Mean Square Force in Simple Liquids and
Solids from Isotope Effect Studies

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ABSTRACT

The vapor pressure isotope effect in the rare gases, neon, argon, and krypton, has been used to determine $\langle \nabla^2 U \rangle$, mean Laplacian of the intermolecular potential, as a function of temperature in the rare gas solids and liquids. An abrupt discontinuity is found at the triple point which is closely correlated with the density change on melting. The mean square force between rare gas atoms in the liquid is linear in ρ , the density, divided by T from the triple point to near the critical temperature. Deviations of the order of ten per cent have been found from the law of corresponding states for $\langle \nabla^2 U \rangle$. It is shown that excellent agreement is obtained between measured values of $\langle \nabla^2 U \rangle$ and radial distribution functions calculated by molecular dynamics and statistical mechanics.

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I. INTRODUCTION

The determination of the vapor pressure ratio of isotopes or the related vapor-liquid, vapor-solid isotope fractionation factors are important sources of information about intermolecular forces, the motion of molecules in the condensed phase, and the perturbation of the energy states of the gaseous molecule by the intermolecular force. In the case of a monatomic substance, the vapor pressure ratio or the separation factor, α , is directly related to properties of the intermolecular potential. Other thermodynamic properties which may be used to obtain useful information about the intermolecular potential, $U(r)$, are the internal energy, E ,

$$\beta E/N = \frac{3}{2} + 2\pi n \int_0^{\infty} r^2 \beta U(r) g(r) dr, \quad (1)$$

and the virial pressure, P ,

$$\beta P/n = 1 - \frac{2\pi n}{3} \int_0^{\infty} r^3 \beta \frac{dU(r)}{dr} g(r) dr. \quad (2)$$

β , n , and $g(r)$ are $(kT)^{-1}$ the number density, and the radial distribution function respectively. The mean square

force, $\langle F^2 \rangle$, is related to the Laplacian of the intermolecular potential by

$$\langle F^2 \rangle = kT \langle \nabla^2 U \rangle$$

Liquid pressures are very sensitive to the collision diameter, σ ; the internal energy is most sensitive to the potential well depth, ϵ . The isotope separation factor is a very sensitive probe of the steeply repulsive part of the potential. The regions of the intermolecular potential that contribute to the pressure, energy and $\langle \nabla^2 U \rangle$ are shown in Fig. 1. In the remainder of this paper, we shall be mainly concerned with the measurement of the isotope separation factor and vapor pressure ratio and the information about the potential that may be obtained from them.

The experimental quantities P'/P and $\alpha \equiv (N'/N)_g / (N'/N)_c$ give directly the ratio of the reduced partition function ratio in the condensed phase to that in the ideal gas, f_c/f_g , by the relations¹⁻³

$$\ln(f_c/f_g) = [\ln(P'/P)] \{1 + P[B_0 - (V/RT)]\} \quad (3)$$

$$\ln(f_c/f_g) = \ln \alpha + [(V' - V)^2 / 2\beta VRT]. \quad (4)$$

N' and N are the mole fractions of light and heavy isotope, respectively; V is the molal volume of the condensed phase, and β is its compressibility. B_0 is the second virial coefficient of the equation of state written in the form

$$PV/RT = 1 + B_0 P. \quad (5)$$

For a monatomic substance with small quantum effects^{1,4,5}

$$\ln(fc/fg) = \frac{1}{24}(h/kT)^2 [(1/m') - (1/m)] (\langle v^2 U \rangle_c - \langle v^2 U \rangle_g) + \dots \quad (6)$$

and

$$\langle v^2 U \rangle = 4\pi n \int_0^\infty g(r) \frac{d}{dr} \left[r^2 \frac{dU}{dr} \right] dr. \quad (7)$$

m' and m are the atomic masses of the light and heavy isotope;

For a harmonic lattice

$$\ln \left[\frac{fc}{fg} \right] = \sum_{j=1}^{\infty} (-1)^{j+1} \frac{3B_{2j-1}}{2j(2j)!} \left(1 - \frac{m'}{m} \right) \mu'_{2j}, \quad \frac{h\nu_{\max}'}{kT} < 2\pi, \quad (8)$$

where μ'_{2j} is the $2j$ 'th moment of the frequency distribution.

For a Debye solid μ'_{2j} is

$$\mu'_{2j} = 3(k\theta'/h)^{2j}/(2j+3). \quad (9)$$

II. RESULTS

The vapor-pressure ratio of isotopic liquids can be determined by differential manometry; the separation factor is just the isotopic fractionation in liquid-vapor distribution equilibria. Each of the methods has inherent advantages and disadvantages. The method of differential manometry requires high chemical purity, enriched isotopes in quantities of the order of a tenth of a liter or more (NTP) of gas, good thermal equilibrium between two samples, constant temperature of the sample for periods of the order of an hour, and precise measurements of small pressure differences. The liquid-vapor equilibration method has modest requirements of chemical purity and temperature stability, and does not require significant quantities of enriched isotopes. Frequently the natural abundance is sufficient. The method depends entirely on isotope ratio determinations with a precision of the order 0.01-1.0%. In the liquid-vapor equilibration method it is essential to achieve equilibrium with respect to mass transport. Finally, if one desires the vapor-pressure ratio, then one must consider the problem of nonideal solution behavior. Mass transfer equilibrium is not easily established between a solid and a vapor because of the slow diffusion in the solid. Thus a conventional distribution experiment is not applicable to the solid.

Although Eq. (6) was derived by Lindemann⁶ for the special case of a Debye solid as early as 1919, it was not until 1960

that it received experimental verification through the experiments of Bigeleisen and Roth on the vapor pressures of the neon isotopes^{7,8}. Their results, since confirmed by others^{9,10}, shown in Fig. 2, gave a Debye θ of 74.6°K for solid neon in good agreement with the value of 73°K obtained both from the temperature dependence of neutron scattering (Debye-Waller factor) and theoretical calculations using a Lennard-Jones potential with ϵ and σ derived from the equation of state of the gas. These results differ in a fundamental way from the heat capacity value of 63° K as a result of the anharmonicity of the lattice vibrations. An interesting finding in the neon work was the sharp discontinuity in $\langle v^2 \rangle$ at the melting point. To study the change in $\langle v^2 \rangle$ on melting quantitatively and to follow its behavior to the critical point, where the separation factor must vanish, the studies were extended to the rare gases Ar and Kr. The results on argon are the most extensive; the behavior of all three rare gases, Ne, Ar, and Kr, will be discussed with reference to the argon data. Figure 3 shows the temperature dependence of $\ln(f_c/f_g)$ for Ar in the solid and the low temperature liquid.¹¹ Figure 4 shows the temperature dependence of the separation factor from the triple point to the critical temperature.¹² Results similar to those shown in Fig. 3 have been obtained for krypton¹³ where the measured vapor pressure differences divided by the total pressure between two enriched samples covered the small range 0.7×10^{-3} to 1.8×10^{-3} between 130° K and 94° K.

To include the anharmonic effects in the solid,
we write

$$\langle \nabla^2 U \rangle = \langle \nabla^2 U \rangle_0 (1 - \alpha T) \quad (10)$$

Then

$$\ln f_c/f_g = A/T^2 - B/T \quad (11)$$

where $A = \frac{1}{24} (h/k)^2 \left(\frac{1}{m'} - \frac{1}{m} \right) \langle \nabla^2 U \rangle_0$ and $B = \alpha A$. Least square values of A and B for Ar and Kr are given in Table I.

Table I

Least Square Coefficients to Eq. (11)

	A (°K ²)	B (°K)
Ar (⁴⁰ Ar/ ³⁶ Ar)	63.3 ± 0.4	0.124 ± 0.005
Kr (⁸⁴ Kr/ ⁸⁰ Kr)	18 ± 2	0.02 ± 0.01

Within the limits of experimental error the values of α are the same for argon and krypton. The Debye θ_0 values derived from the A values in Table I are 87.2° and 70° K for ^{40}Ar and ^{84}Kr respectively. These values are in good agreement with θ_0 values, 93.3 and 71.7 respectively, from heat capacity measurements on natural material (atomic weights 39.95 and 83.80 respectively). The discrepancy is not surprising if one considers the rather complicated temperature dependence of $\theta_0(T)$ derived from heat capacity measurements.¹⁴

The ratio $\langle \nabla^2 U \rangle_s / \langle \nabla^2 U \rangle_l$ at the triple point is 1.20 ± 0.01 , 1.20 ± 0.01 and 1.24 ± 0.02 for neon, argon and krypton respectively. This result is in accord with expectations from corresponding states arguments for the quantity $\langle \nabla^2 U \rangle$ and represents a confirmatory check on the absolute magnitudes of the values for $\ln(fc/fg)$ for these three substances. If nearest neighbors only are considered in summing

$\sum u(r_{ij})$, the ratio $\langle \nabla^2 U \rangle_s / \langle \nabla^2 U \rangle_l$ should be $12/8.8 = 1.36$.

The fact that the experimental value is significantly lower shows the important contribution made by the interactions of atoms at a distance less than the first maximum in the radial distribution function to $\langle \nabla^2 U \rangle$ in the liquid. A statistical approach which averages over all configurations of the liquid is the "significant structure theory".¹⁵ It leads to the relation

$$\langle \nabla^2 U \rangle_{\text{liq}} = (v_s/v_l) \langle \nabla^2 U \rangle_s \quad (12)$$

for a monatomic substance. The density ratio for the solid to the liquid is 1.16 for the condensed rare gases at the triple point. Thus the close agreement of $\langle v^2 U \rangle_s / \langle v^2 U \rangle_l$ with V_l/V_s shows the near equality of the integral in Eq. (7) in the liquid with the corresponding lattice sum in the solid. This result explains the success of many lattice models of the liquid state.

Calculations of $\ln(f_c/f_g)$ for solid argon in the anharmonic approximation for 13-6 and 12-6 Mie potentials have been made from the free energy calculations of Klein, Blizard and Goldman.¹⁶ They employed an improved modification of Choquard's reformulation of the Born theory. A pseudo 13-6 potential fits the experimental data in the solid better than does the 12-6 potential.

A useful correlation of the experimental data on $\langle v^2 U \rangle$ for the rare gases is made by means of a reduced plot, $(r_{\min}^2 / (\epsilon/k)) \langle v^2 U \rangle = \langle v^2 U^* \rangle$ vs $T^* = kT/\epsilon$. Such a plot is given in Fig. 5. The molecular parameters are taken from the recent theoretical calculation of the two body potentials of the rare gases by Kim and Gordon.¹⁷ The reduced pair potentials for Ar and Kr derived from spectroscopic and thermophysical data^{18,19} are in good agreement with the theoretical curves. Each of these sets of potentials lead to concordant values of the reduced triple points for argon and krypton. The reduced triple point of neon is somewhat lower as a result of quantum

effects. To correct for the latter we multiply the neon reduced temperatures by a quantum correction factor, $\beta = 1.065$, and $\langle v^2 U^* \rangle$ for neon by β^2 . The measured values of $\ln(fc/fg)$ differ by a factor of 20 between neon and krypton; the reduced plots of $\beta^2 \langle v^2 U^* \rangle$ vs T^* show a spread of at most 10%. This constitutes a remarkable confirmation of the self-consistency of all of the rare gas measurements of $\langle v^2 U \rangle$.

The temperature dependence of $\ln \alpha$, the separation factor, is conveniently made through a correlation with the density difference, $\rho_c - \rho_g$, between the liquid and the gas along the equilibrium saturation line from the triple point to the critical point. Below 130° K it is found¹² that $T^2 \ln \alpha$ for Ar is linear in $\rho_c - \rho_g$. Below 130° K both $\langle v^2 U \rangle_g$ and ρ_g are individually small compared with $\langle v^2 U \rangle_c$ and ρ_c , respectively. Inasmuch as the integral in Eq. (7) is fairly insensitive to temperature, $T^2 \ln \alpha$ will be linear in $(\rho_c - \rho_g)$ between 84 - 130° K. $T^2 \ln \alpha$ has the familiar non-classical approach to the critical point. We define an index, b for $T^2 \ln \alpha$, analogous to the β index associated with $\Delta \rho$, by

$$T^2 \ln \alpha = (1 - T/T_c)^b. \quad (13)$$

Our data give a value of b equal to 0.42 ± 0.02 in the temperature range, $0.1 > (1 - T/T_c) > 3 \times 10^{-3}$. The data are insufficient to decide whether the limiting value of b approaches the limiting value of β , which is currently taken as 0.36.

INTERPRETATION

The important theoretical quantity for the isotope effect in the liquid is the integral of the Laplacian of the intermolecular potential weighted by the radial distribution function, which appears in Eq. (7). This integral also appears in the statistical mechanical theory of the Brownian motion friction constant²⁰ and was first evaluated by Kirkwood, Buff, and Green²¹ for liquid argon. We shall consider the reduced dimensionless quantity

$$v^* \langle \nabla^2 U^* \rangle = \int g(r^*) \left(\frac{d}{dr^*} \right) [r^{*2} (du^*/dr^*)] dr^* d\Omega, \quad (14)$$

where $r^* = r/\sigma$ (for the L-J potential we use the characteristic length σ). $v^* \langle \nabla^2 U^* \rangle$ is equal to $96\pi C$, the dimensionless quantity used by Casanova and Levi.²² Kirkwood, Buff, and Green estimated the integral in Eq. (14) by employing an analytical approximation to the radial distribution function in liquid argon derived by Eisenstein and Gingrich²³ from their x-ray. The parameters were adjusted to fit a Lennard-Jones potential, the equation of state of gaseous argon, and the energy of vaporization. The Kirkwood, Buff, and Green value is 904 at 89° K while our experimental value is 910 at the same temperature. A comparison is made of the experimental value of $v^* \langle \nabla^2 U^* \rangle$ with calculations from the x-ray²³⁻²⁵ and neutron²⁶ diffraction $g(r)$ values and the L-J potential in Fig. 6. A similar result is found for

krypton. $v^* \langle v^2 U^* \rangle$ calculated from radial distribution functions and the L-J potential exhibits a maximum at $T^* \approx 1.0$ in contrast with the monotonic small decrease between $T^* = 0.7$ to 1.2 found experimentally.

Casanova and Levi found that much better agreement could be obtained with experiment for the L-J potential if $v^* \langle v^2 U^* \rangle$ were calculated by the Rowlinson correlation method rather than through Eq. (14). Rowlinson²⁷ has related $\langle v^2 U \rangle$ to the intermolecular virial function, and its derivative

$$\gamma = -\frac{1}{3} \sum v(R_{ij}), \quad v(R) = R[du(R)/dR] \quad (15)$$

$$\mathcal{W} = \frac{1}{9} \sum w(R_{ij}), \quad w(R) = R[dv(R)/dR] \quad (16)$$

and

$$\overline{\gamma} = PV - NkT. \quad (17)$$

For a pair potential of the Lennard-Jones type one gets in reduced units

$$\langle v^2 U^* \rangle = 6[(n + m - 1) \langle \gamma^* \rangle - nm \langle U^* \rangle / 3], \quad (18)$$

where

$$\langle U^* \rangle = \frac{2}{V^*} \int_0^\infty u(r^*) g(r^*) r^{*2} dr^*. \quad (19)$$

In Fig. 6 we intercompare $V^* \langle \nabla^2 U^* \rangle$ obtained from Casanova and Levi's calculation of the right-hand side of Eq. (18) for a 12-6 potential with the experimental data for argon. This immediately shows that the experimental radial distribution functions in the region $0.9 < r^* < 1.1$ are inconsistent with the L-J potential.

High speed computers and recent perturbation methods permit the calculation of the radial distribution function in a fluid from the pair potential. Such calculations have been made for argon by Rahman²⁸ and by Verlet²⁹. These workers used the Lennard-Jones 12-6 potential. Computer generated radial distribution functions give good agreement with the experimental values of $V^* \langle \nabla^2 U^* \rangle$ (Fig. 6). Mandel^{30,31} has calculated $g(r^*)$ for a number of potentials using the WCA³² perturbation technique. Barker and Henderson³³ showed that WCA method gives good agreement with the molecular dynamics calculation of the radial distribution function. Mandel's results for $V^* \langle \nabla^2 U^* \rangle$ are compared with the argon experimental data in Fig. 6. This result, using a 12-6 potential, are in excellent agreement with experiment over the entire temperature range $0.7 < T^* < 1.2$.

Contrary to the excellent agreement that is obtained between values of $\langle \nabla^2 U \rangle$, E , and P of liquid argon from a two body L-J (12-6) potential derived from gas data and experiment, no such agreement is found for krypton. Mandel³¹ has found

that the thermodynamic data on liquid krypton require a much steeper repulsive two body potential ($r^{-18.5}$) than argon. The parameters associated with such a potential lead to very poor corresponding states plots for argon and krypton. The fact that the best fit for $\langle v^2 U \rangle$ and other properties of solid argon is obtained with a 13-6 rather than a 12-6 potential, which gives a better fit to the liquid data than does a 13-6 potential, shows that neither of these effective two body potentials is correct. They are useful working approximations.

Theoretical calculations of Kim and Gordon show the steepness and its derivatives of the repulsive part of the two body potential to increase monotonically for the substances $\text{Xe} < \text{Kr} < \text{Ar} < \text{Ne} < \text{He}$. This would suggest an inverse order for $\langle v^2 U^* \rangle$. If anything the data shown in Fig. 5 for both the solid and the liquid do not follow the expected sequence. The calculations of Kim and Gordon give small deviations of the individual rare gases from a common reduced potential. The spread in our values of $\langle v^2 U^* \rangle$ among the rare gases is at most ten per cent. Deviations of the values of $\langle v^2 U^* \rangle$ for each of the rare gases from a universal value are to be expected from the Kim and Gordon potentials. Quantitative comparison can only be made by calculation of the radial distribution functions consistent with the potentials and integration of Eq. (7). Such an analysis will give an assessment of the importance of three body forces, which are

not included in the present analysis, to $\langle v^2 U \rangle$. The present reduced plots of $\langle v^2 U^* \rangle$ as well as the theoretical calculations of $U^*(r_{ij})$ by Kim and Gordon show the utility of the use of corresponding states analysis of the thermodynamic properties of the condensed rare gases.

CONCLUSION

Isotope effect studies are good probes to study molecular and intermolecular forces at the site of isotopic substitution. This property, which is manifest in all quantum mechanical systems, is the basis of the use of the isotopic discrimination method in the study of molecular forces, chemical kinetics, and chemical equilibria. In the present study it has been used to derive information about the intermolecular potential in the rare gases and the mean square force, $kT\langle v^2 \rangle$, acting on these atoms in the solid and liquid. It is shown that the quantity $v\langle v^2 \rangle$ is rather constant over a wide temperature range, which spans the solid, the melting process, and the liquid up to within 10% of the critical temperature. The law of corresponding states has been found to hold (within ten per cent) for the mean square force between rare gas atoms in the solid and the liquid. Comparisons of $\langle v^2 \rangle$ calculated directly from experimental diffraction data with isotope effect determinations, shows that radial distribution functions for simple liquids are better calculated by computer simulation of the liquid or statistical mechanics than measured experimentally.

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Captions

Fig. 1. The integrand of the internal energy, the virial pressure, $\langle v^2 u^* \rangle$, the radial distribution function, $g(r)$ and the intermolecular potential, $u(r)$, as a function of the intermolecular separation. These functions are evaluated at $T^* = 0.719$ and $\rho^* = 0.85$ for the Lennard-Jones (12 - 6) potential.

Fig. 2. Plot of $\ln f_c[\text{Ne}^{22}/\text{Ne}^{20}]$ vs $1/T^2$. The sharp break in the curve comes at the triple point.

Fig. 3. $T \ln f_c / f_g$ vs $100/T$ for Ar.

○, Lee, Fuks, and Bigeleisen (1971)

△, Boato, Casanova, Scoles and Vallauri (1961)

□, Clusius, Schleich, and Vogelmann (1963).

The lines are theoretical calculations for 13 - 6 and 12 - 6 potentials by Klein, Blizard, and Goldman (1970).

Fig. 4. $T \ln \alpha$ vs $100/T$. Dashed line, Lee, Fuks, and Bigeleisen; ○, Phillips, Linderstrom-Lang, and Bigeleisen; □, Boato, et al.

Fig. 5. Plot of $\beta^2 \langle v^2 u^* \rangle$ vs βT^* for solid and liquid neon, argon, and krypton; x neon, $\beta = 1.065$, * argon, $\beta = 1$, □ krypton, $\beta = 1$. (In this plot $r^* = r/r_{\min}$).

Fig. 6. Comparison of $v^* \langle v^2 u^* \rangle$ vs T^* as determined by: ○, isotope effect; ●, neutron scattering; ★, ◇, and ✱, x-ray diffraction; □, and △, molecular dynamics calculation; +, semiempirical from viscosity. The dashed curve refers to Rowlinson's correlation. The solid curve refers to a WCA perturbation calculation. T_c^* and T_{mp}^* are the reduced temperatures of the critical and triple points, respectively.

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