, J. Chem. Phys. 39, 474 (1963).
23. E. A. Guggenheim, J. Chem. Phys. 13, 253 (1945).
24. In the neighborhood of the critical temperature the exponent $1/3$ becomes an irrational number close to 0.36.

Fig. 1

Fig. 2

Fig. 3

Figs

Fig 6