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Compressibility of Liquids: Theoretical Basis for a Century of Empiricism

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We show how the successful empirical results of the past century for the compressibility of liquids can be obtained from a recent statistical-mechanical theory that includes dense fluids as well as low-density gases and vapors. The theory also shows to what extent the results for liquids can be extended to dense supercritical fluids and how they can be generalized to any number of dimensions. For simplicity only argon and a Lennard–Jones (12,6) fluid are examined in detail, but the results can probably be extended to real molecular fluids.

KEY WORDS: argon; equation of state; Lennard–Jones fluid; liquid compressibility; Tait equation.

1. INTRODUCTION

There exists no general simple analytical equation of state for liquids based on fundamental theory, although many empirical ones have been proposed for practical use [1–3]. The empirical formulas can be classified into those that treat the bulk modulus (reciprocal compressibility) as a proper derivative and those that represent it by its finite-difference analogues. A successful equation valid over a wide range of pressure can be expressed as

$$\left(\frac{\partial B}{\partial p}\right)_T = \left[\frac{\partial(1/\kappa_T)}{\partial p}\right]_T = -\left(\frac{\partial \ln \kappa_T}{\partial \ln \rho}\right)_T = C(T) \tag{1}$$

where p is the pressure, ρ is the density, B is the bulk modulus, and κ_T is the isothermal compressibility,

$$\kappa_T = \frac{1}{B} \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial p}\right)_T \tag{2}$$

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The dimensionless temperature-dependent coefficient $C(T)$ is referred to here as the Moelwyn–Hughes number, in recognition of his use of it to determine intermolecular-potential parameters, via a lattice-model theory of the liquid state [4–6]. Although Eq. (1) has been mainly used for highly compressed liquids and solids, it also holds for ideal gases with $C(T)=1$.

Integration of Eq. (1) can be carried out with either p or ρ as the independent variable. The first integrals are

$$\frac{1}{\kappa_T}-\frac{1}{\kappa_T^0}=C(p-p_0) \tag{3}$$

or

$$\kappa_T/\kappa_T^0=(\rho_0/\rho)^C \tag{4}$$

where κ_T^0 is the compressibility at the reference pressure p_0 and reference density ρ_0. The second integral is the p–V–T equation of state,

$$\frac{V_0}{V}=\frac{\rho}{\rho_0}=[1+C\kappa_T^0(p-p_0)]^{1/C} \tag{5}$$

where V_0 is the reference volume. This form was derived by Murnaghan [7], starting from an expression for the bulk modulus of an elastic solid, and has been called the Murnaghan equation [2]. The third integrals give the Gibbs free energy as a function of either pressure or density and are easily found by straightforward integration [6].

The linear relation between bulk modulus and pressure exemplified by Eq. (1) is essentially due to Tait [1–3] but was originally expressed in terms of an average or finite-difference modulus, $\bar{B}$, now usually called the secant bulk modulus,

$$\bar{B}\equiv\frac{V_0(p-p_0)}{V_0-V}=\frac{p-p_0}{1-\rho_0/\rho} \tag{6}$$

This is a more convenient quantity than the differential modulus B, since differentiation of experimental data greatly amplifies errors.

The purpose of this paper is to show how the successful empirical results follow from a statistical-mechanical theory that includes dense fluids as well as low-density gases and vapors [8]. This seems to be the first time that these results have been given a strong basis in statistical mechanics. It also shows to what extent they can be extended from compressed liquids to dense supercritical fluids. For simplicity we consider here only spherical particles with central-force interactions and test the results on computer simulations of a Lennard–Jones (12,6) fluid and on argon. However, the arguments are not essentially changed for nonspherical molecules [9], although of course many details are different.

2. THEORY

The crucial ingredients that have made possible a successful statistical-mechanical equation of state are two in number. The first is the recognition that the structure of simple dense fluids is determined largely by the repulsive intermolecular forces, so that a fluid of hard spheres can serve as a reference system on which to base perturbation theories. This is the basis of successful modern theories of liquids. A succinct review of the rather involved history of this view has been given by J. S. Rowlinson in Section 5.5 of his Introductory Essay to the recent printing of an English translation of the Leiden thesis of van der Waals [10]. A statistical-mechanical theory based on this idea yields an equation of state of the following form [8]:

$$\frac{p}{\rho kT} = 1 + B_2(T)\rho + \alpha(T)\rho\{g[b(T)\rho] - 1\} \tag{7}$$

where ρ is the number (molar) density, kT has its usual meaning, and $g[b(T)\rho]$ has the same mathematical form as the pair distribution function at contact for equivalent hard spheres (whose temperature-dependent effective diameter is determined by the true intermolecular potential).

It should be emphasized that this equation of state is in fact a new result. Although related to them, it differs from modern liquid theories in that it is an analytic result, rather than a purely numerical one, and its three parameters depend only on the temperature. The parameters are related to the intermolecular pair potential $u(r)$ by straightforward quadratures:

$$B_2(T) = 2\pi \int_0^\infty [1 - e^{-u(r)/kT}]r^2\,dr \tag{8}$$

$$\alpha(T) = 2\pi \int_0^{r_m} [1 - e^{-u_0(r)/kT}]r^2\,dr \tag{9}$$

$$b(T) = \alpha + T\frac{d\alpha}{dT} = 2\pi \int_0^{r_m} \left[1 - \left(1 + \frac{u_0}{kT}\right) e^{-u_0(r)/kT}\right] r^2\,dr \tag{10}$$

Here $u_0(r)$ is the repulsive part of $u(r)$,

$$u_0(r) = \begin{cases} u(r) + \varepsilon, & r < r_m \\ 0, & r > r_m \end{cases} \tag{11}$$

where ε is the depth of the potential well and r_m is its minimum position. This is the Weeks–Chandler–Andersen [11] decomposition of $u(r)$. The physical interpretation of these parameters is as follows: $B_2(T)$ is the second virial coefficient; $\alpha(T)$ is the contribution to $B_2(T)$ from the intermolecular repulsive forces and acts as a scaling factor for the "softness" of these forces; and $b(T)$ corresponds to a van der Waals covolume for equivalent hard spheres [8].

The second crucial ingredient of the equation of state is the availability of an accurate simple approximation for the equation of state of a hard-sphere fluid, from which the mathematical form of $g[b(T)\rho]$ can be found. Carnahan and Starling [12] found such an approximation by noticing some algebraic regularities in the known virial coefficients of hard spheres. Their result is virtually indistinguishable from computer simulations of hard-sphere fluids; possible reasons for this outstanding success have been advanced [13]. The form of $g[b(T)\rho]$ found from the Carnahan–Starling equation of state is especially simple when written in terms of the variable $\eta \equiv \frac{1}{4}b(T)\rho$ [12, 13],

$$g(\eta) = \frac{1-\eta/2}{(1-\eta)^3} \tag{12}$$

where η is interpreted to be the packing fraction (the fraction of space filled by particles) for the equivalent hard spheres. This expression for $g(\eta)$ is very accurate up to the freezing density but fails at the still higher densities that correspond to metastable compressed liquid. Other, more elaborate, expressions for $g(\eta)$ are available that are accurate at these higher densities [14, 15], but we do not need them here.

On substituting Eq. (12) into Eq. (7), we obtain an explicit analytic form for the equation of state (we here drop the explicit notation for the temperature dependence of B_2, α, and b),

$$p = \rho kT\left[1 + (B_2 - \alpha)\rho + 8\alpha\rho\,\frac{(8-b\rho)}{(4-b\rho)^3}\right] \tag{13}$$

The accuracy of this expression has previously been tested on computer simulations and on a number of selected real fluids over a wide range of densities [8], but little attention was paid to the regions of compressed liquid, which we now wish to examine. It is straightforward to evaluate the isothermal compressibility from Eq. (13),

$$B = \frac{1}{\kappa_T} = \rho\left(\frac{\partial p}{\partial \rho}\right)_T = \rho kT\left[1 + 2(B_2 - \alpha)\rho + 32\alpha\rho\,\frac{(16-b\rho)}{(4-b\rho)^4}\right] \tag{14}$$

Equations (13) and (14) constitute the fundamental theoretical relation between κ_T and pressure, expressed parametrically with the density as the parameter. It is not obvious that elimination of ρ between Eq. (13) and Eq. (14) will lead to a linear or nearly linear relation between $1/\kappa_T$ and p below the critical temperature, as suggested by Eq. (3) in Section 1. However, it is not necessary to eliminate ρ analytically in order to investigate this point; it is just as easy to carry out the elimination numerically, as described in the following section.

A final comment is in order on the approximations contained in Eqs. (13) and (14). We have already mentioned the restriction to spherical particles with central-force interactions and the fact that these approximations can be relaxed. A more serious assumption is that of pairwise additivity of the intermolecular forces, which enters primarily through Eq. (12) for $g(\eta)$. Many-body forces are still included in the $g(\eta)$ appearing in the general form given by Eq. (7), but Eq. (12) involves pairwise additivity.

3. NUMERICAL CALCULATIONS

Given $u(r)$, it is straightforward to calculate $B_2(T)$, $\alpha(T)$, and $b(T)$ from Eqs. (8)–(10), and then to generate numerical values of $1/\kappa_T$ from Eq. (14) and corresponding values of p from Eq. (13). We have carried out such calculations over a wide range of pressures and temperatures for fluids obeying a Lennard–Jones (12,6) potential,

$$u(r) = \varepsilon\left[\left(\frac{r_m}{r}\right)^{12} - 2\left(\frac{r_m}{r}\right)^{6}\right] \tag{15}$$

The results are shown in Fig. 1 in terms of the reduced quantities,

$$\kappa_T^* \equiv \kappa_T \varepsilon / r_m^3 = 1/B^*, \qquad p^* \equiv p r_m^3/\varepsilon, \qquad T^* \equiv kT/\varepsilon \tag{16}$$

where ε/r_m^3 has the dimensions of pressure.

The liquid range in Fig. 1 is the roughly triangular region enclosed by the critical isotherm, T_c^*, and the dashed curves. In this range, the curves are quite straight; even the critical isotherm (T_c^*) has only a small amount of curvature. Above the critical temperature the curves start off with the slope of the ideal-gas relation, $1/\kappa_T = p$, but eventually bend upward and become straight at the very high pressures corresponding to dense supercritical fluid. Notice that the scale in Fig. 1 extends to quite high pressures, since the critical pressure on this scale is only $p_c^* \approx 0.2$. The corresponding results for argon as calculated from the best available pair potential [16]

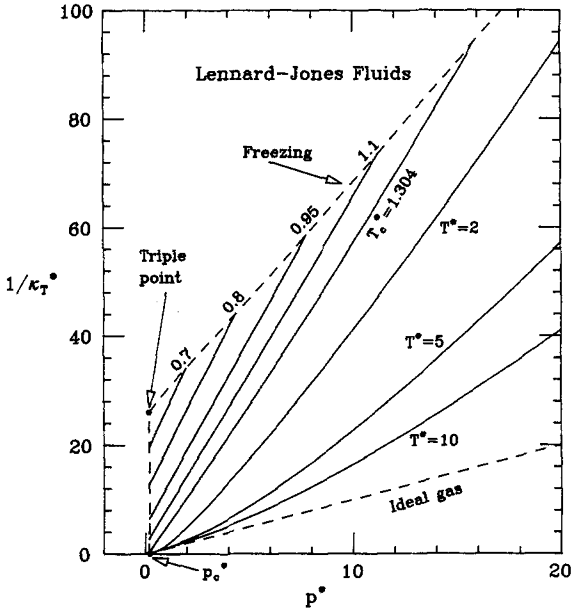

Fig. 1. Reciprocal isothermal compressibility as a function of pressure at different temperatures for a Lennard-Jones (12,6) fluid. The reduced quantities used are defined in Eq. (16).

are so similar to those shown in Fig. 1 that it is not worth displaying them separately.

It is convenient to fit straight lines to the liquid isotherms in Fig. 1,

$$B^* = \frac{1}{\kappa_T^*} = \frac{1}{(\kappa_T^0)^*} + Cp^* = B_0^* + Cp^* \qquad (17)$$

where the slope C is the Moelwyn–Hughes number and $1/(\kappa_T^0)^* = B_0^*$ is the (extrapolated) intercept at $p^* = 0$. Both C and B_0^* are functions of temperature, and the fitted values are given in Table I for both the (12,6) potential and the accurate Aziz–Slaman [16] argon potential. It happens that C varies linearly with reciprocal temperature for both potentials, as shown in Fig. 2. This is only an empirical observation on our part. The intercept and slope for the (12,6) potential are 3.253 and 3.417, respectively, and those for the Aziz–Slaman argon potential are 2.953 and 3.244. However, the temperature dependence of $(\kappa_T^0)^*$ is more complicated, and Fig. 3 shows that B_0^* vs. $1/T^*$ is noticeably curved.

On integration, Eq. (17) yields the so-called Murnaghan equation [2, 7], given as Eq. (5) in Section 1. In his original paper, Murnaghan also

Table I. Reduced Bulk Modulus as a Linear Function of Reduced Pressure: $B^* = B_0^* + Cp^*$

Lennard–Jones (12–6)			Ar		
T^*	C	B_0^*	T^*	C	B_0^*
0.70	8.150	18.23	0.60	8.392	18.45
0.75	7.810	14.48	0.65	7.942	13.85
0.80	7.518	11.48	0.70	7.571	10.41
0.85	7.262	9.040	0.75	7.257	7.755
0.90	7.040	7.021	0.80	6.991	5.662
0.95	6.845	5.327	0.85	6.762	3.978
1.00	6.667	3.902	0.90	6.556	2.618
1.05	6.511	2.680	0.95	6.382	1.485
1.10	6.368	1.636	1.00	6.221	0.5596
1.15	6.232	0.7517	1.05	6.071	−0.1904
1.20	6.110	−0.0109	1.122[a]	5.876	−0.9842
1.25	5.994	−0.6469			
1.304[a]	5.877	−1.1766			

[a] These are the critical temperatures as calculated from Eq. (13).

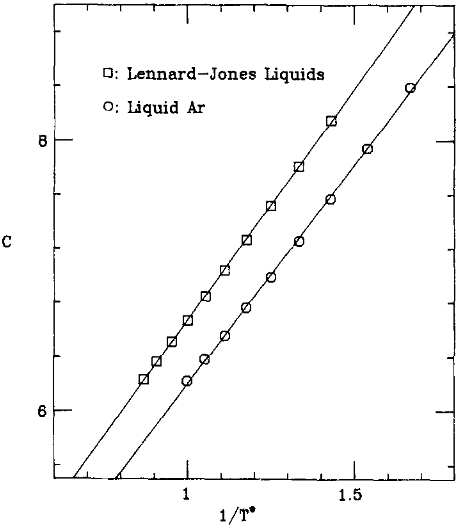

Fig. 2. Temperature dependence of the Moelwyn-Hughes number C (the slopes of the liquid isotherms in Fig. 1) for a (12,6) liquid and for liquid argon.

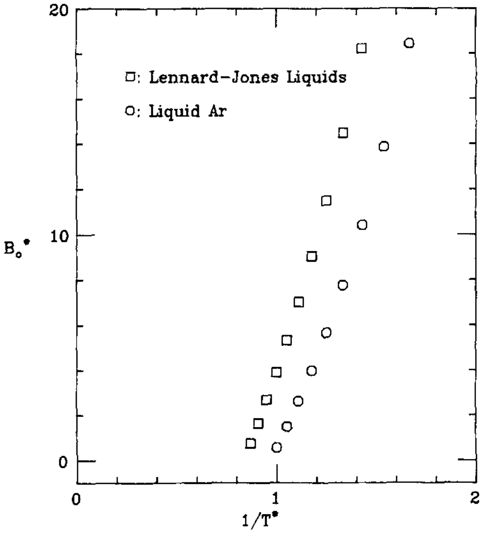

Fig. 3. Temperature dependence of the intercepts of the liquid isotherms in Fig. 1.

considered modifying his equivalent of Eq. (17) by adding higher terms in p^2, p^3, etc. Although we could easily do this as an exercise in curve-fitting, we believe it is more sensible to work directly with the statistical-mechanical Eqs. (13) and (14), rather than bother with an extended Taylor expansion.

4. COMPARISON WITH EXPERIMENT

We now wish to compare the theoretical results from Eqs. (13) and (14), as summarized by the simple linear Eq. (17), with computer simulation data for the (12,6) liquid [17, 18] and with experimental data for liquid argon [19]. This is best done with the equations in integrated form to avoid error amplification. It is convenient to use the secant bulk modulus $\bar{B}$ defined in Eq. (6). Theoretical values of $\bar{B}$ can be numerically generated from Eq. (13) for the pressure or can be calculated analytically from the integrated form of Eq. (17),

$$\bar{B}=\frac{p-p_0}{1-[1+C\kappa_T^0(p-p_0)]^{-1/C}} \tag{18}$$

where κ_T^0 is the compressibility at the reference pressure p_0.

The results for the (12,6) liquid are shown in Fig. 4 in terms of the reduced quantities $\bar{B}^* \equiv \bar{B}r_m^3/\varepsilon$ and $p^* \equiv pr_m^3/\varepsilon$, for three temperatures, the highest of which ($T^* = 1.35$) is very close to the critical temperature. We

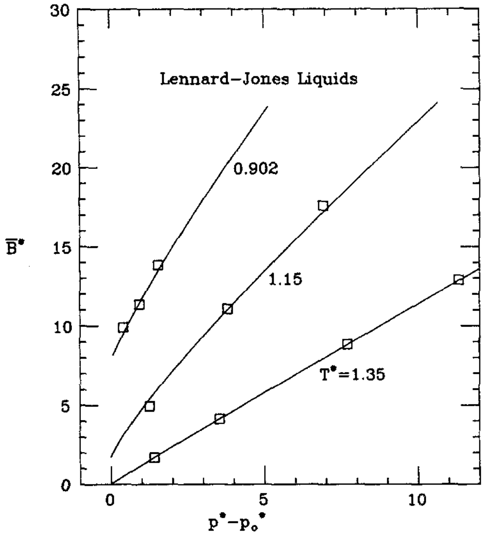

Fig. 4. Calculated and computer-simulated values of the reduced secant bulk modulus, $\bar{B}^*$, as a function of reduced pressure for a Lennard–Jones liquid at three temperatures. The points are the computer simulations [17, 18] and the curves are calculated from Eq. (13).

have used Eq. (13) to calculate $\bar{B}^*$ and have chosen the reference pressure to be $p_0^* = 0.15$. For consistency we have used the value of ρ_0 from Eq. (13) throughout. The agreement is remarkably good.

Similar results for liquid argon are shown in Fig. 5, with the reference pressure p_0 chosen to be the actual saturated vapor pressure at the specified temperature. The reference densities for the experimental points were taken to be the experimental densities of the saturated liquid. The curves were calculated from Eq. (13) using the Aziz–Slaman potential, with ρ_0 also calculated from Eq. (13). The agreement is fairly good, but there are some obvious systematic deviations; these may possibly be caused by many-body forces, which are absent in the (12,6) liquid.

An interesting feature shown in both Fig. 4 and Fig. 5 is the nonlinearity of the $\bar{B}$ vs p isotherms. The original Tait equation takes these isotherms as linear, and Hayward [1] has claimed that this is the best two-constant representation of the equation of state of liquids. He has also asserted that no two-constant equation is satisfactory at very high pressures. Both the points and the curves in Figs. 4 and 5 show that neither of these assertions is true. The statistical-mechanical result predicts distinct curvature of the secant bulk modulus $\bar{B}$, in agreement wih experiment.

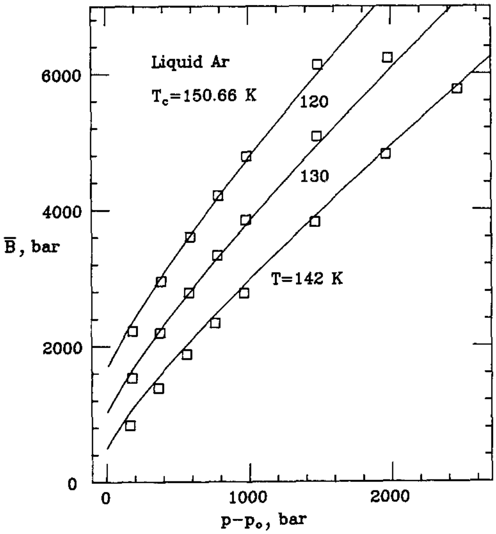

Fig. 5. Calculated and experimental values of the secant bulk modulus of liquid argon as a function of pressure at three temperatures. The points represent experimental data [19] and the curves are calculated from Eq. (13).

5. COMPARISON WITH LATTICE THEORIES

Although lattice theories are now regarded as a rather unsuccessful chapter in the history of the theory of liquids [20], they do show some interesting features that are worth comparing with the present results. By attributing the modulus entirely to the intermolecular potential energy and assuming a Lennard-Jones (n, m) potential, Moelwyn-Hughes [4, 5] obtained from lattice theory the relation,

$$C = \tfrac{1}{3}(n + m + 6) \tag{19}$$

This should apply best at the lowest temperature available, since thermal kinetic energy is neglected. From Table I we find $C \approx 8.15$ near the triple point for the (12,6) potential; Eq. (19) predicts a value of 8.00, which is not a bad agreement. Perhaps more significantly, the lattice theory indicates that C depends only on T, which is indeed the case.

Another connection to lattice theories, whether classical or quantum, comes from the relation between the characteristic vibrational frequency ν and the Grüneisen number Γ,

$$-\frac{d \ln \nu}{d \ln V} = \Gamma = \frac{\alpha_p V}{\kappa_T C_V} \tag{20}$$

where $\alpha_p = V^{-1}(\partial V/\partial T)_p$ is the coefficient of thermal expansion and C_V is the constant-volume heat capacity. In the application of the lattice theories the Grüneisen number is usually taken to be constant. It is never made clear in such theories why it must be so; the power law implied by Eq. (20) means there is no preferred macroscopic volume scale. It is only through a constant Γ that lattice theory can deliver any result for the coefficient of thermal expansion.

Grüneisen [21] was the first to observe that the ratio α_p/C_V is approximately independent of T. The dimensionless number Γ, which now bears his name, has been observed to be essentially constant for solid metals from low to moderate temperatures and up to high pressures. This constancy also is found for liquid mercury; compilations of Γ for other liquids do not appear to be easily accessible. As with the Moelwyn-Hughes number the Grüneisen number is constant for ideal gases, at least to the extent that C_V can be taken as constant.

The expression for Γ can also be written in an equivalent form that emphasizes its dependence on the equation of state,

$$\frac{1}{\Gamma} = \frac{C_{V_0} + \int_{V_0}^{V} T(\partial^2 p/\partial T^2)_V \, dV}{V(\partial p/\partial T)_V} \tag{21}$$

Thus only one value of C_V at each T is required.

The thermal expansion coefficient is readily found from Eq. (13) to be

$$\alpha_p = \frac{1}{T}\left[1 + \left(B_2 + T\frac{dB_2}{dT} - b\right)\rho + \frac{8b\rho(8-b\rho)}{(4-b\rho)^3} + 16\alpha\rho^2\left(T\frac{db}{dT}\right)\frac{(10-b\rho)}{(4-b\rho)^4}\right] \times\left[1 + 2(B_2-\alpha)\rho + 32\alpha\rho\frac{(16-b\rho)}{(4-b\rho)^4}\right]^{-1} \tag{22}$$

An equation of state alone cannot determine the temperature dependence of C_V. We have therefore used experimental values of C_V for liquid argon [19] but have calculated α_p, κ_T, and V from the equation of state. The results are shown in Fig. 6 for liquid argon, where it is clear that Γ is not constant, but depends quite significantly on both temperature and pressure. Moelwyn-Hughes [4, 5] calculated Γ for the (n, m) potential by means of lattice theory and obtained,

$$\Gamma = \tfrac{1}{6}(n+m+1) \tag{23}$$

which yields $\Gamma = 3.17$ for the (12,6) potential. Figure 6 shows that this is likely to be only roughly true, and only at low temperatures and high pressures.

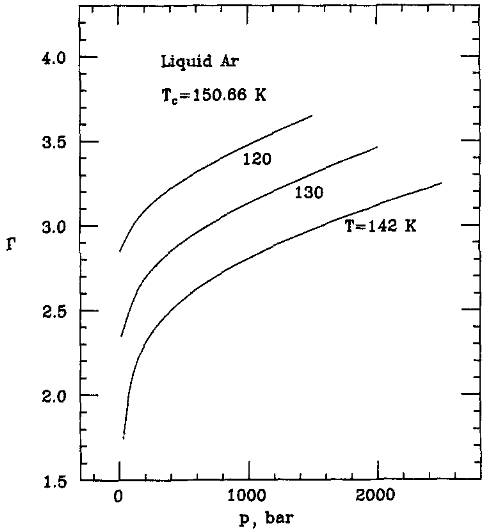

Fig. 6. Grüneisen number, $\Gamma \equiv \alpha_p V/\kappa_T C_V$, of liquid argon as a function of pressure at three temperatures. It is clear that Γ is far from constant.

6. OTHER DIMENSIONALITIES

It is often informative to investigate how results depend on the dimensionality of space. This is easily done in the present case because the statistical-mechanical Eq. (7) for the p–V–T relation has been generalized to d dimensions [22]. The form of Eq. (7) remains unaltered, but Eq. (12) for the contact pair distribution function $g(\eta)$ becomes

$$g(\eta) = \frac{1 - \gamma\eta}{(1 - \eta)^d} \tag{24}$$

where $\eta = b\rho/2^{d-1}$ is the packing fraction in d dimensions, and γ is a known constant that depends on d. The definitions of the parameters $B_2(T)$, $\alpha(T)$, and $b(T)$ are also generalized in a straightforward way [22], but there is no need to write down the expressions here.

We have calculated κ_T and examined plots of $1/\kappa_T^*$ vs ρ^* for Lennard-Jones (12,6) molecules in spaces of 1, 2, 4, and 5 dimensions. Except that the numerical scales increase with increasing d, the results resemble Fig. 1 for $d = 3$ in that the liquid isotherms ($T^* < T_c^*$) are well approximated by straight lines. If anything, a linear approximation of the liquid isotherms becomes better as d increases. Thus the present results seem to be valid in all dimensions.

7. CONCLUSIONS

The most important conclusion to be drawn from the present results is that the nearly linear pressure dependence of the bulk modulus of a liquid can be given a strong basis in statistical mechanics. Thus the Murnaghan equation turns out to have the best theoretical pedigree of all the empirical equations of state for liquids.

The present results also show to what extent the results for liquids can be extended to supercritical fluids. From Fig. 1 we can see that the supercritical isotherms do not approach liquid-like behavior until rather high pressures are reached—roughly $p^* \approx 10$, or pressures about 50 times the critical pressure.

The Moelwyn-Hughes number C is indeed found to be a function of temperature, almost independent of pressure. However, the Grüneisen "constant" Γ is found to depend rather strongly on both T and p. Thus C is a useful quantity for compressed liquids, whereas Γ is not.

There are, of course, a number of limitations to the present theoretical results. We have ignored the effects of nonspherical intermolecular forces and of possible many-body forces and considered only pairwise additive central forces. However, recent work on the theory of molecular fluids [9] gives the prospect that at least some of these restrictions can be eased and the results applied to real molecular fluids.

If the theory can indeed be extended to molecular liquids, the practical question arises as to how to find scale factors corresponding to ε and r_m, in order that the theory can have real predictive power. The present statistical-mechanical theory would take ε and r_m from experimental values of $B_2(T)$, the second virial coefficient of the vapor [8]. But $B_2(T)$ would not be known experimentally for many compressed liquids of interest, and another method for finding suitable scale factors would be needed.

In summary, the present work shows how the equation of state of compressed liquids can be given a statistical-mechanical basis, but further work is needed for application to real molecular liquids.

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