ON THE STRUCTURAL PART OF THE COMPRESSIBILITY OF LIQUIDS

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Abstract

The 'structural' part of the bulk modulus, represented by the contribution of the entropy term in the free energy, is examined and related to the temperature coefficient of the bulk modulus. This quantity is computed for the harmonic oscillator and free volume models, as also on the basis of a simple kinetic theory treatment. The values agree with experiment as regards the order of magnitude.

1. Introduction

It has been suggested[1] that the compressibility of a liquid can be expressed as the sum of two contributions:

(*a*) a geometrical part due to the simultaneous contraction of the intermolecular spacing under the influence of pressure,

(*b*) a structural part that stems from a molecular rearrangement as a result of the increased regularity and compactness.

It was also shown[2] that the second contribution can be expressed in terms of the temperature coefficient of the compressibility. Thus considering the Bulk Modulus,

$$\begin{aligned} K_T &= -V\left(\frac{\partial P}{\partial V}\right)_T = V\left(\frac{\partial^2 F}{\partial V^2}\right)_T \\ &= V\left(\frac{\partial^2 U}{\partial V^2}\right)_T - TV\left(\frac{\partial^2 S}{\partial V^2}\right)_T \\ &= K_T{}^g + K_T{}^s \end{aligned}$$

where $K_T{}^g$ and $K_T{}^s$ are the geometrical and the structural parts. Now, $K_T{}^s$ can be expressed in terms of the dK_T/dT for,

$$\left(\frac{\partial^2 S}{\partial V^2}\right)_T = \frac{\partial}{\partial V}\left[\frac{\partial p}{\partial T}\right]_v = \frac{\partial}{\partial T}\left[\frac{\partial p}{\partial V}\right]_T = \left[\frac{1}{V}\frac{\partial K_T}{\partial T} + K_T\alpha\right]$$

where α is the thermal expansivity.

Since, dK_T/dT is negative for most liquids,

$$K_T = V\left(\frac{\partial^2 U}{\partial V^2}\right)_T - T\left[\left|\frac{dK_T}{dT}\right| + K_T\alpha\right].$$

Further,

$$\frac{1}{K_T}\frac{dK_T}{dT} \sim 1\%$$

for most liquids, so that the second term is about 3 to 4 times K_T at room temperatures, and the first correspondingly greater by a factor 4 to 5 K_T.

The first term $V\,\partial^2 U/\partial V^2$ is the one employed in the computation of the K_T in solids, where the entropy contribution is negligible. Thus

$$\frac{1}{K_T}\cdot\frac{dK_T}{dT} \sim 0{\cdot}1\%$$

in solids, and K_T' 10 to 20% of K_T. In liquids, however, the second term resulting from a more favourable distribution of the molecules under pressure, is the major contribution to the decrease in Bulk Modulus as compared to a solid. In fact, it can be shown that the effect of enhanced molecular distance alone cannot account for the drop in Bulk Modulus by a factor of nearly 10 from that of the solid.

A similar situation exists, as was pointed out by Frenkel, when the expression for the pressure is considered

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = -\left(\frac{\partial U}{\partial V}\right)_T + T\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial U}{\partial V}\right)_T + T\left(\frac{\partial P}{\partial T}\right)_V .$$

The first term is the static or elastic part of the pressure, and the second the thermal part, the volume of the body representing a condition of equilibrium between the thermal pressure tending to expand it and the elastic force tending to restore the original volume. The two contributions to K_T will now be evaluated on the basis of the two simple models adopted for liquids, the harmonic oscillator and smoothed potential models.

2. THE HARMONIC OSCILLATOR MODEL

A quasi-lattice of equilibrium positions of potential minima—χ_0 is chosen, and the molecules regarded as simple harmonic oscillators of frequency ν. For convenience, the lattice can be regarded as face-centred cubic. Then, from the partition function, the following expressions are obtained for the free energy, pressure, and the Bulk Modulus.[3]

$$F = -N\chi_0 + 3RT\,ln\,\frac{kT}{h\nu} + RT$$

$$P = N\left(\frac{\partial\chi_0}{\partial V}\right)_T + 3RT\,\frac{\partial}{\partial V}(ln\,\nu)_T.$$

Hence,

$$K_T = -NV\left(\frac{\partial^2\chi_0}{\partial V^2}\right)_T - 3RTV\,\frac{\partial^2}{\partial V^2}(ln\,\nu)_T.$$

Assuming a Lennard-Jones potential,

$$-\chi_0 = \frac{z}{2}\left[-\frac{a}{r^6} + \frac{b}{r^{12}}\right]$$

where z is the co-ordination number, the equilibrium is then given by,

$$-\mathrm{N}\left[\frac{\partial\chi_0}{\partial\mathrm{V}}\right]_{\mathrm{T}} = 3\mathrm{RT}\cdot\frac{\partial}{\partial\mathrm{V}}(ln\ \nu)_{\mathrm{T}}$$

where the frequency

$$\nu = \frac{1}{2\pi}\sqrt{\frac{f}{m}}$$

and the restoring force,

$$f = \frac{4}{\sqrt{2}}\left(\frac{\partial^2\chi_0}{\partial r^2}\right)_{eq.}$$

for a face-centred cubic lattice, taking account of only nearest neighbour interactions.

Now, assuming the equilibrium distance in a crystal is given by R_0,

$$(\partial\chi_0/\partial r) = 0.$$

$$b = a\mathrm{R}_0^{6}/2$$

and in the liquid,

$$\mathrm{R}' = \mathrm{R}_0(1+\delta):\quad \delta \ll 1,$$

substitution in the equation gives,

$$6\cdot\frac{\mathrm{N}z}{2}\cdot\frac{a}{\mathrm{R}_0^{7}}\cdot 6\delta = \frac{3\mathrm{RT}}{2}\cdot\left[\frac{8-156\delta}{1-14\delta}\right]\cdot\frac{1}{\mathrm{R}}.$$

Now, a can be eliminated by the relation,

$$\frac{\mathrm{N}z}{2}\cdot\frac{a}{\mathrm{R}^6} \bumpeq \lambda_m$$

where λ_m is the molar latent heat. Hence,

$$\delta \bumpeq 0\cdot 5\,\frac{\mathrm{RT}}{\lambda_m} \sim \mathbf{0\cdot 025},$$

by *Trouton's Rule*

$$\frac{\lambda_m}{\mathrm{RT}_b} \bumpeq 20 \text{ and } \mathrm{T}_b \sim \mathrm{T}.$$

This, of course, is in accordance with the fact that the increase in volume on passage to the liquid state is $\sim 10\%$.

Hence the two components of K_T are obtained,

$$-NV\left[\frac{\partial^2 \chi_0}{\partial V^2}\right]_T = -NV\left[\left(\frac{r}{3V}\right)^2 \cdot \frac{\partial^2 \chi_0}{\partial r^2} + \frac{2}{9} \cdot \frac{r}{3V^2} \cdot \left(\frac{\partial \chi}{\partial r}\right)^2\right]$$

and this value comes out as nearly

$$2 \cdot \frac{Nza}{R^6 V} \sim 4 \frac{\lambda_m}{V} \sim 4 \times 10^{10} \text{ dynes/cm.}^2$$

Similarly, for the structural contribution,

$$3RTV \frac{\partial^2}{\partial V^2}(ln\, v) \doteqdot \frac{3RTV}{2} \cdot \frac{R_0^2}{9V^2} \cdot R_0^{-2}\left[\frac{390 - 4\delta}{1 - 14\delta}\right].$$

Substituting the values, the L.H.S. has a value,

$$|\, K_T^s \,| \sim 10RT \sim 2{\cdot}4 \times 10^{10} \text{ dynes/cm.}^2,$$

at $T = 300°$ K., which is of the right order of magnitude.

3. THE SMOOTHED POTENTIAL MODEL

The intermolecular potential is replaced by a value averaged over all configurations and a free volume is introduced. The expressions for the free energy, pressure, and Bulk Modulus are given by (3).

$$F = -N\chi_0 - RT\, ln\, V_f + RT\, ln\left[\frac{2\pi mkT}{h^2}\right]^{3/2} + RT$$

$$P = N\left(\frac{\partial \chi_0}{\partial V}\right)_T + RT \frac{\partial}{\partial V}(ln\, V_f)_T.$$

Hence,

$$K_T = -NV\left(\frac{\partial^2 \chi_0}{\partial V^2}\right)_T - RTV \frac{\partial^2}{\partial V^2}(ln\, V_f)_T.$$

The geometrical contribution to K_T is the same as in the previous case, while to find the structural part, some assumption has to be made regarding the free volume V_f. The simplest is to assume

$$V_f = (V - V_0)$$

where V_0 is analogous to the Van der Waals co-volume.

The structural part is thus negative, and

$$K_T^s = -\frac{RT}{V} \cdot \left[\frac{V}{V - V_0}\right]^2$$

values of V_0 from latent heat and thermal pressure data give,

$$\left[\frac{V}{V - V_0}\right] \sim 10^2$$

so that

$$K_T^s \sim 10^{11} \text{ dynes/cm.}^2$$

which is too high by about a factor of ~ 10. Using a more refined '*cage*' model (3),

$$V_f = \frac{4}{3}\pi\sqrt{2} \cdot [V^{\frac{1}{3}} - V_0^{\frac{1}{3}}]^3$$

$$= \frac{4}{3}\pi\sqrt{2} \, . \, V[1-\theta]^3; \;\; \theta = \left(\frac{V_0}{V}\right)^{\frac{1}{3}}$$

$$\frac{\partial^2}{\partial V^2} \ln (V_f) = \frac{-1}{V^2} \cdot \frac{1 - \frac{4}{3}\theta}{(1-\theta)^2}$$

so that the structural part is,

$$| K_T^s | = \frac{RT}{V} \cdot \frac{\left(\frac{4}{3}\theta - 1\right)}{(1-\theta)^2} \cdot$$

With values of $(1 - \theta) \approx 10^{-3}$,

this yields values of nearly the right order of magnitude for $| K_T^s |$.

4. THE KINETIC THEORY TREATMENT

Finally, we shall consider the expressions for K_T and its temperature coefficient on the basis of the kinetic theory, starting from the expression for the pressure,

$$P = nkT - \tfrac{1}{6}\int \bar{n}_2(r) \cdot r \cdot \frac{d\phi(r)}{dr} \cdot 4\pi r^2 dr$$

[the integral being extended over the volume of the liquid and $\bar{n}_2(r)$ being the radial distribution function] the differentiation with respect to V can be carried out by the method following Green.[4, 5]

The integral involves a magnitude,

$$R = \gamma V^{\frac{1}{3}}: \qquad\qquad \gamma = \text{constant}$$

so that the limits can be got rid of by the substitution,

$$\rho = V^{-\frac{1}{3}} r,$$

then,

$$\frac{\partial}{\partial V}(dr) = \frac{dr}{3V}$$

$$\frac{\partial}{\partial V}[\bar{n}_2 \, . \, \phi' \, . \, r^3] = \frac{r}{3V} \cdot \frac{\partial}{\partial r}[\bar{n}_2 \, . \, \phi' \, . \, r^3].$$

The latter differentiation involves $\partial \bar{n}_2/dr$ and this can be calculated as follows:—

For a uniform stress, the distance between the molecules changes to

$$r' = r\left[1 - \frac{dr}{r}\right]$$

while the molecular density changes by

$$n' = n\left[1 - \frac{dV}{V}\right] = n\left[1 - 3\frac{dr}{r}\right].$$

Since the probability of finding a molecule in a volume element dV at a distance r from an occupied position, in the undeformed state is the same as that of finding it a distance r' in the deformed state, in dV',

$$\frac{\bar{n}_2}{n_1} \cdot dV = \frac{\bar{n}_2'}{n_1'} \cdot dV'.$$

$$\bar{n}_2' = \bar{n}_2\left[1 - 6\frac{dr}{r}\right]$$

$$\therefore \quad \frac{d\bar{n}_2}{dr} = -6\frac{\bar{n}_2}{r}.$$

$$\therefore \quad \frac{\partial}{\partial V}\left[\int \bar{n}_2 \cdot \phi' \cdot r^3\, dr\right] = \frac{1}{3V}\int\left[\bar{n}_2 \cdot \phi'' \cdot r^4 - 2\bar{n}_2 \cdot \phi' \cdot r^3\right] dr$$

$$\therefore \quad K_T = \frac{NkT}{3V} + \frac{4\pi}{18}\int \bar{n}_2 \cdot \phi''(r) \cdot r^4\, dr.$$

This is practically the same as the expression as that derived by Green, taking into account a shear modulus as well, except for a difference in the numerical factor.

The evaluation of K_T can be effected by the method of steepest descents. This is because the integral distribution function rises to a steep value at $r = R_1$ the nearest distribution function maximum distance, and is but little displaced when account is taken of the multiplying factors $r^4 \cdot \phi''(r)$.

$$K_T = \frac{4\pi}{18}\bar{n}_2 \cdot \phi''(R_1) \cdot R_1^4\sqrt{\pi/\beta}$$

$$\beta = \frac{d^2}{dr^2}\left[\ln \bar{n}_2 + \ln \phi'' + 4\ln r\right].$$

Finally substituting

$$\bar{n}_2 = n^2 \cdot e^{-\phi/KT}\ ;\ \phi = \frac{-a}{r^6} + \frac{b}{r^{12}}\ ;$$

and evaluating β,

$$K_T = \frac{4\pi^{3/2}}{18} \cdot 78 \cdot a \sqrt{\frac{KT}{42a}} \cdot \left[\frac{R_1}{R_0}\right]^6 \cdot n^2 \cdot e^{-\phi/KT}$$

$$= A \cdot n^2 \cdot \left(\frac{R_1}{R_0}\right)^6 \cdot e^{-\phi/KT}.$$

where a is the coefficient in the Lennard-Jones potential and $R_0 =$ P.E minimum distance.

Now, the temperature coefficient is governed mainly by the exponential term, so that

$$\left|\frac{dK_T}{dT}\right| = K_T \cdot \frac{\phi}{kT^2}.$$

Hence,

$$\left|T\frac{dK_T}{dT}\right| = \left|\frac{\phi}{kT}\right| \cdot K_T.$$

Now making use of the molar latent heat, $\lambda_m = Nz/2 \,.\, \phi$

$$T\frac{dK_T}{dT} \sim \frac{2\lambda_m}{zRT}:$$

which for $z = \mathbf{12}$, is of the order of **3**, in accordance with the previous treatment.

DISCUSSION

It is thus seen that under ordinary conditions, the structural part of the Bulk Modulus is a few times K_T itself. Further, this term is necessary to explain the decrease in the Bulk Modulus of liquids by a factor of 10 as compared to solids. For if we consider only the term $V\,\partial^2U/\partial V^2$ with $dU/dr = 0$,

$$V\frac{\partial^2 U}{\partial V^2} \sim \frac{4}{3}V \cdot \frac{a}{R_0^{12}}.$$

An increase of the order of 3% in R would entail a decrease in K_T by a factor **1·4**, only.

Finally, the case of water is peculiar, as it is the only known liquid with positive temperature coefficient of the Bulk Modulus. This is probably connected with a transition from tridymite to ice-like structure, supposed to take place in this range of temperatures according to the theories of Bernal and Fowler.[6] This might account for the positive term $T\,dK_T/dT$.

The presence of two contributions to compressibility molecular and structural (the latter relaxing under pressure) has been postulated by Hall[7] to explain the anomalous ultrasonic absorption in water. Calculations by Hall indicate that the two components are nearly equal in magnitude.

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