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vestigations are presently under way in our laboratories.

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

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Although a difference in vapor pressures of isotopic substances was predicted and demonstrated about a decade before chemical equilibrium and kinetic isotope effects, vapor pressure isotope effects have not been as significant in the development of chemical and related sciences as either of the latter two.

Like the chemical equilibrium and kinetic isotope effects, the vapor pressure isotope effect has its physical origin in the fact that the zero-point energy of a light molecule is larger than that of a heavy molecule. This leads to a smaller energy of vaporization and a higher vapor pressure for light isotopic species compared with heavy isotopic species of simple molecules (e.g., $P_{H_2} > P_{D_2}$). Yet it was demonstrated early in the thirties that deuteriocarbons usually have higher vapor pressures than their related hydrocarbons.

In the case of methane, vapor pressures are in the sequence $P_{12_{CH_3D}} > P_{12_{CH_4}} > P_{13_{CH_4}}$ at 93 K. At 80 K the sequence is $P_{12_{CH_4}} > P_{13_{CH_4}} > P_{12_{CH_3D}}$. Clearly there is an interplay of isotope effects on the enthalpy and entropy changes in vaporization as well as on details of molecular structure which play an important role in the vapor pressure isotope effect.

The vapor pressure isotope effect is typically one to two orders of magnitude smaller than chemical equilibrium or kinetic isotope effects. The determination of such a quantity, of order between a few hundredths and a few tenths of a percent, and equally important of its temperature coefficient, clearly requires careful quantitative work. The requisite ex-

perimental techniques were developed during the last 15 years simultaneously with significant advances in the statistical mechanical theory of the phenomenon. The latter took into account the structure of a molecule, which the methane experiments among many others showed to be of major significance in determining even the qualitative aspects of vapor pressure isotope chemistry.

Systematic pursuit of vapor pressure isotope studies on polyatomic molecules has led to important information about translation, hindered rotation, the perturbation of molecular vibrations in solids and liquids, and the coupling of molecular translation, rotation, and internal vibration in the condensed state.[1]

In the development of the condensed phase isotope chemistry of polyatomic molecules, it became evident that it would be necessary to understand in as complete detail as possible the differences in vapor pressures of the simple rare gases—neon, argon, and krypton. The statistical mechanical theory of this phenomenon revealed that such measurements could supply complementary and even unique information about anharmonic forces in solids, liquid structure, and their relationship to intermolecular forces.

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

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

and the virial pressure, P.

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

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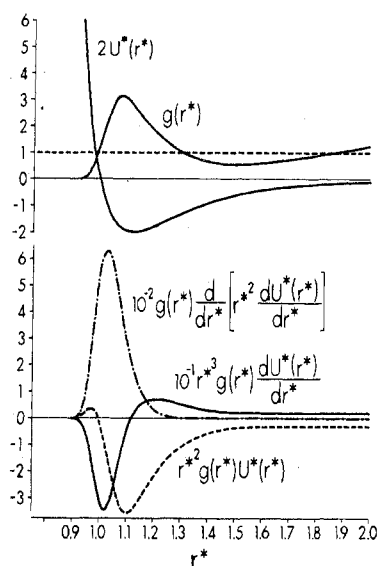
Figure 1. The integrand of the internal energy, the virial pressure, $\langle \nabla^2 U^* \rangle$, the radial distribution function, $g(r)$, and the intermolecular potential, $u(r)$, as a function of the intermolecular separation. These functions are evaluated at $T^* = 0.719$ and $\rho^* = 0.85$ for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

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 sensitive to the collision diameter, σ; the internal energy is most sensitive to the potential well depth, ϵ. The isotope separation factor is a 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 Figure 1.

In this Account, we shall be mainly concerned with measurement of the isotope separation factor and vapor pressure ratio in the rare gases and information 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 relations[2-4]

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

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

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[2,5,6]

$$\ln (f_c/f_g) = \frac{1}{24}(\hbar/kT)^2[(1/m') - (1/m)](\langle \nabla^2 U \rangle_c -$$

$$\langle \nabla^2 U \rangle_g) + \ldots \quad (6)$$

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If the total potential energy is pairwise additive and the latter has spherical symmetry, then

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

m' and m are the atomic masses of the light and heavy isotope; For a harmonic lattice

$$\ln \frac{f_c}{f_g} = \sum_{j=1}^\infty (-1)^{j+1} \frac{3B_{2j-1}}{2j(2j)!} \left[1 - \frac{m'}{m} \right] \mu_{2j}' \quad (8)$$

$$\frac{h\nu_{max}'}{kT} < 2\pi$$

where μ_{2j}' is the $2j$th moment of the frequency distribution.[2] For a Debye solid μ_{2j}' is

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

Results

The vapor pressure ratio for isotopic liquids can be determined by differential manometry; isotopic fractionation factors can be measured 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 (normal temperature and pressure) 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 Lindemann[7] 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.[8,9] Their results, since confirmed by others,[10,11] shown in Figure 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

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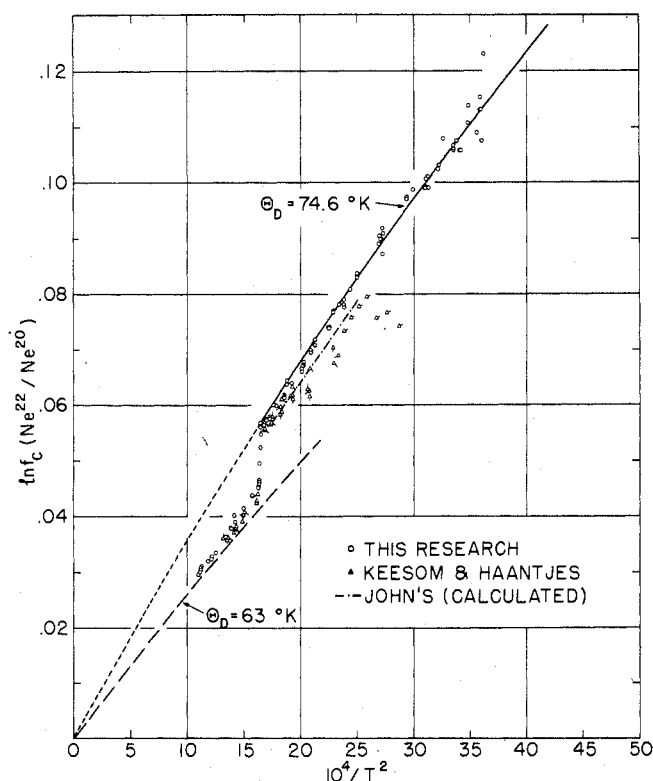(11) G. T. McConville, *J. Low Temp. Phys.*, **15**, 647 (1974).

Figure 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.
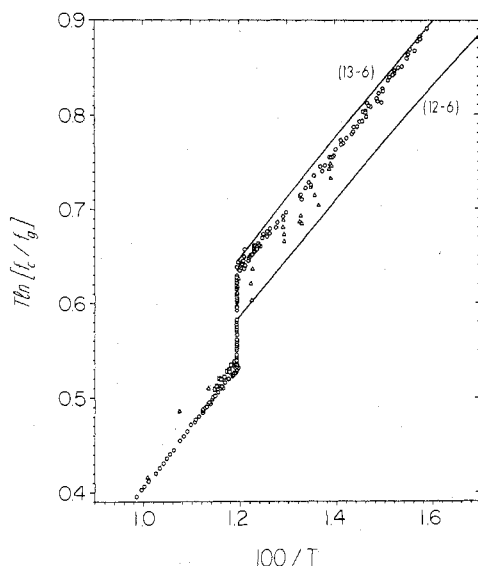

Figure 3. $T \ln (f_c/f_g)$ vs. $100/T$ for Ar: O, Lee, Fuks, and Bigeleisen;[12] △, Boato, Casanova, Scoles and Vallauri (1961); □, Clusius, Schleich, and Vogelmann (1963). The lines are theoretical calculations for 13-6 and 12-6 potentials by Klein, Blizard, and Goldman.[17]

Figure 4. $T \ln \alpha$ vs. $100/T$. Dashed line, Lee, Fuks, and Bigeleisen;[12] O, Phillips, Linderstrom-Lang, and Bigeleisen;[13] □, Boato et al.

Table I
Least-Squares 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

Figure 3 shows the temperature dependence of ln (f_c/f_g) for Ar in the solid and the low-temperature liquid.[12] Figure 4 shows the temperature dependence of the separation factor from the triple point to the critical temperature.[13] Results similar to those shown in Figure 3 have been obtained for krypton[14] 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

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

Then

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

where $A = (1/24)(\hbar/k)^2[(1/m') - (1/m)]\langle \nabla^2 U \rangle_0$ and $B = \alpha A$. Least squares values of A and B for Ar and Kr are given in Table I.

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.[15]

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heat capacity value of 63 K as a result of the anharmonicity of the lattice vibrations.

McConville has used the vapor pressure isotope effect data to obtain an improved value for the lattice energy of neon.[11] An interesting finding in the neon work was the sharp discontinuity in $\langle \nabla^2 U \rangle$ at the melting point. To study the change in $\langle \nabla^2 U \rangle$ 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.
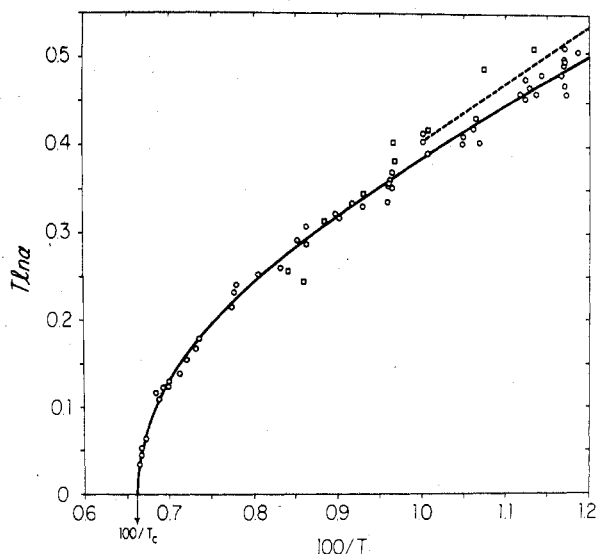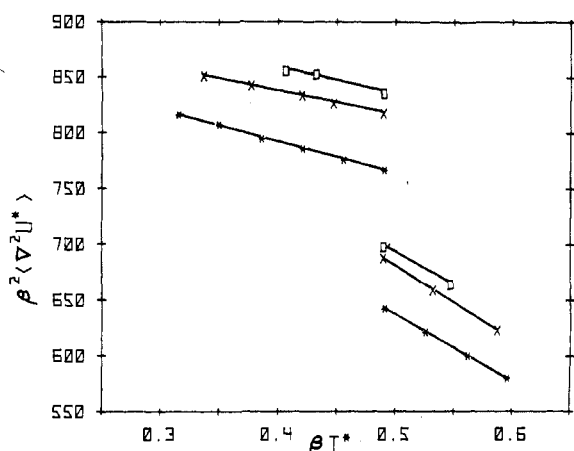
Figure 5. Plot of $\beta^2\langle\nabla^2U^*\rangle$ vs. βT^* for solid and liquid neon, argon, and krypton; $\times$ neon, $\beta = 1.065$; *, argon, $\beta = 1$; $\square$, krypton, $\beta = 1$. (In this plot $r^* = r/r_{min}$).

The ratio $\langle\nabla^2U\rangle_s/\langle\nabla^2U\rangle_l$ 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 $\langle\nabla^2U\rangle$ and represents a confirmatory check on the absolute magnitudes of the values for ln (f_c/f_g) for these three substances. If nearest neighbors only are considered in summing $\Sigma u(r_{ij})$, the ratio $\langle\nabla^2U\rangle_s/\langle\nabla^2U\rangle_l$ 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 $\langle\nabla^2U\rangle$ in the liquid.

A statistical approach which averages over all configurations of the liquid is the "significant structure theory."[16] It leads to the relation

$$\langle\nabla^2U\rangle_{liq} = (V_s/V_1)\langle\nabla^2U\rangle_s \qquad (12)$$

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 $\langle\nabla^2U\rangle_s/\langle\nabla^2U\rangle_l$ with V_1/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.[17] 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 $\langle\nabla^2U\rangle$ for the rare cases is made by means of a reduced plot, $(r_{min}^2/\epsilon)\langle\nabla^2U\rangle = \langle\nabla^2U^*\rangle$ vs. $T^* = kT/\epsilon$. Such a plot is given in Figure 5. The molecular parameters are taken from the recent theoretical calculation of the two-body potentials of the rare gases by Kim and Gordon.[18] The reduced pair potentials for Ar and Kr derived from spectroscopic and thermophysical data[19,20] are in good agreement with the the-

oretical 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 an empirical quantum correction factor, $\beta = 1.065$, and $\langle\nabla^2U^*\rangle$ for neon by β^2. The measured values of ln (f_c/f_g) differ by a factor of 20 between neon and krypton; the reduced plots of $\beta^2\langle\nabla^2U^*\rangle$ 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 $\langle\nabla^2U\rangle$.

The temperature dependence of ln α, 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 found[13] that T^2 ln α for Ar is linear in $\rho_c - \rho_g$ ($\sim\rho_c$). Below 130 K both $\langle\nabla^2U\rangle_g$ and ρ_g are individually small compared with $\langle\nabla^2U\rangle_c$ and ρ_c, respectively. Inasmuch as the integral in eq 7 is fairly insensitive to temperature, T^2 ln α will be linear in $\rho_c - \rho_g$ between 84 and 103 K. If the integrals in eq 7 are about equal for liquid and vapor near the critical point, T^2 ln α will show the familiar nonclassical approach to the critical point. We define an index, b, for T^2 ln α, analogous to the β index associated with $\Delta\rho$, by

$$T^2 \ln \alpha \simeq (1 - T/T_c)^b \qquad (13)$$

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 constant[21] and was first evaluated by Kirkwood, Buff, and Green[22] for liquid argon. We shall consider the reduced dimensionless quantity

$$V^*\langle\nabla^2U^*\rangle = \int g(r^*)(d/dr^*)[r^{*2}(du^*/dr^*)]dr^*d\Omega \qquad (14)$$

where $r^* = r/\sigma$ (for the LJ potential we use the characteristic length σ). Casanova and Levi[23] employed a related dimensionless quantity, $C = (96\pi)^{-1}V^*\langle\nabla^2U^*\rangle$.

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 Gingrich[24] from their X-ray studies. The parameters were adjusted to fit a Len-

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nard-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 $V^*\langle\nabla^2U^*\rangle$ with calculations from the X-ray[24-26] and neutron[27] diffraction $g(r)$ values and the L-J potential in Figure 6. A similar result is found for krypton. $V^*\langle\nabla^2U^*\rangle$ calculated from radial distribution functions and the LJ potential exhibits a maximum at $T^* \simeq 1.0$ in contrast with the monotonic small decrease between $T^* = 0.7$ and 1.2 found experimentally.

Casanova and Levi found that much better agreement could be obtained with experiment for the LJ potential if $V^*\langle\nabla^2U^*\rangle$ were calculated by the Rowlinson correlation method rather than through eq 14. Rowlinson[28] has related $\langle\nabla^2U\rangle$ to the intermolecular virial function, and its derivative

$$v = -\frac{1}{3}\sum v(R_{ij}) \tag{15}$$

$$v(R) = R[du(R)/dR]$$

$$w = \frac{1}{9}\sum w(R_{ij}) \tag{16}$$

$$w(R) = R[dv(R)/dR]$$

$$\overline{v} = PV - NkT \tag{17}$$

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

$$\langle\nabla^2U^*\rangle = 6[(n + m - 1)\langle v^*\rangle - nm\langle U^*\rangle/3] \tag{18}$$

where

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

In Figure 6 we intercompare $V^*\langle\nabla^2U^*\rangle$ 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 LJ potential.

High-speed computers and 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 Rahman[29] and by Verlet.[30] These workers used the Lennard-Jones 12–6 potential. Computer-generated radial distribution functions give good agreement with the experimental values of $V^*\langle\nabla^2U^*\rangle$ (Figure 6). Mandel[31,32] has calculated $g(r^*)$ for a number of potentials using the Weeks–Chandler–Anderson WCA[33] perturbation technique. Barker and Henderson[34] showed that the WCA method gives good agreement with the molecular dynamics calculation of the radial distribution
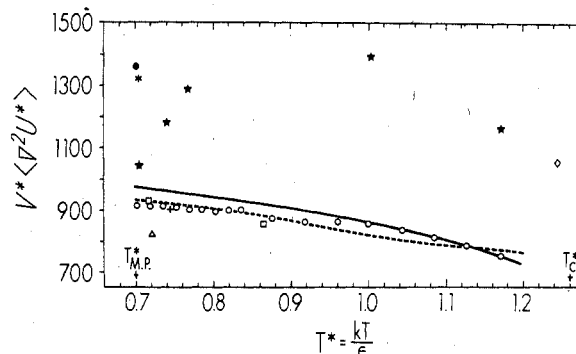

Figure 6. Comparison of $V^*\langle\nabla^2U^*\rangle$ vs. T^* as determined by: O, isotope effect; ●, neutron scattering; ★, ◊, and *, X-ray diffraction; □ and △, molecular dynamics calculation; +, semiempirical from viscosity. The dashed curve refers to Rowlinson's correlation. The solid curve refers to a WCA perturbation calculation. T^*_c and T^*_{mp} are the reduced temperatures of the critical and triple points, respectively.

function. Mandel's results for $V^*\langle\nabla^2U^*\rangle$ are compared with the argon experimental data in Figure 6. These results, 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 $\langle\nabla^2U\rangle$, E, and P of liquid argon from a two-body LJ (12–6) potential derived from gas data and experiment, no such agreement is found for krypton. Mandel[32] has found that the thermodynamic data of liquid krypton require a much steeper repulsive two-body potential $(r^{-18.5})$ than has been found for 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 $\langle\nabla^2U\rangle$ 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 rupulsive part of the two-body potential to increase monotonically for the substances Xe < Kr < Ar < Ne < He. This would suggest an inverse order for $\langle\nabla^2U^*\rangle$. If anything, the data shown in Figure 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 $\langle\nabla^2U^*\rangle$ among the rare gases is at most 10%. Deviations of the values of $\langle\nabla U^*\rangle$ 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 $\langle\nabla^2U\rangle$. The present reduced plots of $\langle\nabla^2U^*\rangle$ 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 mo-

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lecular and intermolecular forces at the site of isotopic substitution. When the physical phenomenon investigated is the vapor pressure, new independent information is obtained about the characteristic temperature of a solid and the mean square force, $kT\langle\nabla^2 U\rangle$, acting on the molecules in the liquid. Because anharmonic effects strongly influence many properties of liquids and solids, vapor pressure isotope effect studies on the rare gases have led to significant improvement in our knowledge of such quantities as the lattice energy and the thermal properties of simple solids and liquids. It has been shown that the logarithm of the isotope vapor pressure ratio for the solid rare gases has a T^{-2} rather than a T^{-1} temperature dependence as a leading term, in accord with expectations for an equilibrium phenomena which is quantum mechanical in origin and small in magnitude.

$\langle\nabla^2 U\rangle$ associated with translational motion in a condensed phase when multiplied by the molar volume, V, has been shown to be 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. As a result many properties of solids and liquids, particularly thermodynamic properties, are insensitive to structural details of the condensed phase.

The law of corresponding states has been found useful to correlate the mean square force between rare gas atoms in the solid and the liquid. Deviations of the order of 10% have been demonstrated. The failure of the law of corresponding states, even for such simple substances as the rare gases, is a consequence of the fact that the repulsive part of the interatomic rare gas potentials cannot be scaled and of the influence of three-body forces. The magnitude of the effect of the latter on the law of corresponding states has yet to be investigated.

Experimental values of $\langle\nabla^2 U\rangle$ for the liquid rare gases provide quantitative confirmation of the radial distribution function of simple fluids calculated by molecular dynamics. Experimental radial distribution functions determined by scattering, X-ray and neutron, when combined with a variety of reasonable interatomic potentials give poor agreement with $\langle\nabla^2 U\rangle$ determined from vapor pressure isotope effect studies.

We can anticipate that the information obtained about the translational motion in rare gas solids and liquids, in particular $\langle\nabla^2 U\rangle$ as a function of temperature, density, and phase, will provide a base for the more complicated behavior of polyatomic molecules.