ABOUT LIQUIDS

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Introduction

Under ordinary terrestrial conditions matter appears in three states of aggregation: solids, liquids, and gases. The existence and the general properties of solids and gases are relatively easy to understand once it is realized that atoms or molecules have certain typical properties and interactions that follow from quantum mechanics. Liquids are harder to understand. Assume that a group of intelligent theoretical physicists had lived in closed buildings from birth such that they never had occasion to see any natural structures. Let us forget that it may be impossible to prevent them to see their own bodies and their inputs and outputs. What would they be able to predict from a fundamental knowledge of quantum mechanics? They probably would predict the existence of atoms, of molecules, of solid crystals, both metals and insulators, of gases, but most likely not the existence of liquids.

The essay does not show how the existence of liquids necessarily follows from quantum mechanics. Its aim is much less ambitious. It tries to present oversimplified models of the three states of aggregation that may help to get a better intuitive understanding of simple liquids, of the processes of melting and evaporation, their temperatures and energies, and, in particular, of the viscosity and of the self-diffusion coefficients of liquids.

Nothing in this essay is original, a lot is vastly oversimplified, but the author was happy when he could use these models in order to clarify a few points, which for him, before, were in the well-known gray area of "I should understand this better but I don't."

The Questions

In what follows we will consider simple substances only, that is, substances consisting of atoms or molecules that are exactly spherical and whose internal degrees of freedom do not participate in the heat exchange. We will refer to the constituents as "atoms," even when they may be molecules. The examples on which we will test our ideas are argon, oxygen, sodium, copper, mercury, methane, and water. The molecules of the last substance cannot be considered spherical nor can their internal degrees of freedom be neglected. Water, however, is such an important liquid that we nevertheless will try to use our simplified methods, which do indeed yield the right order of magnitude of the different properties.

We distinguish an energy ϵ_s which is the binding energy per atom of the solid at zero-temperature. This energy assumes very different values for different substances, depending on the type of binding between the "atoms." For example, for noble gases, $\epsilon_s \sim 0.1$ eV whereas for some metals it is of the order of several eV. We distinguish ϵ_B which is the boiling heat per atom at atmospheric pressure, and ϵ_M, the melting heat per atom. The following relation,

$$\epsilon_s \cong \epsilon_B + \epsilon_M + \tfrac{1}{2}kT_B, \tag{2.1}$$

is a reasonable approximation under the assumption that the heat content of a solid and a liquid is $3kT$ per atom (Dulong-Petit law), whereas it is $(5/2)kT$ in the gas under constant pressure. We will never take into account any quantum effects in this paper. Usually kT_B and ϵ_M is much smaller than ϵ_s so that we may put roughly $\epsilon_s \sim \epsilon_B$. Indeed when we put

$$\epsilon_M = \frac{\epsilon_s}{a} \approx \frac{\epsilon_B}{a}, \tag{2.2}$$

we find that, roughly speaking, a is of the order 10 to 30 for simple substances as seen in TABLE 1. We will give reasons for this relation. The melting temperature T_M depends somewhat but not very much on the pressure. We observe the following relation

$$kT_M \sim \epsilon_M, \tag{2.3}$$

where k is Boltzmann's constant. Indeed the ratio ϵ_M/kT_M is always of the order unity as seen in TABLE 1. We will give reasons for this relation too.

The boiling temperature depends strongly on the pressure; in the vacuum it is zero; every substance evaporates in empty space. We define T_B as the boiling temperature at atmospheric pressure. There exists a relation referred to as Troutons rule:

$$kT_B = \frac{1}{b}\epsilon_B, \tag{2.4}$$

where b is very near to 11 as seen in TABLE 1. We will explain this relation and indicate how the value of b can be calculated.

We also will apply our considerations to an estimate of the self-diffusion coefficient D of a liquid and its viscosity η. The coefficient D is defined as follows: consider an atom at $t = 0$ at $r = 0$; after a time t the average distance $\bar{r}$ of the atom from the point $r = 0$ is:

$$\bar{r} = \sqrt{Dt}. \tag{2.5}$$

From purely dimensional reasons it follows that we can write

$$D = \frac{w_{\text{th}}d}{3} \cdot \zeta, \quad \zeta \sim \frac{1}{15} \text{ at } T \sim T_M \tag{2.6}$$

where w_{th} is the thermal velocity of an atom, d is the average distance between atoms (there are d^{-3} atoms per unit volume). For simple liquids near the melting

TABLE I

OBSERVED AND CALCULATED VALUES FOR VARIOUS SIMPLE LIQUIDS*

Magnitude	Description, Equation Referred to	Ar	O_2	Na	Cu	Hg	CH_4	H_2O
ϵ_B	in eV	0.068	0.071	1.02	3.11	0.61	0.085	0.42
ϵ_M	in eV	0.012	0.0046	0.027	0.136	0.024	0.010	0.062
kT_B	in eV $\times 10^2$	0.75	0.78	9.9	24.5	5.43	0.96	3.22
kT_M	in eV $\times 10^2$	0.73	0.47	3.2	11.7	2.02	0.78	2.35
d	in 10^{-8} cm	3.4	3.3	3.4	2.3	2.9	4.0	3.1
$\log_{10} p^G$	obs†	2.35	−0.15	−7.1	−3.1	−5.7	1.96	+0.66
$\log_{10} p^G$	calc†, 3.10	2.50	+0.12	−6.7	−3.4	−6.0	1.83	[−0.31]
$x = \epsilon_M/kT_M$	‡	1.64	0.98	0.84	1.16	1.19	1.26	2.64
$b = \epsilon_B/kT_B$		9.1	9.1	10.3	12.7	11.2	8.85	13.0
b (theor.)	4.18	8.8	9.1	10.4	13.1	10.9	8.8	12.0
$\omega_E \times 10^{-12}$	3.2	6.7	6.9	12	26	5.5	9.6	14.6
$\omega_E \times 10^{-12}$	3.4	3.7	4.2	17.8	27.9	5.5	5.1	14.9
$\bar{\omega}_E \times 10^{-12}$	mean of the two above	5.2	5.6	14.9	27.0	5.5	7.4	14.6[30]§
$\delta_S(T = T_M)$	in 10^{-8} cm, 3.6	0.63	0.53	0.61	0.39	0.45	0.72	[0.30]
$\delta_L(T = T_M)$	in 10^{-8} cm, 4.3	0.92	0.69	0.76	0.52	0.60	0.98	[0.50]
$\delta_L^*(T = T_B)$	in 10^{-8} cm, 4.14	0.93	0.81	1.17	0.66	0.83	1.04	[0.54]
$d/\delta_L = \alpha$	4.1	3.7	4.5	4.5	4.4	4.8	4.1	[6.2]
d^3/v_L	obs, 3.5, 4.8	28	88	74	63	84	49	80
d^3/v_L	calc, 4.5, 4.6	35	91	70	68	95	56	[226]
d^3/v_L^*	obs, 4.19	49	49	13.2	18.4	47	53	585
d^3/v_L^*	calc, 4.15	34	50	13.4	28	28	41	[185]
ξ	obs, 2.6¶	1/15		1/18	1/12	1/11	1/22	1/65
κ	obs, 2.8**	6.4	26	11.1	7.3	9.4	10.6	28

observed values are taken from Landolt-Boernstein Numerical Data, 1965. Vol. II, 5, Springer Verlag, Berlin, and the A.I.P. Handboo
. McGraw Hill, New York, 1972.

is the vapor pressure over the solid near melting temperature in millimeter mercury.

calculated value is unity according to Equation 4.10.

ıntroduce a fictitious value for water, $\omega_E = 30$, which gives better results. All values calculated for water with this value are put in brackets.

theoretical value is 1/12 according to Equation 5.3.

e theoretical value is 12 according to Equation 5.4.

point, we find that the pure number ζ is of the order of 1/15, as seen in TABLE 1. It will be understandable on the basis of our model.

The viscosity coefficient η of a liquid substance is defined as follows: assume that the substance moves with a velocity u in the x direction, but the magnitude of u changes in the z direction, so that there is a gradient (du/dz) of the overall velocity u. Then a certain amount P of momentum is transferred per unit time through a cm^2 of a plane perpendicular to z. P is proportional to du/dz:

$$P = \eta \frac{du}{dz} \tag{2.7}$$

and the coefficient η is the viscosity. Again, for purely dimensional reasons we write

$$\eta = \frac{mw_{th}}{3d^2}\kappa, \quad \kappa \sim 12 \text{ at } T \sim T_M, \tag{2.8}$$

where m is the mass of the atom and κ is a dimensionless number which, at or near melting temperature, is of the order 10 for simple liquids as indicated in TABLE 1. Also this relation will be made plausible by our model.

The size of the constant in Equation 7 is surprising when one compares it with the well-known formula for the viscosity of an ideal gas

$$\eta_{Gas} = \frac{nmw_{th}l}{3}, \quad l = \frac{1}{\sqrt{2}n\pi(2r)^2}. \tag{2.9}$$

Here n is the number of atoms per unit volume, r is the radius of the atom, and l is the mean-free path. It is well known that this expression does not depend on the density. Surely, expression 8 is only valid for dilute gases but, since η_{Gas} is density independent, one would have thought that it should at least give the right order of magnitude also for a liquid. However, when we put $d \approx 2r$ for the liquid in which the atoms touch each other, we get formula 7 but with $\kappa = (\sqrt{2}\pi)^{-1} = 0.23$; that is about 50 times too small. We will be able to explain this discrepancy.

Gases and Solids

We begin with a discussion of solids and gases and of the equilibrium between these two states of aggregation. This will serve to fix our models and to describe the simplified methods that we will use in order to treat the equilibrium between two phases. We consider the gaseous state as a dilute ideal gas of N spherical atoms without any internal degrees of freedom, enclosed in a volume V. We introduce the volume per atom $v_G = V/N$ which fulfills the ideal gas equation:

$$v_G = \frac{kT}{p}, \tag{3.1}$$

where p is the pressure.

We now describe our model of a solid (the Einstein model): Here we assume that each atom or molecule is a mass-point (mass m) tied elastically to its rest-

position; the latter being fixed in place at cubic lattice points, with d as the nearest distance. The elastic bond has a frequency ω_E which we will determine as follows. The frequency ω_E is connected with the Debye temperature θ:

$$\omega_E = c\frac{k\theta}{h} = c\omega_D \quad c = \frac{1}{\sqrt{3}} \tag{3.2}$$

where c is a numerical factor. The choice of $c = 1/\sqrt{3}$ is based upon the following reasoning: ω_D is the highest frequency of the lattice in the Debye model, which assumes a frequency distribution proportional to $\omega^2\,d\omega$. The value of c depends upon what average one wants to choose. We are interested mainly in the determination of the square of the average amplitude δ of the oscillators at a given thermal energy. δ^2 is proportional to ω^{-2} at a fixed energy and the average of ω^{-2} in the Debye model is $3\omega_D{}^{-2}$. Hence we get $\omega_E{}^2 = 3\omega_D{}^2$ and $c = 1/\sqrt{3}$.

The Debye frequencies are determined experimentally from the behavior of the specific heat at low temperatures. They are characteristic of the bond strength at small vibrational amplitudes. We get an idea of the behavior at large amplitudes by interpreting ω_E in the following way: In the Einstein model of a solid we would imagine that the energy ϵ_s necessary to lift the atom from its rest position within the solid to a rest position in empty space (we neglect quantum effects such as zero-point energies) must be given approximately by

$$\epsilon_s \cong \tfrac{1}{2} m\omega_E{}^2(d/2)^2, \tag{3.3}$$

where d is the distance between the atoms in the solid. It is the potential energy when the atom is displaced by $d/2$. The binding energy ϵ_S is determined from the melting heat ϵ_M and the boiling heat ϵ_B according to relation **2.1.** Thus we get another way to determine ω_E:

$$\omega_E = [8(\epsilon_B + \epsilon_M + \tfrac{1}{2}kT_B)/md^2]^{1/2}. \tag{3.4}$$

We will use the arithmetic mean of the values calculated by **3.2** and **3.4.** The resulting values are found in TABLE 1. In the case of water it turned out that the agreement with facts is much better if a fictitious Einstein frequency is used which is two times higher than the mean of **3.2** and **3.4.**

In all our examples $h\omega_E$ turns out to be reasonably small compared to the melting temperatures. We therefore are allowed to neglect quantum effects when we are dealing with temperatures near melting or higher as we will do throughout this paper.

We now introduce the concept of "available volume" of an atom at a given temperature T. It is easy to visualize that concept in the Einstein-model of a solid. The available volume v_s is a measure of the volume in which the motion of the atom takes place; it will be of the order of the cube of the amplitude of vibration, that is proportional to $[kT/(m\omega_E{}^2)]^{3/2}$. A more exact definition of this volume is

$$v_S = \int dx^3 \exp\,[-\pi(x)/kT] = \left(\frac{2\pi kT}{m\omega_E{}^2}\right)^{3/2}, \tag{3.5}$$

where $\pi(x) = \frac{1}{2}m\omega_E{}^2x^2$ is potential energy of the oscillator. This expression

represents an integral over the volume weighted by the probability of binding the atom there.

It is useful to introduce a length δ_s indicating the linear dimension of the available volume:

$$\delta_s = v_s^{1/3} = \left(\frac{2\pi kT}{m\omega_E^2}\right)^{1/2}. \tag{3.6}$$

The length δ_s is of the order of 0.1 of the lattice distance d below the melting point. The volume v_s is of the order 10^{-3} of the cell volume d^3 and reaches about 1/250 of d^3 at the melting point. Notice that δ_s is the cube root of the available volume and not the average amplitude of the oscillator vibrations. The latter amplitude R_s would be approximately equal to the radius of a sphere of that volume:

$$R_s \approx \left(\frac{3}{4\pi}\right)^{1/3} \delta_s \tag{3.6a}$$

It probably is intuitively plausible that the corresponding available volume v_G for a gas is the volume per atom, namely, V/N as given by **3.1**:

$$v_G = V/N. \tag{3.7}$$

At atmospheric pressure this volume is about 1000 times larger than the cell volume d^3 of a solid and therefore several 10^5 times larger than the available volume in a solid.

We will use the available-volume concept in order to express the condition of equilibrium between two phases I and II. Such equilibrium exists when

$$\frac{v_{\mathrm{I}}}{v_{\mathrm{II}}} = e^{\Delta\epsilon/kT} \quad \Delta\epsilon = \epsilon_{\mathrm{I}} - \epsilon_{\mathrm{II}}. \tag{3.8}$$

Here v_i are the available volumes in the two phases and ϵ_i are the energies per atom of the two phases, but without counting the thermal energies, that is, when the atoms are at rest. So ϵ_i is zero in the gas phase and $\epsilon_i = -\epsilon_s$ in the solid phase. The relation **3.8** is intuitively plausible. Two phases can coexist if the difference between the available volumes is compensated by the Boltzmann factor corresponding to the difference in energy. The relation **3.8** is derived from the general laws of statistical mechanics in the Appendix.

Applying the relation **3.8** to the gas-solid equilibrium we get

$$\frac{v_G}{v_S} = e^{\epsilon_S/kT}. \tag{3.9}$$

In the gas, the atom has a much larger available volume to its disposition than in the solid, but the energy in the solid is lower by ϵ_S. We can transform **3.9** into an expression of the vapor pressure $p^{(G)}$ above a solid by means of **3.1** and get

$$p_G = \frac{kT}{v_s} e^{-\epsilon_S/kT}. \tag{3.10}$$

This equation says that, in our model, the vapor pressure is that of an ideal gas compressed so that the volume per atom is v_s, but then reduced by the Boltzmann factor exp $(-\epsilon_s/kT)$.

We will show a few examples of how our model works. Of course, our simplified model can only give very approximative results. As mentioned before, all quantum effects including zero-point energies are neglected.

All data, the ones that enter into our models, the results and the actual values, are assembled in TABLE 1. We see by comparing lines 6 and 7 that the values for the vapor pressures near the melting point are not too badly reproduced. Although the pressures differ by nine orders of magnitude, our results are good within a factor 2.5, except for water where we are off by a factor of 8.

Liquids

In an idealized solid the "location" x_i of each atom is fixed at the lattice points. We understand by "location" not its exact position but the position of the center of that volume $\delta_s^3 = v_s$ within which it performs harmonic vibrations (in the Einstein picture) with an amplitude of the other δ_S. This is long-range order. We now make the following assumption. When δ_S reaches a certain critical value δ_L the location x_i of the atoms do no longer remain fixed; the structure then is loosened such that the atoms do no longer oscillate around a fixed position; the locations change due to combinations of vibrations of neighboring atoms: the long-range order disappears. Then the individual atom rather performs a random motion with steps of the order δ_L instead of an exact oscillation around a fixed location. This will be our description of the liquid state. We picture it by imagining spherical atoms of size $\sim d$, almost closely packed but with spaces inbetween, allowing relative motions of neighbors against each other, of order δ_L. They move oscillator like for distances δ_L but do not necessarily return to the same point when the restoring force pushes them back. They perform a "hindered" random walk. The term "hindered" expresses the fact that the small ratio δ_L/d prevents them from moving freely in all directions.

It is very difficult to determine from first principles the critical distance δ_L at which the long-range order disappears. We will get from an analysis of the conditions that the transition from long-range order to the liquid state occurs when

$$\delta_L \geq \frac{d}{\alpha}, \quad \alpha \sim 4.5, \tag{4.1}$$

that is, the random displacements are of the order of one quarter to a fifth of the lattice distance d or larger.*

This loosening up of the solid state long-range order needs energy. It is the energy necessary to increase the δ_S given by **3.6** to δ_L as defined above. The melting heat ϵ_M is just that energy necessary to increase δ_S to δ_L at T_M. Assuming that the binding forces roughly have the character of a restoring force in an oscilla-

*Here and in the rest that follows, we neglect the difference in density of liquids and solids. We always define d as $d^3 = V/N$, where V is the volume of N atoms in the solid or liquid.

tor, the energy ϵ_M necessary to extend the displacements from δ_S to δ_L in the solid should be nearly equal to the difference in potential energy of an oscillator with those displacements. The potential energy is proportional to the square of the displacement. At the temperature T_M, the average potential energy is $(3/2)kT_M$. Thus we get

$$\frac{(3/2)kT_M + \epsilon_M}{(3/2)kT_M} = \frac{\delta_L{}^2}{\delta_S{}^2}. \tag{4.2}$$

So ϵ_M is the energy to stretch δ_S to δ_L at T_M. This equation allows us to calculate δ_L at the melting point from δ_S, which is given by **3.6**:

$$\delta_L = \left(1 + \frac{2\epsilon_M}{3kT_M}\right)^{1/2}\left(\frac{2\pi kT}{m\omega_E{}^2}\right)^{1/2} \tag{4.3}$$

TABLE 1 shows the values δ_L according to **4.3** for a few simple liquids. Now we can determine empirically $\alpha = d/\delta_L$ at the melting point; the values are listed in the TABLE 1, line 17. They are the basis for our claim that α lies between 4 and 5.

The motion of the atom in the liquid is no longer exactly that of an oscillator since it does not return to the same point. But its motion still is "back and forth" with an amplitude corresponding to δ_L. If we want to approximate the force that drives it back by an oscillator-type restoring force, that oscillator would have a different (smaller) frequency ω'_E. It is easy to determine ω'_E, since that new oscillator has an amplitude corresponding to δ_L at T_M, whereas the oscillator describing the solid state had an amplitude corresponding to δ_S. Since the amplitudes at fixed T are proportional to ω^{-1}, we get

$$\omega'_E = (\delta_S/\delta_L)\omega_E, \tag{4.4}$$

where δ_S/δ_L is given by **4.2.** We emphasize again that the motion of the atom in our model of the liquid state is an oscillator motion only in a very approximative sense because it does not return to the same point of origin. Our model of the solid, however, deals with exact oscillatory motions of the atom.

The energy of the atom at rest in that oscillator which approximately describes the motion in the liquid, is not $-\epsilon_S$ as it is in the oscillator of the Einstein model of the solid, but $-\epsilon_L = -\epsilon_S + \epsilon_M$; it is higher by the melting heat. We therefore get

$$\epsilon_S - \epsilon_L = \epsilon_M. \tag{4.4a}$$

We now determine the increase of the available space v_S when a solid becomes liquid. In order to do this we must try to describe the liquid state a little more accurately. The liquid consists of atoms moving through distances δ_L before turning into another direction because of the presence of neighboring atoms. Since δ_L is rather much smaller than the average distance d between the atoms, the displacements of neighboring atoms cannot be completely independent of each other, they must be coordinated; one must make room for the other. Actually there will be a continuous transition from nearby atoms whose locations are tightly correlated and others further away that are less tightly correlated. We try to simplify the situation by introducing the concept of a "clump" of f neighboring atoms

whose relative positions are as tightly correlated as in a solid (they form a lattice), whereas the positions of the atoms outside the clump are not at all correlated to those inside the clump. We do not assign definite atoms to definite clumps; whenever we look at the neighborhood of an atom we assume that f surrounding atoms form a clump.

The size of a clump is connected with the ratio $\alpha = d/\delta_L$ for the following reason: The position of an atom, α lattice distances away, should be independent of the position of a reference atom. Since our clump describes the continuously diminishing dependence by a sharp break from complete lattice to complete independence, we believe that the linear dimensions of a clump should be $\xi\alpha d$ where ξ is less than unity, say about 0.6. This choice will give reasonable results. We then have

$$f = \left(\xi \frac{d}{\delta_L}\right)^3 = (\xi\alpha)^3, \quad \xi \sim 0.6 \tag{4.5}$$

which, with the choice of $\alpha \approx 4.5$ would give $f \sim 20$. It should be noted that the values of α and f are connected; in principle, we have introduced only one arbitrary constant α to describe the transition from the solid to the liquid state.

This rough picture allows us to calculate the available space volume v_L in a liquid. We determine it on the basis of our clump model: if the position of all the atoms were completely free like in a gas, we would get $v_L \sim V/N = d^3$. Actually among the f atoms of a clump only one—we call it the reference atom—is completely free, whereas the other $(f - 1)$ atoms have only a volume $\delta_L{}^3$ at their disposition since their locations are coordinated to that of the reference atom. Therefore the position phase space for the f atoms of the clump is

$$(v_L)^f = d^3 \delta_L{}^{3(f-1)},$$

and the available volume of a single atom in the liquid becomes

$$v_L = \delta_L{}^3 \left(\frac{d}{\delta_L}\right)^{3/f} = \delta_L{}^3 \alpha^{3/f}. \tag{4.6}$$

Note that the available volume is larger than the $\delta_L{}^3$ by the factor $(d/\delta_L)^{3/f}$. This is because the motion of the atom is not really oscillatory in the liquid. The above factor expresses the increase in available volume due to the fact that the atom does not return to the same place in its oscillations within a volume $\delta_L{}^3$.

The expression **4.6** allows us to determine directly the ratio v_L/d^3, from the ratio $\alpha = d/\delta_L$ at the melting point. We get

$$\frac{v_L}{d^3} = \alpha^{(-3+3/f)}. \tag{4.7}$$

As a first orientation, we may put $\alpha = 4.5$ and $f = 20$, and we get $v_L \approx d^3/73$.

We now proceed to calculate the equilibrium between the liquid and solid phase and use again expression **3.8**, which tells us that the ratio of available volumes must equal the Boltzmann-factor corresponding to the energy difference $\Delta\epsilon$ between the two phases. Of course, this difference is equal to the melting heat:

$\Delta\epsilon = \epsilon_M$.† We get

$$\frac{v_L}{v_s} = e^{\epsilon_M/kT_M}. \tag{4.8}$$

We now can check our result **4.7** for v_L in terms of d^3. We determine v_L empirically from **4.8** by using **3.5** for v_S and the empirical values for d^3, ϵ_M, and T_M. The result is found in TABLE 1 line 18. We see that the values are not too far from 1/73, which we would get by using **4.7** with $\alpha = 4.5$ and $f = 20$. If we use the actual values of α as listed in the table, the agreement with the empirical v_L is even better, (see line 19 of the table), except in the case of water.

The relation **4.8** allows us to get an estimate of the ratio between the melting heats ϵ_M and the melting temperature T_M. A very rough result is obtained by noting from TABLE 1 that $v_S \sim d^3/250$ whereas $v_L \sim (1/73)d^3$ according to **4.7** with $\alpha = 4.5$ and $f = 20$. Thus the ratio $v_L/v_S \sim 3$. Then it follows immediately from **4.8** that $\exp(\epsilon_M/kT_M) = 3$ or $\epsilon_M \approx kT_M$.

We can come to the same conclusion without making use of the empirical relation $v_S \sim d^3/250$. We use **3.5** and **4.6** in order to express the volumes v_S and v_L in terms of the lengths δ_S and δ_L, and we express the ratio of these two lengths in terms of ϵ_M/kT_M by means of **4.2.** We then find that **4.8** can be written in the form

$$\left(1 + \frac{2\epsilon_M}{3kT}\right)^{3/2} \alpha^{3/f} = \exp(\epsilon_M/kT_M). \tag{4.9}$$

This relation determines ϵ_M/kT_M; it is equivalent to the following equation for $x \equiv \epsilon_M/kT_M$:

$$\alpha^{3/f}(1 + \tfrac{2}{3}x)^{3/2} = e^x. \tag{4.10}$$

With the previously determined values $\alpha \sim 4.5$, $f \sim 20$ valid at the melting point, we find that the solution of **4.10** is $x \sim 1$.

Our model therefore predicts that $\epsilon_M \sim kT_M$, a relation that indeed is approximately fulfilled as seen in TABLE 1, line 8.

It is interesting to point out that our relations also contain the so-called Lindemann Melting-Point Formula. It connects the Debye temperature θ with the melting temperature T_M and usually is written in the following form:

$$\theta = D\left(\frac{T_M}{\mu V^{2/3}}\right)^{1/2}, \quad \mathrm{D} = 120\ \mathrm{cm\ g^{1/2}\ deg^{1/2}}. \tag{4.11}$$

Here μ is the molar weight in grams and V is the molar volume. In our notation $V = Ad^3$, where A is the Avogadro number and $\mu = Am$. Since $k\theta/h = \omega_D$ we may write **4.11** in the form

$$\omega_D = D'\left(\frac{kT_M}{md^2}\right)^{1/2}, \quad D' = 20.4. \tag{4.12}$$

†Exactly speaking, $\Delta\epsilon$ should be the energy difference without counting the heat content. Since we describe both phases approximately by oscillators, the heat content is the same. The relation $\Delta\epsilon = \epsilon_M$ was shown to be correct in Equation 4.4a.

Now D' is a dimensionless constant. We can derive a similar relation from Equation 4.3 by putting $e_M \sim kT_M$. Then **4.3** becomes

$$\delta_L^2 = \frac{5}{3} \frac{2\pi k T_M}{m\omega_E^2}.$$

This can be written in the form

$$\omega_E^2 = \frac{5}{3} 2\pi \frac{kT_M}{md^2} \frac{d^2}{\delta_L^2}.$$

We use **3.2** to connect ω_E with ω_D and **4.1** to determine (d/δ_L). Then we obtain indeed Lindemann's formula **4.12** with $D' = 25.2$, which is near enough to Lindemann's value, considering the approximations made.

The same equations also permit an estimate of the melting heat in terms of the binding energy of the solid. The melting heat ϵ_M increases the average oscillator amplitude from the one corresponding to δ_S to the one corresponding to δ_L. We call these amplitudes R_L and R_S and they are related to δ_S and δ_L as indicated in **3.6a.** The energy needed for this is

$$\epsilon_M = \frac{1}{2} m\omega_E^2 (R_L^2 - R_S^2) = \frac{1}{2} m\omega_E^2 \left(\frac{3}{4\pi}\right)^{2/3} \delta_L^2 \left(1 - \frac{\delta_S^2}{\delta_L^2}\right)$$

Equation **4.2** tells us that the ratio $(\delta_S/\delta_L)^2$ is $\frac{3}{5}$ with $x = 1$. Thus we obtain

$$\epsilon_M = \frac{1}{5} \left(\frac{3}{4\pi}\right)^{2/3} m\omega_E^2 \delta_L^2 = \frac{8}{5} \left(\frac{3}{4\pi}\right)^{2/3} \left(\frac{\delta_L}{d}\right)^2 \cdot \frac{1}{8} m\omega_E d^2.$$

in the previous section we already have interpreted $\frac{1}{8} m\omega_E^2 d^2$ as approximately equal to ϵ_S. We therefore get with $d = 4.5\,\delta_L$:

$$\epsilon_M \approx \frac{1}{33} \cdot \frac{1}{8} m\omega_E d^2 \sim \frac{1}{33} \epsilon_S. \qquad \textbf{(4.13)}$$

We find that the melting heat is a small fraction of the binding energy or of the boiling heat according to **2.1.** Actually the values of ϵ_M/ϵ_B lie between 1/7 and 1/40 as seen by comparing lines 1 and 2 of TABLE 1. Our considerations give the right order of magnitude. As expected, the first equality in **4.13** is somewhat better fulfilled; the values of $\epsilon_M/(1/8 m\omega_E^2 d^2)$ lie between 1/14 and 1/34. The deviations from the relation **4.13** come from the fact that the binding potential is not exactly an oscillator potential. It rises less steeply than with increasing distance. Equation **4.13** therefore probably is an underestimate of the ratio ϵ_M/ϵ_S.

We want to determine the available volume of a liquid not only at melting temperature but also at boiling temperature T_B. Let us distinguish the magnitudes at boiling by a star, such as v_L^* and δ_L^*. We make the simplest possible assumption, namely, that δ_L^* is the result of an extension of an oscillators amplitude at the temperature T_B when the melting heat ϵ_M is added, just as δ_L was the result of a similar extension of an oscillator at the temperature T_M. Then we get in

analogy to **4.3**:

$$\delta_L^* = \delta_S^* \left(1 + \frac{2}{3}\frac{\epsilon_M}{kT_B}\right)^{1/2}, \delta_S^* = \left(\frac{2\pi kT_B}{m\omega_E^2}\right)^{1/2} \tag{4.14}$$

Together with δ_L the value of f will also change with temperature. Expression **4.5** tells us that f is proportional to δ_L^{-3}, so that we find

$$f^* = f\left(\frac{\delta_L}{\delta_L^*}\right)^3, v_L^* = (\delta_L^*)^3 \left(\frac{d}{\delta_L^*}\right)^{3/f^*} \tag{4.15}$$

As a first orientation we may put very approximately $T_B \sim 2T_M$ and $\epsilon_M \sim kT_M$. Then $\alpha^* = d/\delta_L^* \sim 3.6$ and $f^* \sim 10$. The available volume amounts to

$$v_L^* \sim (\alpha^*)^{-3+3/f^*} d^3 \sim \tfrac{1}{32} d^3. \tag{4.16}$$

We may compare this with the equally approximative value of v_L at the melting point: $v_L \sim (1/73)\, d^3$.

Now we construct the equation regulating the boiling process, in analogy to **3.9** and **4.8**:

$$\frac{v_G}{v_L^*} = e^{(\epsilon_S - \epsilon_M)/kT_B}, \epsilon_S - \epsilon_M = \epsilon_B + \frac{1}{2} kT_B \tag{4.17}$$

Here $\epsilon_S - \epsilon_M$ is the difference in energy between liquid and gas; it is equal to $\epsilon_B + \frac{1}{2}kT_B$ according to **2.1**. This relation allows us to get an idea of the ratio ϵ_B/kT_B. We again start with a rough estimate. Remember that gases at atmospheric pressure have a density of about 10^{-3} of solids; hence $v_G/d^3 \sim 10^3$. Furthermore **4.16** tells us that $v_G \sim d^3/32$; thus $v_G/v_L^* \sim 32000$ and $\epsilon_B/kT = ln\ 32000 + \frac{1}{2}$, which is just about 11. We have derived Trouton's rule!

A somewhat more detailed determination of $b = \epsilon_B/kT_B$ uses the ideal gas equation, $v_G = kT_B/p_0$, where p_0 is the atmospheric pressure, and **4.14** and **4.15** for the calculation of v_L^*. One then gets from **4.17**

$$b + \frac{1}{2} = \ln\left[\frac{kT_B}{p_0}/v_L^*\right]. \tag{4.18}$$

TABLE 1 shows that the values calculated with this expression agree quite well with the observed ones.

Trouton's rule can be used to get an upper limit on the melting heat ϵ_M. We previously found that $\epsilon_M \sim kT_M$. Obviously the boiling temperature must be higher than the melting temperature. Thus we get $\epsilon_M < kT_B$ and from Trouton's rule

$$\epsilon_M < \epsilon_B/11.$$

Since our previously derived expression was an underestimate, we conclude that ϵ_M should be somewhere between 1/11 and 1/33 of the boiling heat, which indeed is borne out by TABLE 1.

A more sensitive way to test **4.17** than the calculation of the Trouton coefficient b would be a comparison of v_L^* obtained "theoretically" from **4.14** and

4.15, with the "empirical value":

$$v_L^* = \frac{kT_B}{p_0} e^{-\epsilon_B'/kT} \text{(empirical)}, \tag{4.19}$$

where $\epsilon_B' = \epsilon_B + \frac{1}{2}kT_B$.

TABLE 1 gives the theoretical and the empirical values in terms of d^3 (lines 20 and 21). Here, as well as in the calculation of v_L at the melting point, the semi-quantitative agreement is gratifying, particularly in view of the fact that the vL values depend on the heats of transformation and on the corresponding temperatures through the Boltzmann exponential, which, in particular in the case of the boiling process, is a strongly varying function. Note that v_L^* for sodium is abnormally small, a fact that is reproduced by the theory and is caused by the very high ratio between boiling and melting temperature. Our assumptions do not really apply to the case of water where we find factors of three between observed and calculated values.

Diffusion and Viscosity

Our model allows us to figure out the approximative values of the self-diffusion constant D and the viscosity η of a liquid. D is defined as follows: Consider an atom at $t = 0$ at $r = 0$; after a time t its average distance from the center is $\bar{r} = \sqrt{Dt}$. In our model of the liquid the atom performs a "hindered" random walk with δ_L as the length of the step. It is "hindered" because of the fact that δ_L is small compared to the distance d between the atoms. The direction of the next step is not completely independent of the previous one; it is more probable that it is in or near the opposite direction. This would decrease the diffusion coefficient compared to a true random motion. Were it a true random motion, we would get $D_r = \delta_L w_{\text{th}}/3$ where w_{th} is the average (thermal) velocity of the atom. Actually we write

$$D = F(f) \frac{\delta_L w_{\text{th}}}{3}, \tag{5.1}$$

where the function F expresses the deviation from random. We expect F to be a decreasing function of the clump size f and, naturally $F = 1$ for $f = 1$. We may imagine that $F(f)$ has something to do with the ratio of the number of atoms at the clump surface to the total number in the clump, since the atoms at the surface have more freedom of moving. We therefore expect an approximate proportionality to $f^{-1/3}$ and we will tentatively put

$$F(f) \sim f^{-1/3}. \tag{5.2}$$

We then get

$$D \approx \frac{\delta_L w_{\text{th}}}{3f^{1/3}} = \frac{dw_{\text{th}}}{3} \xi, \quad \xi = \frac{\delta_L}{df^{1/3}}. \tag{5.3}$$

With $d/\delta_L \sim 4.5$ and $f \sim 20$ near the melting point we find $\xi \sim 1/12$ which is the right order of magnitude according to TABLE 1, line 21. Our formula gives a temperature dependence proportional to T^n with n lying between 1 and 3/2, since w_{th} is proportional to $T^{1/2}$ and δ_L and $f^{-1/3}$ are both proportional to a power slightly less than $\frac{1}{2}$ (see **4.14** and **4.15**). Actually, however, D rises at least as fast as T^2. The stronger temperature dependence can probably be explained by the anharmonicity of the atomic vibrations which makes the amplitude δ_L rise faster than **4.14.** In water the increase is even stronger and is caused by the breakage of hydrogen bonds with rising temperature.

We now try to determine the viscosity of a liquid. We have defined the viscosity coefficient η in Equation **2.7** as the factor between the momentum transfer P in the z direction per cm^2 and second when there is a gradient du/dz of the overall velocity u of the liquid in the x direction. We make use of the concept of "clump" and assume that all atoms in a clump have the same average velocity u. Let us look at an area in the x-y plane. There are d^{-2} atoms per cm^2 in or near (within d) that area, each of them performing vibrations with a frequency ω'_E which we have determined in **4.4.** One third of them vibrate perpendicular to the plane. Each of them moves (ω'_E/π) times per second up or down. Assume that the area separates one clump above from one below. Then each time an atom vibrates downwards it transfers the average momentum that it has in the upper clump to the lower clump and vice versa. The average momentum of each atom in the upper clump is larger by $M(du/dz)\Delta$ than the one in the lower clump, where $\Delta \sim f^{1/3}d$ is the linear dimension of a clump. We then get

$$P = \frac{1}{3}\frac{M}{d^2}\frac{\omega'_E}{\pi} f^{1/3} d \frac{du}{dz}$$

or

$$\eta = \frac{M\omega'_E}{3\pi d} f^{1/3}.$$

The atoms move back and forth over distances δ_L with an average velocity w_{th}. Hence $\omega'_E/\pi = w_{th}/\delta_L$. So we get:

$$\eta = \frac{Mw_{th}}{3d^2} k, \quad \kappa = f^{1/3}\frac{d}{\delta_L}. \tag{5.4}$$

We put again $d/\delta_L = \alpha \sim 4.5$ and $f = 20$ near the melting point; this gives us a value of $\kappa \approx 12$, in reasonably good agreement with the observed values found in TABLE 1, line 22. Again the temperature dependence of our expression is too weak. The coefficient κ goes as $f^{1/3}/\delta_L$ which would be somewhat less than T^{-1}, w_{th} goes with $T^{1/2}$. Altogether we would get T^m with m between 0 and $-\frac{1}{2}$ whereas, in fact, the viscosity diminishes strongly with increasing temperature with powers somewhat larger than unity. Simple liquids show a decrease of viscosity of about a factor two to four of the viscosity between melting and boiling. This effect can perhaps be understood qualitatively by the following corrections to our picture: the momentum delivered when "entering" in the adjacent clump might be larger than $M(du/dz)\Delta$, since the atom is to some extent "rigidly" tied to the clump.

This can be expressed by replacing M in **5.4** by $M' > M$. The ratio M'/M certainly decreases with temperature since the clumps become "looser" with rising T.

Water, as usual, is a special case again since the viscosity changes by a factor more than six between melting and boiling. Here the rising of temperature breaks more hydrogen bonds between the molecules; thus the momentum transfer is reduced considerably.

Complicated liquids, especially those with long chain molecules have a much larger viscosity, in particular near the melting point. Here the chains are mutually entangled; one chain winds itself around another. This is a phenomenon called "reptation" by L. DeGennes and causes a direct momentum transport over distances much longer than the chain length. The corresponding increase of viscosity may reach factors of a million at lower temperatures. Our simple expression represents only a lower bound for the viscosity in the case of complicated liquids.

Let us compare the expression **5.4** with the well-known formula of the viscosity of an ideal gas as given by **2.9**. This expression does not depend on the density, but it would be wrong to consider a liquid a highly compressed gas and use **2.9** for the viscosity. Indeed, the ratio of **5.4** to **2.9** is

$$\frac{\eta}{\eta_{\text{gas}}} = \sqrt{2}\,\frac{(2r)^2}{d\delta_L}\,f^{1/3}.$$

In the liquid we may put approximately $2r \approx d$, and we get with $\alpha = d/\delta_L \sim 4.5$ and $f = 20$, near the melting point:

$$\frac{\eta}{\eta_{\text{gas}}} = \sqrt{2}\pi\alpha\, f^{1/3} \sim 50.$$

The viscosity of the liquid is roughly two orders of magnitude higher than the one of a gas at the same temperature. The physical reasons for this factor are these: In the gas, the distance of momentum transfer is of the order of the mean free path l and the number of atoms crossing a unit area per second is $\nu_G \sim \frac{1}{3}\, w_{\text{th}}/d^3$. In the liquid the distance of momentum transfer is $\Delta \sim f^{1/3}d$, and the number of atoms crossing a unit area per second (by vibration) is $\nu_L \sim \frac{1}{3}\, w_{\text{th}}/(\delta_L d^2)$. At densities for which the atoms touch each other, $2r \sim d$, and the gas-kinetic expression $l = d^3/[\sqrt{2}\,\pi(2r)^2]$ becomes $l \sim d/\sqrt{2}\,\pi$ which, very roughly, is equivalent to $l \sim \delta_L$. Thus the viscosity of a liquid is larger because the distance of momentum transfer is $f^{1/3}d$ instead of $l \sim \delta_L$ (a factor about 12), and because there are ν_L crossings instead of ν_G (another factor about 4.5).

Thus we have shown that our oversimplified model of a liquid indeed gives rise to a viscosity and diffusion coefficient of the right order of magnitude. It is true, however, that the temperature dependences of these magnitudes are only rather qualitatively interpreted and probably insufficiently explained. Our model emphasizes the atomic rearrangements rather than the penetration of potential barriers in contrast to most of the models used in the current literature.‡

‡An excellent survey about the present state of our knowledge of liquids by John A. Barker and Doug Henderson has appeared recently in the *Review of Modern Physics*, 1976. **48**:587.

Acknowledgments

The author is grateful for most valuable advice from Richard Feynman and Kerson Huang and many others.

Appendix

In an equilibrium between two phases I and II, the Gibbs function G must not change when an atom is transferred from one phase to another and temperature, pressure and total number N of atoms is kept constant; $N = N_{\mathrm{I}} + N_{\mathrm{II}}$, where N_{I} and N_{II} are the number of atoms in the two phases:

$$\left(\frac{\partial G}{\partial N_{\mathrm{I}}}\right)_{T,p,N} = 0; \tag{A.1}$$

the Gibbs function of the two phase system can be expressed by the partition functions in the following way:

$$G = -kT \log (Q^{(\mathrm{I})} \cdot Q^{(\mathrm{II})}).$$

Here $Q^{(i)}$ is the partition function of the phase i containing N_i particles. In our simple models the partition function $Q^{(i)}$ can be written as the N_ith power of a magnitude $Z^{(i)}$:

$$Q^{(i)} = (Z^{(i)})^{N_i}, \tag{A.2}$$

where $Z^{(i)}$ is independent of N_i. We may call $Z^{(i)}$ the one-particle partition function. We then get

$$G = -kT(N_{\mathrm{I}} \log Z^{(\mathrm{I})} + (N - N_{\mathrm{I}}) \log Z^{(\mathrm{II})}).$$

Equation **A.1** then becomes for $T \neq 0$,

$$\log \frac{Z^{(\mathrm{I})}}{Z^{(\mathrm{II})}} = 0 \quad \text{or} \quad Z^{(\mathrm{I})} = Z^{(\mathrm{II})}. \tag{A.3}$$

We now calculate the partition functions. The general formula for a system of N equal particles is

$$Q = \frac{1}{N!} \int \mathrm{d}x \, \mathrm{d}p \, e^{-E(x,p)/kT}.$$

Here x stands for all $3n$ position coordinates and p stands for all $3n$ momentum coordinates. $E(x, p)$ is the energy of the system which can be split into three parts:

$$E(n, p) = N\epsilon + P(x) + \kappa(p), \tag{A.4}$$

where ϵ is the energy per atom when the atoms are at rest, $P(x)$ is the potential energy, and $\kappa(p)$ the kinetic energy. The potential energy P is measured such that it is zero if all atoms are at their rest position. $P(x)$ also includes the potential energy pV of the gas container which keeps the pressure constant. Then the par-

tition function can be factorized:

$$Q = \frac{1}{N!} e^{-N\epsilon/kT} \int dx\, e^{-P(x)/kT} \int dp\, e^{-\kappa(p)/kT}. \tag{A.5}$$

In our model the kinetic energy will always be

$$\sum_i p_i^2/2m,$$

so that the integral over the momenta will be the same in all phases:

$$\int dp\, e^{-\kappa(p)/kT} = (2\pi mkT)^{3N/2}. \tag{A.6}$$

We now introduce the definition of the "available volume" v_i of the phase i:

$$v_i = \left(\frac{1}{N!} \int dx\, e^{-P_i(x)/kT}\right)^{1/N}. \tag{A.7}$$

We then get from **A.2**

$$Z^{(i)} = e^{-\epsilon_i/kT} v_i (2\pi mkT)^{3/2},$$

and the equilibrium condition **A.3** becomes

$$\frac{v_{\mathrm{I}}}{v_{\mathrm{II}}} = e^{(\epsilon_{\mathrm{I}} - \epsilon_{\mathrm{II}})/kT}. \tag{A.8}$$

This is the expression that we have used.

It is easy to show that the definition **A.7** indeed yields the expression **3.7** for v_G and **3.5** for v_S. In the Einstein model for the solid the potential energy is

$$P(x) = \frac{1}{2} \sum_k m\omega_E^2 x^2$$

where the sum is taken over all particles coordinates. The factor $1/N!$ in **A.7** is cancelled by the fact that N atoms can be distributed over the N oscillator sites in $N!$ ways. Hence we get

$$v_S = \int dx^3 \exp\left(-\frac{1}{2} m\omega_E^2 x^2/kT\right) = \left(\frac{2\pi kT}{m\omega_E^2}\right)^{3/2}.$$

When we apply **A.7** to an ideal gas at a constant pressure p, the only potential energy entering is $P(x) = pV$, that is, the work exerted against the containers wall. Now $pV = NkT$ so that we get

$$v_G{}^N = \frac{1}{N!} \int dx\, e^{-P(x)/kT} = e^{-N} V^N.$$

We make use of the Stirling formula $e^N N! = N^N$ and obtain

$$v_G = V/N.$$

The determination of v_L from v_S is described in the section entitled "Liquids."