ABOUT LIQUIDS

Herbert J. Bernstein
School of Natural Science
Hampshire College
Amherst, Massachusetts 01002 U.S.A.
and
Department of Physics
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139 U.S.A.

and

Victor F. Weisskopf
Department of Physics
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139 U.S.A.

Submitted to: American Journal of Physics

October 1986


d This work was supported in part by funds provided by the U. S. Department of Energy (D.O.E.) under contract #DE-AC02-76ER03069 and N.S.F. grant # 8316209-DMR. One of us (H.J.B.) thanks Professor C. G. Shull and M.I.T. for support and hospitality during the work reported here.


ABOUT LIQUIDS

Herbert J. Bernstein
and
Victor F. Weisskopf

ABSTRACT

On the basis of a simplified depiction of liquids, solids and gases, we present a qualitative understanding of certain properties of liquids with spherically symmetric atoms: their heats of solidification and vaporization, and the corresponding temperatures, their coefficients of viscosity and self-diffusion. Results are compared to data for neon, argon, sodium, aluminum, copper, silver and mercury. We also include water for order-of-magnitude comparison, although its molecules are not spherically symmetric and internal degrees of freedom cannot be neglected.

1. INTRODUCTION

Under ordinary terrestrial conditions, matter appears in three states of aggregation: solids, liquids and gases. Because of the close connection between liquids and life itself, the liquid state is perhaps the most important of these. But it also provides physics with the most severe challenge of the three. The existence and properties of solids and gases are relatively easy to understand on the basis of characteristic atomic or molecular properties and interactions which follow from basic quantum mechanics. Liquids are harder to understand. Why should there be a state with density nearly equal to that of the solids, but with such relatively low viscosity that the shape can vary readily at virtually no change in volume? 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 impossible to prevent them from seeing their own bodily inputs or outputs. They 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.

This paper does not show how the existence of liquids necessarily follows from quantum mechanics. Its aim is much less ambitious. It tries to present simplified depictions of the three states of aggregation that may help provide 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.

Little in this paper is original, a lot is vastly oversimplified, but the authors are happy that the result, at least for each of us, clarified a few points which previously resided in the well-known grey area of "I should understand this better, but I don't."
2. THE QUESTIONS

In what follows we will consider simple substances only, that is, substances consisting of atoms or molecules that act as spherical objects. We will refer to the constituents as "atoms", even when they may be molecules. The examples on which we will test our ideas are neon, argon, sodium, aluminum, copper, silver, mercury 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.

Our approach emphasizes certain geometric aspects of atomic thermal motion in each state of aggregation. At the melting temperature, the mean displacements from equilibrium of atoms in a solid attain a sizeable fraction of the distance between them. This fraction, similar for all substances, is one of two key semi-empirical ratios in our analysis. The second ratio measures the increase in volume available to the motion of atoms in a liquid, when allowed to drift away from their equilibrium points fixed in the solid. That increase does not necessarily imply a decrease in density since it is based on processes where one atom replaces another. This ratio, too, is quite similar for all our examples. Fig. 1 gives a graphic demonstration of both ratios.

There are several ways to define these two ratios, all giving approximately the same conclusions. We have chosen those definitions which seemed to us to give the best overall agreement with the data. We also restrict ourselves to normal atmospheric pressure throughout. Still, it is quite remarkable that our calculated values come so close to experimental results, especially in view of the wide variety of substances with such a large range of melting and boiling temperatures and heats.

Our results reproduce several well-known qualitative relationships for liquid properties. We obtain approximate expressions for the melting heats, for the relation between boiling and melting heats, and the corresponding temperatures; in particular for the ratio of the boiling heats to the boiling temperatures known as Trouton's rule, and for Lindemann's formula which connects the Debye temperature with the melting point. We also get approximate values for viscosity and self-diffusion coefficients. These conclusions all follow from the two semi-empirical ratios mentioned above, combined with a few arguments based on classical statistical mechanics. All data, the ones that enter into our analysis, the results and the actual values, are assembled in the table.

We denote the energy \( \epsilon \), as the binding energy per atom of the solid at zero-temperature. It is given in line 1 of our table. This energy assumes very different values for different substances, depending on the type of binding between the "atoms". For example, for noble gases, \( \epsilon \approx 0.1 \text{ eV} \); whereas for some metals it is of the order of several eV. We distinguish \( \epsilon_V \) which is the boiling heat per atom at atmospheric pressure, and \( \epsilon_M \), the melting heat per atom. The following relation \( (k) \) is the Boltzmann constant:

\[
\begin{align*}
\epsilon_V & \propto \text{vol} \times \text{heat} \\
\epsilon_M & \propto \text{et} \times \text{heat}
\end{align*}
\]


* \( p_b \) is the vapor pressure over the solid near melting temperature in millimeters of mercury. The observed values were taken from AIP tables giving the temperature at which \( p_b \) equals various powers of ten times one atmosphere.

** The values of \( \epsilon \) and \( \kappa \) are at melting temperature, \( T_M \). The theoretical values are \( \epsilon \approx 1/60, \kappa \approx 10 \) according to Eqs. (5.6) and (5.9). Some of the values had to be reduced to \( T_M \) by using the approximative relations: \( D \sim (T/T_M)^{2/3} \) and \( \eta \sim (T/T_M)^{1/3} \).
constant and $T_V$ is the boiling temperature

$$
e_s \approx \epsilon_V + \epsilon_M + \frac{1}{2} kT_V ,$$

(2.1)

is a rough approximation under the assumption that the heat content of a solid or a liquid is $3kT$ per atom (Dulong-Petit law), whereas it is $(5/2)kT$ in the gas under constant pressure. We will not account for any quantum effects in this paper. Usually, $kT_V$ and $\epsilon_M$ are much smaller than $\epsilon_s$ so that we may put roughly $\epsilon_s \sim \epsilon_V$. Indeed when we put

$$
\epsilon_M = \frac{\epsilon_s}{a} \approx \frac{\epsilon_V}{a} ,
$$

(2.2)

we find that, roughly speaking, $a$ is of the order 6 to 40 for simple substances as seen in the table. The melting temperature $T_M$ depends somewhat but not very much on the pressure. We observe the following relation

$$
kT_M \sim \epsilon_M .$$

(2.3)

Indeed, the ratio $\epsilon_M/kT_M$ is always of the order unity as seen in lines 3 and 5 of the table. We will give reasons for this relation.

The boiling temperature depends strongly on the pressure: in the vacuum it is zero: every substance evaporates in empty space. We define $T_V$ as the vaporization temperature at atmospheric pressure. $T_V$ is related to $\epsilon_V$ by a relation referred to as Trouton's rule:

$$
kT_V = \frac{1}{b} \epsilon_V ,$$

(2.4)

where $b$ is around 10 as seen in line 16 of the table. We will explain this relation and indicate how the value of $b$ can be calculated.

We also apply our considerations to an estimate of the self-diffusion coefficient $D$ of a liquid and its viscosity $\eta$. The coefficient $D$ is defined as follows: suppose a certain number of atoms in the fluid is "tagged", say, by replacing them by a radioactive isotope. The concentration $c$ of those tagged ones varies along the $z$-direction. There is a concentration gradient $\partial c/\partial z$. Then, the random motions of atoms away from their initial positions will create a net current, $J$, of tagged atoms, the number of such atoms transferred per unit time through each square cm of a plane perpendicular to $z$. $J$ is proportional to $\partial c/\partial z$

$$
J = -D \frac{\partial c}{\partial z} ,
$$

(2.5)

with $D$ the constant of proportionality. From purely dimensional reasons it follows that we can write

$$
D = \nu_{lh} d^2
$$

(2.6)

where $\nu_{lh}$ is the thermal velocity of an atom ($\nu_{lh} = \sqrt{3kT/m}$) and $d$ is the average distance between neighboring atoms. For simple liquids near the melting point, we find that the pure number $\zeta$ is of the order 1/50 as seen in line 18 of the table. It will be understandable on the basis of our considerations.

Display of results from an early computer simulation of hard-sphere atoms moving in the solid (upper photograph) and in the liquid (lower photograph) near the melting point: taken from Alder and Wainwright, Sci. Am. 201, 113 (1959). The upper photograph shows paths of atoms in two layers, one behind the other. For the harmonic interaction of the Einstein model, which we use, each atom would actually trace a curve like a Lissajous' figure.

These photographs give graphic demonstration of the two semi-empirical parameters of Eqs. (4.3) and (4.5). The ratio of linear motion to atomic separation in the solid is roughly 1/6. The ratio of available volumes, approximately 1.5, appears by comparing the upper and lower photographs. Note, too, that approximately 1/10 of the steps in the liquid are large – of the order of $d$, the atomic separation – while the remainder are approximately the same size as in the solid.
The viscosity coefficient \( \eta \) 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 \( \eta \) is the viscosity. Again, for purely dimensional reasons we write

\[
\eta = \frac{mn_0 k}{3d^2} \kappa , \tag{2.8}
\]

where \( m \) is the mass of the atom and \( \kappa \) is a dimensionless number which, at or near melting temperature, is of the order 10 for simple liquids as seen in line 19 of the table. This relation will also be made plausible by our analysis.

The size of the constant in Equation (2.8) is surprising when one compares it with the well-known formula for the viscosity of an ideal gas

\[
\eta = \frac{nmn_0 k}{2} \ell , \quad \ell = \frac{1}{\sqrt{2n_0(2\pi)^2}} . \tag{2.9}
\]

Here, \( n \) is the number of atoms per unit volume, \( r \) is the radius of the atom, and \( \ell \) is the mean-free path. It is well-known that this expression does not depend on the density. Surely, expression (2.9) is only valid for dilute gases, but since \( \eta \) is density independent, one would have thought that it should at least give the right order of magnitude also for the liquid. However, when we put \( d \approx 2r \) for the liquid in which the atoms touch each other, we get formula (2.8) but with \( \kappa = (\sqrt{2\pi})^{-1} \approx 0.23 \); that is, about 40 times too small. We will be able to explain this discrepancy.

3. 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 ideas 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 neighbor distance. The elastic bond has a frequency \( \omega_B \) which we will determine as follows. The frequency \( \omega_B \) is connected with the Debye temperature \( \theta \):

\[
\omega_B = \frac{k\theta}{h} = \omega_D ; \quad \epsilon = \frac{1}{\sqrt{3}} \tag{3.2}
\]

where \( \epsilon \) is a numerical factor. The choice of \( \epsilon = 1/\sqrt{3} \) is based upon the following reasoning: \( \omega_D \) 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 \( \epsilon \) depends upon what average one wants to choose. We are interested mainly in the determination of the square of the average amplitude \( \delta \) of the oscillators at a given thermal energy. \( \delta^2 \) is proportional to \( \omega^{-2} \) at a fixed energy and the average of \( \omega^{-2} \) in the Debye model is \( 3\omega_D^{-2} \). Hence, we get \( 3\omega_D^2 = \omega_B \), and \( \epsilon = 1/\sqrt{3} \).

The values of \( \omega_B \) are listed in line 6 of the table for the liquids under consideration, in their frozen form. In all our examples, \( \omega_B \) turns out to be lower than the melting temperature, with the exception of neon where it is not much higher. Nevertheless, even for neon we neglect quantum effects when we deal 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 \( v_B \) 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 \( |kT/(nm^2\varepsilon)|^{3/2} \). A more exact definition of this volume is (see Appendix)

\[
v_B = \int d^3r \exp\left[-W(r)/kT\right] = \left(\frac{2\pi kT}{nm^2\varepsilon^2}\right)^{3/2} \tag{3.3}
\]

where \( W(r) = \frac{1}{2}m\omega_B^2r^2 \) is the potential energy of the oscillator.

It is useful to introduce a length \( \delta \) indicating the linear latitude of motion:

\[
\delta = \frac{v_B^{1/3}}{2\pi kT} \tag{3.4}
\]

The length \( \delta \) is of the order of a tenth of the lattice distance at temperatures somewhat below the melting point. The volume \( v_B \) is between 100 and 350 times smaller than the cell volume at the melting point, for the materials considered.

In a gas there is no restriction in the motion of the atoms, so that the available volume per atom is given by (3.1)

\[
v_g = V/N . \tag{3.5}
\]

At atmospheric pressure this volume is about 1000 times larger than the cell volume \( d^3 \) of a solid and therefore several hundred thousand times larger than the available volume of a solid.
We will use the available-volume concept in order to express the condition of equilibrium between the gas and the solid phase. Such equilibrium exists when

\[
\frac{v_s}{v_g} = e^{-\epsilon_s/kT}.
\]  

(3.6)

Here, \(v_s\) are the available volumes in the two phases and \(\epsilon_s\) is the binding energy of an atom in the solid at \(T = 0\). The relation (3.6) is intuitively plausible. The probability of finding an atom in the solid or gaseous state is proportional to the Boltzmann factor and to the available phase space. The latter is proportional to the available volume because the momentum part of the phase space depends only on the temperature, which is the same in the two states of aggregation. The solid and the gas can coexist if the difference between the available volumes is compensated by the Boltzmann factor corresponding to the difference in energy. The relations (3.5) and (3.6) are derived from the general laws of statistical mechanics in the Appendix.

In the gas, the atom has a much larger available volume at its disposition than in the solid, but the energy in the solid is lower by \(\epsilon_s\). We can transform (3.6) into an expression of the vapor pressure \(p_v\) above a solid by means of (3.1) and get

\[
p_v = \frac{kT}{\epsilon_s} e^{-\epsilon_s/kT}.
\]  

(3.7)

This equation says that, in our approach, 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 \(e^{-\epsilon_s/kT}\). Of course, our simplified approach can only give very approximate results. As mentioned before, all quantum effects including zero-point energies are neglected. We see by comparing lines 11 and 12 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 to within a factor 2.5, with the exception of H2O and Ne for which our simple arguments should not hold. In water we expect the phase-space for the motion in the gaseous state to be larger because of the additional motions of the internal degrees of freedom within the molecule which are restricted in the solid phase. Neon, on the other hand, has important quantum effects, because the melting temperature is only 1/3 the Debye temperature.

4. LIQUIDS

A. Atomic Motion in Liquids

In an idealized solid the "location" of each atom is fixed at the lattice points. We understand by location not its exact position but the position of the center of the spherical volume \(v_s\) within which it performs harmonic vibrations [in the Einstein picture] with an amplitude of the order \(\delta_s\). This is a long-range order. If the forces between neighboring atoms were exactly harmonic — exemplified by ideal springs — the long-range order would be maintained even at high temperature. But the forces are not exactly harmonic: they become weaker than harmonic at distances of the order of the lattice separation and stronger at very small distances. Therefore, when the temperature reaches the melting point \(T_M\) the structure is loosened. The individual atoms no longer oscillate around a fixed position. Rearrangements occur. The atoms do not always return to the same place, and the long-range order disappears. Since the whole structure loosens up at the melting point, the available volume \(v_G\) in the liquid is somewhat larger than \(v_s\) at the melting temperature \(T_M\). But it cannot be very much larger since the motion of an atom is still strongly confined by its neighbors. Let us also define a length \(\delta_l\) which relates to \(v_G\) as \(\delta_s\) relates to \(v_s\) in (3.4):

\[
\delta_l = \left(\frac{v_G}{v_s}\right)^{1/3}.
\]  

(4.1)

It is a measure of the average step length in the back and forth motion in the liquid. We may picture it by imagining that atoms move almost like oscillators for distances of the order \(\delta_l\) but do not necessarily return to the same point when restoring forces push them back. They perform a "hindered" random motion. The term "hindered" expresses the fact that the ratio \(v_G/d^3\) is rather small although larger than \(v_s/d^3\). The particles are still far from moving freely and randomly as in a gas. Note that an increase in the available volume does not necessarily imply a decrease in density. In the liquid, an atom may change place with another, or move its way through between its neighbors; these displacements would not appreciably decrease the density, if at all.

As shown in the Appendix, a relation similar to (3.6) holds for the ratio \(v_G/v_s\) and the melting heat \(\epsilon_M\):

\[
\left(\frac{v_G}{v_s}\right)_M = \left(\frac{\delta_l}{\delta_s}\right)_M^3 \exp\left(\frac{\epsilon_M}{kT_M}\right)
\]  

(4.2)

where the subscript \(M\) signifies \(T = T_M\). Since \(v_G/v_s\) cannot be very large, we conclude from (4.2) that \(\epsilon_M/kT_M\) must be near unity or smaller, a fact borne out by the data. This contrasts sharply with the ratio \(v_G/kT_v\) which is of the order of 10 according to Trouton's rule. The reason lies in the very large difference between the available volumes of the gas and the liquid as will be shown below.

It is difficult to determine from first principles the melting temperatures or the increase in step-length from \(\delta_s\) to \(\delta_l\). Therefore, we introduce two ratios which are derived semi-empirically from an analysis of the data, but whose values are in the expected range. First, we ask ourselves, what is the value of \(\delta_l/d\) when melting occurs? We get \(\delta_l\) at \(T_M\) from (3.4) and compare it with the lattice distance \(d\). We then find from line 9 of the table that \((d/\delta_s)_{T=T_M}\) lies between 4.4 and 7.1 despite the large differences in \(T_M\) and \(\omega_F\). Thus, we may put down our first approximate ratio

\[
\frac{\delta_s}{d} \approx 1.6
\]  

(4.3)

This is the rough average of the values given by line 9 of the table. It is a reasonable value for the onset of liquidity.

The other ratio is \(\delta_l/\delta_s\) for \(T = T_M\). It measures the increase in step-length in the liquid compared to the solid at the melting point. We expect it to be larger than
one but not very large. After all, the motion of an atom in a liquid is still a strongly hindered random motion: it is a back and forth movement although not restoring the exact original position. We can determine it empirically from $\epsilon_M$ and $T_M$ by making use of (4.2). The results are found in line 10 of the table. In spite of the very different input values the ratios are close to each other, again with the exception of water, where the breaking of hydrogen bonds adds to the melting heat. We may put

$$\left( \frac{\delta}{\delta_s} \right)_{T=T_M} \approx 1.5 . \tag{4.5}$$

The loosening up of the liquid compared to the solid gives the atom about 50% more latitude in its motion. Eqs. (4.3) and (4.5) are the two semi-empirical ratios that we need for the understanding of liquids. Note that they are both of a size that one would expect intuitively from the circumstances.

It is useful to note our estimates of $v_s$ and $v_t$ in terms of $d^2$. Following from (4.1), (4.3) and (4.5):

$$v_s \approx \left( \frac{d^2}{d} \right)^{3/2} \approx \frac{d}{200} \quad \text{at} \quad T = T_M \tag{4.6}$$

Later we will need the dependence of the ratios (4.3) and (4.5) on the temperature. Neglecting the weak change of density of a liquid we assume $d$ remains constant. Then, we get according to (3.4)

$$\frac{\delta}{d} \approx \frac{1}{6} \left( \frac{T}{T_M} \right)^{1/2} \quad \text{at} \quad T = T_M \tag{4.3a}$$

The temperature dependence of (4.5) is not so easy to determine. We will see in section 5 that it can be found from (5.6) with the help of (4.3a) and (5.4). It turns out to be roughly (within 5%) proportional to $T^{1/3}$, so that we get

$$\frac{\delta}{\delta_s} \approx 1.5 \left( \frac{T}{T_M} \right)^{1/3} \quad \text{at} \quad T = T_M \tag{4.5a}$$

We do not investigate, in this paper, how these ratios depend on the pressure. They are all meant to be valid at atmospheric pressure. It is expected that (4.3) increases, and (4.5) decreases with rising pressure.

B. Lindemann Melting Point Formula

Our relations also contain the so-called Lindemann melting-point formula. It connects the Debye temperature $\theta$ with the melting temperature $T_M$ and usually is written in the following form:

$$\theta = D \left( \frac{T_M}{\mu V^{1/3}} \right)^{1/2} , \quad D \approx 150 \text{ cm} \cdot \text{g}^{1/2} \text{ cm}^{1/2} .$$

Here $\mu$ is the molar weight in grams and $V$ is the molar volume. In our notation $V = \Lambda d^3$, where $\Lambda$ is the Avogadro number and $\mu = Am$. The value of $D$ varies somewhat: Ne and Ar are nearer to 180, the alkali metals are around 120. Since $k\theta/\hbar = \omega_D$ we may write the above in the form:

$$\omega_D = D' \left( \frac{kT_M}{md^2} \right)^{1/2} . \tag{4.7}$$

The value of the pure number $D'$ corresponding to $D = 150$ would be $D' = 25$.

We can express the number $D'$ in terms of $\delta_s/d$ using Eqs. (3.4) and (3.2):

$$\left( \frac{kT_M}{md^2} \right)^{1/2} = \frac{1}{\sqrt{2\pi}} \frac{\omega_D}{\sqrt{3}} \left( \frac{\delta_s}{d} \right) = 0.23 \omega_D \left( \frac{\delta_s}{d} \right) \tag{4.7}$$

The ratio $(\delta_s/d)$ at the melting point was found to be about 1/6. We then get an expression for $\omega_D$ of the form (4.7) and we arrive at a value $D' \approx 26$, a good value considering the approximations made. The fact that the Lindemann relation (4.7) holds with roughly the same constant for most substances, again indicates that $(\delta_s/d)$ is more or less independent of the substance. The deviations of $D$ in the noble gases and in the alkalis derive from the abnormally low values of $(\delta_s/d)$ in the former cases and in the abnormally high value for the alkalis (Na), according to line 9 of the table. (The other alkali metals also have a high value of $(\delta_s/d)$.)

C. Melting and Boiling Heats

We can determine the melting heat $\epsilon_M$ by combining Eqs. (3.4) and (4.2). Extracting $kT_M$ from (3.4) at $T = T_M$ we can write

$$kT_M = \frac{1}{2\pi} m \omega_D d^2 \left( \frac{\delta_s}{d} \right)^2 ,$$

and we get from (4.2)

$$\epsilon_M / kT_M = 3 \ln \left( \frac{\delta_s}{\delta_s} \right) .$$

This enables us to obtain an expression for $\epsilon_M$:

$$\epsilon_M = \frac{1}{2\pi} m \omega_D d^2 \left( \frac{\delta_s}{d} \right)^3 \cdot 3 \ln \left( \frac{\delta_s}{\delta_s} \right) . \tag{4.8}$$

This determines $\epsilon_M$ by means of our semi-empirical ratios (4.3) and (4.5). The results are found in line 14 of the table: they agree reasonably well with the observed values in line 3, with the exception of water. There the actual melting heat is considerably higher because the melting not only creates additional displacements of the molecules; it also breaks a number of hydrogen bonds.
Let us now discuss $\epsilon_a$, the binding energy in the solid. We assumed that the atoms in the solid are bound by a harmonic restoring force to their rest positions. The potential energy $W$ is

$$W = \frac{1}{2} m \omega^2 d^2 \delta^2$$  \hspace{1cm} (4.9)

where $\delta$ is the displacement. $W$ should be of the order of (but larger than) the binding energy $\epsilon_a$ when $\delta \sim d$. The liquid state sets in, as we saw, when $\delta \sim d/6$. It means that already for this displacement the potential energy is less than the harmonic value. There would be no melting if all bonds in the solid remained harmonic however great their extension. $W$ as given by (4.9) will become equal to $\epsilon_a$ when $\delta = f d$, where $f < 1$ but larger than $1/6$ since certainly the energy per atom at melting must be less than $\epsilon_a$. If $f$ were $1/6$ or less the solid would sublimate directly to gas. We write

$$\epsilon_a = \frac{1}{2} m \omega^2 (f d)^2$$  \hspace{1cm} (4.10)

Eqs. (4.8) and (4.10) allow us to obtain a simple relation for $\epsilon_a/\epsilon_M$:

$$\frac{\epsilon_a}{\epsilon_M} = \pi f^2 \left( \frac{d}{\delta_a} \right)^2 \frac{1}{3 \ln \left( \delta_a/\delta_s \right)}$$

We realize that the boiling heat is never less than 80% of $\epsilon_a$. We then get with the help of (4.3) and (4.5) an approximate expression for the ratio of boiling and melting heats by setting $\epsilon_a \approx \epsilon_V$:

$$\frac{\epsilon_V}{\epsilon_M} \approx 93 f^2$$  \hspace{1cm} (4.11)

According to line 13 of the table, the values of $f$ lie around 0.5, except for Ne and Ar for which the boiling point lies so close to the melting point that these substances almost sublimate. We may therefore use (4.11) for a rough estimate of $\epsilon_V/\epsilon_M$ by setting $f = 0.5$ for all substances for which $T_V/T_M > 1.4$ and $f = 0.25$ for the others. Then we get $\epsilon_V/\epsilon_M \approx 23$ for the former, and $\approx 5.8$ for the latter substances. The observed ratios are found in line 15 of the table. They are reasonably close to the predictions considering the assumptions, with the usual exception of water. Sodium has a considerably higher ratio than 23 because of its abnormally high value of $f$.

D. Trouton's Rule

Trouton's rule says that the boiling heat $\epsilon_V$ per atom is of the order of ten times $kT_V$. This relation can be understood on the basis of an equilibrium condition similar to (3.6) for the vaporization process, which is explained in the Appendix:

$$\left( \frac{v_g}{v_v} \right)_{T=T_V} = \exp \left( \frac{\epsilon_V}{kT_V} \right)$$  \hspace{1cm} (4.12)

where $v_g$ is the available volume per atom in the gas and $\epsilon_V$ the difference in energy in the liquid and in the gas. We may argue roughly as follows. The density of a gas at atmospheric pressure is about a thousand times less that in a liquid: $v_g \approx 10^3 d^3$. According to (4.6), the available volume in a liquid is approximately $(1/60) d^3$. Hence, $\epsilon_V/kT_V$ should be about near the natural logarithm of $60,000$, which is 11. Here is a more exact evaluation of (4.12). Let us call $v_T$ the volume per atom of an ideal gas at atmospheric pressure: at $T_0 = 273 K$, $v_0 = 3.72 \times 10^{-4} A^3$ (this is the well-known 22.4 liter per mol). According to the gas law (3.1) $v_T$ is proportional to $T$: $v_T = v_0 (T/T_0)$. The available volume in the liquid is $v_L = (1/6)^3 v_T (T/T_M)$ according to (4.5a). Eq. (4.3a) tells us that $v_L = (65/6)^3 (T/T_M)^{3/2} d^3$ so that we find

$$v_L (T=T_V) = \left( \frac{1}{6} \right)^3 \left( \frac{T_V}{T_M} \right)^{3/2} d^3$$

We then get from (4.12)

$$\frac{\epsilon_V}{kT_V} = \ln \left( \frac{v_T^3}{(1/6)^3 d^3} \right) + \ln \left( \frac{T_M^{5/2}}{T_V^{5/2}} \right)$$  \hspace{1cm} (4.13)

Neglecting the relatively smaller second term and setting $d = 3 \times 10^{-10}$, we obtain

$$\frac{\epsilon_V}{kT_V} \approx 11.4$$

which is Trouton's rule. A better agreement with the observed values is reached when the complete expression (4.13) is evaluated with the actual values of $d$, as seen by comparing lines 16 and 17 of the table.

5. SELF-DIFFUSION AND VISCOITY

We have assumed that the motion of an atom in a solid is strictly harmonic; it always returns to a fixed position in the lattice. Under this simplified assumption, the diffusion is zero and the viscosity infinite since the solid is not deformable in that approximation.

In order to estimate diffusion and viscosity of fluids, we must study the displacements of atoms in liquids. The motion in the liquid is "quasi-harmonic". Sometimes it returns to its previous place, sometimes it returns to a place nearby, sometimes it may exchange place with neighbors, and sometimes it may even end up in one step at a distance larger than $d$. Let us simplify the situation by assuming that the atom has a probability of $(1 - L)$ to make a strictly harmonic motion (returning to its original place), and a probability $L$ to land in one step at a distance $d$. All intermediary steps are either counted as harmonic steps or as the steps by $d$ in such a way that the same average step-length $\delta_L$ results. $L$ can be easily determined from our two semi-empirical numbers (4.3) and (4.5). The displacement is $\delta_L$ in the harmonic motion, and $d$ otherwise. The average should be $\delta_L$. So we get $(1 - L)\delta_L + Ld = \delta_L$

$$L = \frac{(\delta_L/\delta_x) - 1}{(d/\delta_x) - 1}$$  \hspace{1cm} (5.1)
Using the values (4.3) and (4.5) we get
\[ L \approx \frac{1}{10} \text{ for } T = T_M \]  
(5.2)

The temperature dependence of \( L \) can be obtained by the following consideration:
\( L \) is the fraction of atoms displaced by the distance \( d \). In order to do so a potential barrier \( \epsilon_A \) must be overcome. We may call \( \epsilon_A \) the activation energy of the displacement. Then the temperature dependence of \( L \) should have the form:
\[ L(T) = \exp \left( \frac{-\epsilon_A}{kT} \right), \]  
(5.3)

where \( \epsilon_A \) is chosen such that \( L(T_M) = 0.1 = \exp(-2.30) \). Then we get
\[ L(r) = \exp \left( \frac{-2.30}{r} \right), \quad r = \frac{T}{T_M} \]  
(5.4)

For \( r < 1.5 \), Eq. (5.4) can be approximated by
\[ \frac{L(r)}{L(r = 1)} \approx r^2 \]  
(5.5)

The introduction of only one activation energy \( \epsilon_A \) represents a considerable simplification. Surely the exchange of place with a neighbor requires an energy different from the squeezing between two neighbors. We may use (5.2) for the determination of the \( T \)-dependence of \( \delta_t/\delta_s \):
\[ \frac{\delta_t}{\delta_s} = \left( \frac{d}{\delta_s} - 1 \right) L + 1 \]  
(5.6)

Using (5.4) and (4.3a) we find that we can approximate within 8% the \( T \)-dependence of \( \delta_t/\delta_s \) in the interval \( 1 < r < 3 \). (In our examples \( r \) is never larger than about 3.)

In our simplified picture, a fraction \((1 - L)\) atoms stay put, but a fraction \(L\) move a distance \(d\).

We now are able to estimate the self-diffusion coefficient \(D\) as defined by Eq. (2.5). When the concentration \(c\) of tagged atoms is uniform, random thermal motion carries just as many atoms upwards as downwards. On the average, the net current \(J\) across a unit area perpendicular to the \(z\)-axis vanishes. But if there is a positive \(dc/dz\), the density is greater above the unit area than below, more atoms move downwards than upwards simply because there are more of them above.

In our simplified picture, only a fraction \(L\) of the atoms is displaced by \(d\) and contributes to the self-diffusion. Let us look at the particle flux through a unit area perpendicular to the \(z\)-axis. If the concentration \(c\) of atoms increases upward by \(dc/dz\) the effective increase in concentration at a distance \(d\) above the unit area is \((dc/dz)d\). The volume from which atoms might reach the unit area in a single step has the height \(d\). Then one would think that the number that could cross downwards from above in a single step exceeds that from below by
\[ N'_{ex} \approx \left( \frac{\partial c}{\partial z} \right) d^2 \]  
(5.7)

Actually, that number is reduced for two reasons. First, only one-sixth of the atoms from above (or below) are headed across the unit area, since the directions up or down along the \(z\)-axis are equally probable as the forward and backwards movements in the \(x\)- and \(y\)-directions. Only motion down the \(z\)-axis contributes to diffusion. Second, only \(L\) of the atoms displace themselves. Therefore, the net excess is not given by Eq. (5.7) but by
\[ N_{ex} = \frac{L}{6} \frac{\partial c}{\partial z} d^2 \]  
(5.8)

The time for the one step is \(d/w_{th}\), so that the net number crossing the unit area in the \(z\)-direction is (the excess is downward)
\[ J = -\frac{\partial c}{\partial z} \frac{d w_{th} L}{6} \]

and we get for \(D\) according to Eq. (2.5)
\[ D = \frac{w_{th} d L}{6} \]  
(5.9)

We obtain for the dimensionless constant \(\zeta\) defined in (2.6):
\[ \zeta = \frac{L}{6} \approx \frac{1}{60} \]  
(5.10)

Our result is in qualitative agreement with observed values, line 18 of the table. The actual values are a little higher, but of the same order, except for water where the non-spherical shape of the molecule impedes diffusion. Since \(w_{th}\) is proportional to \(T^{1/2}\), we get a temperature dependence of \(D\) from (5.4): \(D = D_M T^{1/2} \exp(-\frac{\epsilon_A}{r})\), where \(D_M\) is the value near the melting point. For \(r < 1.5\), this is approximately \(D = D_M T^{1/2}\), in reasonable agreement with the facts, except for water.

Let us now turn to viscosity. As long as the atoms are bound by a harmonic force, the viscosity is practically infinite. The crystal is perfectly stiff except for extremely high shearing forces. We have assumed that, in the liquid, a fraction \(1 - L\) of the atoms vibrate harmonically, and a fraction \(L\) move by steps of the size \(d\). The latter steps are responsible for the finite viscosity of liquids.

The viscosity coefficient \(\eta\) was defined by Eq. (2.7). We must find the momentum transfer \(P\) per cm\(^2\) through a plane perpendicular to \(x\), when the increase of the velocity is in the \(z\)-direction is given by \(du/dz\). For this purpose, we simplify our picture even more: Instead of having a fraction \(L\) of atoms, all over the liquid, performing steps of length \(d\), we assume they all lie in monoatomic layers parallel to the \(x - y\) plane. In order to maintain the right ratio \(L\), these layers must have a distance \(d/L\) from one
another. In between those layers all atoms are considered harmonically bound. This implies that the region between the layers are stiff and all atoms move with the same velocity in the $x$-direction. Then there must be a jump of $u$ through the layers by an amount

$$\Delta u = \frac{d}{L} \frac{du}{dz} . \tag{5.11}$$

The momentum transfer between two adjacent stiff regions is effected by the atoms in the layer between them. When an atom moves up it transfers a momentum $m(u - \Delta u)$ to the upper region; when an atom moves down it transfers a momentum $m(u + \Delta u)$ to the lower region. There is a net transfer of $m\Delta u$ per atom. How many of such displacements occur per second in a layer? There are $d^{-2}$ atoms per cm$^2$. One third of them moves up or down parallel to the $x$-direction and takes the time $\ell = d/w_{th}$ to travel the distance $d$. Thus, the momentum $P$ per cm$^2$ per second transferred from the upper to the lower region is roughly

$$P \approx -m\Delta u \frac{1}{3d^2} \frac{w_{th}}{d} .$$

Inserting (5.11) we get

$$P = -\eta \frac{ds}{dz}, \quad \eta = \frac{m w_{th}}{3d^2 L} . \tag{5.12}$$

The factor $\eta$ defined in (2.8) is then

$$\eta \approx L^{-1} . \tag{5.13}$$

It would be about 10 at $T = T_M$, which is in good qualitative agreement with line 19 of the table, again with the exception of water, where the asymmetry of the molecules increases viscosity.

Since $w_{th}$ is proportional to $T^{1/2}$ and $L(r)$ is given by (5.5), we expect that the coefficient of viscosity decreases with temperature as $\eta \approx \eta_M T^{-1/2} \exp(-\frac{2}{\theta_0})$ where $\eta_M$ is the value near the melting point and $r = T/T_M$. For $r < 1.5$, this can be approximated by $\eta \approx \eta_M r^{-3/2}$. It is approximately correct, although the temperature dependence in some cases, is somewhat stronger. Water, as usual, is a special case, again since the viscosity changes by a factor more than six between melting and boiling. The rising 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. The chains are mutually entangled: one chain winds itself around another. This phenomenon is called "reptation" by L. de Gennes 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. For example, honey at room temperature is about 10$^5$ times more viscous than water. Our simple expression represents only a lower bound for the viscosity in the case of complicated liquids.

Let us compare expression (5.12) with the formula for 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 as a highly compressed gas in which the atoms touch: $2r = d$. Taking the ratio of (5.12) to (2.9), we get for $T > T_M$:

$$\frac{\eta}{\eta_M} = \sqrt{2\pi(2r)^3} = \sqrt{2\pi} \frac{d}{L} = 44 . \tag{5.14}$$

Here we have put $2r = d$ corresponding to the liquid situation.

The viscosity of liquids is roughly 50 times higher than that of a gas at the same temperature. The reason lies, of course, in the fact that the atoms are much more bound to each other in the liquid. The distance over which the momentum is transferred to the next layer is $d/L$, whereas in a gas it is the mean free path $\ell$. At densities for which the atoms touch each other, $2r = d$ and the gas-kinetic expression $\ell = d^2/(2\pi(2r)^3)$ becomes $\ell \approx d/\sqrt{2\pi}$. Thus, the viscosity of a liquid is larger by the factor $d/L$ is $\sqrt{2\pi}/L$ times larger. This is just the factor 44 appearing in (5.14).

We have shown that our oversimplified picture of a liquid indeed gives rise to a viscosity and diffusion coefficient of the right order of magnitude. Our analysis emphasizes the atomic displacements rather than the energetics of potential barriers, except in (5.5). This is in contrast to most of the approaches in the current literature.

Comparing our expressions for $D$ and $\eta$ in Eqs. (5.9) and (5.12) we arrive at the simple relation

$$D \cdot \eta \approx \frac{m w_{th}^2}{18d} = \frac{kT}{6d} . \tag{5.12}$$

This relation is quoted frequently in the literature; the factor varies, however. Refs. [2] and [3] have no factor 1/6. Ref. [4] has a factor $(2\pi)^{-1}$ instead of 1/6.

6. **WHY IS WATER "WATERY"**

When we try to move a finger placed in a hole of a fixed solid, we feel an almost infinite resistance. Why does liquid such as water seem very different from a solid? When we move a finger through a liquid (in a fixed container), we feel only moderate resistance. It roughly corresponds to accelerating a quantity of water equal to the volume of the dipped finger to the velocity of the finger, in the time the finger moves by approximately its own diameter. The force of resistance to motion in a liquid comes from two sources: the inertial resistance to acceleration $F_i$; and the viscous resistance $F_v$. When the liquid is water and the speed of the finger is "normal" i.e. 10 to 100 cm/sec, we definitely feel a purely inertial resistance: it seems as if the displaced water suffers no frictional resistance.


Let us see how this follows from the value of viscosity. We estimate \( F_i = Ma \), where \( M \) is the mass of the displaced water and \( a \) the acceleration:

\[
|F_i| \approx \Delta^3 \rho \cdot V \frac{V}{\Delta} = \Delta^2 \rho V^2 .
\]  

(6.1)

Here, \( \Delta \) is the linear dimension of the dipped finger, \( \rho \) is the density of the liquid, \( V \) the magnitude of the velocity of the finger, and \( \Delta/V \) the time the water is accelerated from rest to velocity \( V \). The viscous resistance is estimated as follows: There is a viscous momentum transfer \( \Pi \) per second from the water at rest to the moving parts of the water, which is equal to the force \( F_v \):

\[
|F_v| = \Pi \approx \eta \left( \frac{V}{\Delta} \right) \Delta^2 = \eta V \Delta .
\]  

(6.2)

Here, \( V/\Delta \) is a measure of the velocity gradient, and \( \Delta^2 \) a measure of the surface of the moving water volume. The ratio \( |F_i|/|F_v| \) is called the Reynolds number \( \mathcal{R} \):

\[
\mathcal{R} = \frac{|F_i|}{|F_v|} = \frac{\Delta \rho V}{\eta} .
\]  

(6.3)

As seen from Eqs. (6.1) and (6.2), \( F_i \) is proportional to the square of \( \Delta \) and \( V \), whereas they enter \( F_v \) only to the first power. Therefore, the smaller or slower the object, the more important becomes the viscous force.

Reynold’s number can be written in a more instructive form by inserting (5.9) for \( \eta \) and \( M/d^3 \) for \( \rho \):

\[
\mathcal{R} \approx \frac{\Delta}{d} \frac{V}{\nu \kappa} .
\]

For objects of macroscopic size, \( \Delta/d \) is of the order of \( 10^4 \). As line 20 of the table indicates, \( \nu h \) is of the order of several \( 10^4 \) cm/sec; \( \kappa \) is of the order 10. In general, \( \Delta \) is much larger than \( d \), and \( V \) much smaller than \( \nu h \).

Let’s go back to expression (6.3) for Reynold’s number and find its value for the case of moving a finger with a velocity \( V \approx 10 - 100 \) cm/sec through water, for which \( \eta \approx 10^{-2} \) gram/cm sec. We get \( \mathcal{R} \approx 10^3 - 10^4 \). Obviously, the viscous resistance is negligible. That is why water is “watery”.

As long as \( V \) is much larger than about \( 10^{-3} \) cm/sec, water will be “watery” for objects of the size of about 1 cm. It is interesting that water is far from watery for microbes. In that case \( \Delta \approx 10^{-4} \) cm and \( V \approx 10^{-5} \) cm/sec so that we get \( \mathcal{R} \approx 10^{-5} \). For them, the decisive resistance is the viscous force. They feel like we would if we were moving a finger very slowly \( (10^{-5} \) cm/sec) in honey.

**APPENDIX**

In the 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 are kept constant; \( N = N_1 + N_2 \), where \( N_1 \) and \( N_2 \) are the number of atoms in the two phases:

\[
\begin{align*}
\left( \frac{\partial G}{\partial N_i} \right)_{T,P,N} &= 0 .
\end{align*}
\]  

(A1)

The Gibbs function of a two phase system is the sum of the functions of each system:

\[
G = G^{(I)} + G^{(II)}
\]  

(A2)

where

\[
G^{(i)} = -kT \ln Q^{(i)} - \frac{pV_i}{kT}
\]  

(A3)

Here, \( p \) is the common pressure, \( V_i \) is the volume of the phase \( i \) and \( Q^{(i)} \) is the partition function of phase \( i \) containing \( N_i \) particles:

\[
Q^{(i)} = \frac{1}{N_i!} \int d\tau \ e^{-E_i(\tau)/kT}
\]  

(A4)

The integration is taken over all \( 6N_i \) coordinates of the position and momentum space \( r \) of the phase \( i \). \( E_i(r) \) is the total energy as a function of the coordinates.

If the motion of each particle is independent of the others and all particles of one phase are subject to the same conditions – this is so in the Einstein model of a solid and in the ideal gas – \( E_i \) has the form

\[
E_i = \sum_n (U_i(r_n) + K_i(p_n))
\]

\( U_i(r_n) \) and \( K_i(p_n) \) are the potential and kinetic energies of the \( n \)th particle in the phase \( i \), as functions of its position or momentum variables. The sum extended over all \( N_i \) particles.

Let us first evaluate the partition function (A4) when there is only one particle in the phase \( i \). We then call it \( Z_i \) and get

\[
Z_i = A_i B , \quad A_i = \int d\tau \ \exp \left( -U_i(\tau)/kT \right)
\]

\[
B = \int d\tau \ \exp \left( -K_i(\tau)/kT \right)
\]  

(A5)


** About the necessity to introduce the factor \( (N!)^{-1} \) see, for example, F. Reif, *Statistical and Thermal Physics*, (McGraw-Hill, New York, 1965), p. 245.
The factor $B$ does not depend on the phase since $K_i(\tau)$ is always $p^2/2m$. We get
\[ B = (2\pi mkT)^{3/2} \]  
(A6)

In the Einstein model of a solid we have
\[ U_s = -e_s + \frac{1}{2}mv_s^2 \]  
(A7)

where $e_s$ is the energy necessary to liberate the atom from its rest position. Thus, we get
\[ A_s = e^{e_s/kT} \cdot v_s \]  
(A8)

where $v_s$ is the available volume as given by Eq. (3.3).

We now turn to the ideal gas in a volume $V_g$ (from now on we set $V_g = V$ since the volumes of the other phases will not appear). Evidently there are no forces acting on the particles, so that the potential energy vanishes. Thus, we get for a gas with one atom:
\[ Z_g = A_g \cdot B \quad ; \quad A_g = V \]  
(A9)

and $B$ is given by (A6).

What happens if $N_t \gg 1$? In the solid, we must take into account that each atom moves near a different lattice point. Therefore, they can be distributed in $N_s!$ ways over the lattice points. The total coordinate space is $N_s!$ times larger than the product of the $r_a$- and $p_a$-spaces. Hence, the factor $N_s!$ in (A4) is cancelled out. Because of the independence of the particle motions, we may write
\[ Q^{(t)} = (Z_g)^{-N_s} \left( e^{e_s/kT} v_s B \right)^{N_s}. \]  
(A10)

In the ideal gas each atom moves in the same volume $V$ so there is no factor $N_s!$ in the numerator:
\[ Q^{(o)} = \frac{1}{N_g!} (Z_g)^{N_s} = \frac{1}{N_g!} (V B)^{N_s}. \]  
(A11)

The Gibbs’ functions contain the term $pV/kT$ according to (A3). For the gas, this term is equal to $N_g$ according to the gas law, whereas it can be omitted in the solid because its volume is several orders of magnitude smaller than that of a gas with a similar number of particles. This omission expresses the fact that the inner state of the solid is essentially independent of the pressure. We then get
\[ G^{(o)} = -kT N_g \left( \ln v_s + \frac{e_s}{kT} \right) + \ln B \]  
and
\[ G^{(o)} = -kT N_g \left( \ln v_s - \frac{N_s}{N_g} + 1 + \ln B \right) \]  
(A12)

The number 1 in the bracket of $G^{(o)}$ represents the $pV/kT$ term in (A3) which contributes only negligibly to $G^{(o)}$. We use Stirling’s formula $! = N^N e^{-N}$ and get $\ln N_s! + \ln N_g = N_s \ln N_g$. Then we find
\[ G^{(o)} = -kT N_g \left( \ln v_s + \ln B \right) \]  
(A13)

with $v_s = V/N_g$ as in (3.5).

Note that the available volume per atom in the gas is not the total volume $V$ as one might be led to believe. The reason is the factor $(N_s!)^{-1}$. One may also understand it as follows. What counts in our considerations is the ratio between the available volume in the gas and in the condensed state. In the latter case we must take into account the $N_s!$ permutations in the distribution of atoms. Now $N_s! \sim N^N$ and the partition function contains the available volume $v_s$ to the $N_s^2$ power. Thus, the available volume in the condensed phase gets an additional factor $N_s$ or, since only ratios enter, the gas phase gets a factor $N_s^{-1}$. Actually, $N_s! \sim N^N e^{-N}$. The additional factor $e^{-N}$ is taken care of by the term $pV/kT$ in (A3).

Let us now determine the Gibbs function for the solid-gas system according to (A2).
\[ G = -kT \left[ N_s \ln v_s + N_g (\ln v_s + e_s/kT) + N \ln B \right] \]

Here, $N = N_s + N_g$ and is a constant. Taking the derivative (A1) in respect to $N_s$, we obtain the equilibrium condition (3.6):
\[ \frac{v_g}{v_o} = \exp(e_s/kT) \]  
(A14)

Our approximative methods cannot exactly prove the parallel relations (4.2) and (4.12) for the liquid-solid and liquid-gas equilibrium. In liquids the motions of atoms are no longer independent from each other. The potential energy is no longer a sum of terms, each depending only on the coordinates of one particle. But we can extend (A14) to the equilibrium with liquids by the following consideration. We have described the transition from the solid to the liquid and from the liquid to the gas as an increase in available volume for each particle, at constant temperature $T_M$ or $T_B$. Let us approximate the situation by assuming that the atom moves as a free particle within the bounds of the available volume. Then the increase from $v_1$ to $v_2$ requires an energy $\epsilon_2$:
\[ \epsilon_2 = \int_{v_1}^{v_2} p' \, dv' = kT \log \left( \frac{v_2}{v_1} \right) \]

when the gas equation for one particle is used: $p' = kT/v$. Note that $p'$ is the pressure an ideal gas would have if confined to one atom per available volume. In the solid or liquid, this is far higher than the external, atmospheric pressure. It is counteracted by the forces that keep the atoms within the available volume. We therefore get
\[ \frac{v_2}{v_1} = \exp(\epsilon_2/kT) \]  
(A15)

The energy $\epsilon_2$ is the melting heat $\epsilon_M$ for the solid-liquid transition at $T_M$, or the boiling heat $\epsilon_V$ for the liquid-gas transition at $T_V$. We then arrive at Eq. (4.2) and (4.12).

The three relations (3.6), (4.2) and (4.12) are all of the form (A15). They express the fact that the probability of an atom to be in the phase $i$ is proportional to $v_i e^{-\epsilon_i/kT}$. where $\epsilon_i$ is the energy of the atom in phase $i$. In order to have equilibrium between two phases 1 and 2, the probability to be in 1 or 2 must be equal: $v_1 e^{-\epsilon_1/kT} = v_2 e^{-\epsilon_2/kT}$

This is identical to (A15) since $\epsilon_1 - \epsilon_2 = \epsilon_2 - \epsilon_1$. 

21