

The Archimedes force acting on individual molecules of matter in an external field

V. L. Lyuboshitz and M. I. Podgoretskii

Joint Institute for Nuclear Research, Dubna, Moscow Region

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The meaning of the law of Archimedes for microscopic bodies is discussed. On the basis of Boltzmann's principle, it is determined that, in an external field (in particular, in a gravitational field), an additional force, which is identified with the Archimedes force, acts on every molecule of a nonideal gas or liquid. From Boltzmann's principle and the universal character of the Einstein relation between the diffusion coefficient and mobility, it follows that the drift velocity of a molecule in an external field is determined not only by the external force, but also by the Archimedes force. The general thermodynamic equations for the Archimedes forces acting on molecules have been obtained for both one-component and also multi-component media. In the case of a mixture of rarefied gases, the Archimedes forces are expressed linearly by the second virial coefficients. It is shown that the Archimedes forces acting on the molecules of matter are directly connected with the fluctuations of the number of molecules, and thereby with the integrals of the functions describing the pair correlations of their positions.

1. INTRODUCTION. POSING THE QUESTION

In connection with the generally accepted formulation of the law of Archimedes (... the buoyancy equals the weight of the liquid or gas in a volume equal to the volume of the body), a somewhat unexpected question arises: can one consider every molecule of a liquid (gas) as a "body immersed in this same liquid (gas)"? This question is by no means trivial. On the one hand, it is well known that the law of Archimedes is formulated for macroscopic bodies in conditions when hydrodynamics is applicable, and therefore, it would seem that it is not relevant to individual atoms and molecules, but on the other hand, one can consider a molecule as a physical body possessing a certain finite volume, and therefore, an additional "buoyancy" must act on it in the presence of a pressure gradient. The analysis carried out below shows that this is actually so, that there exists an entirely rigorous definition for the Archimedes force acting on individual molecules of matter. At the same time, as will be clear from what is said later on, the law of Archimedes for microscopic objects has a somewhat different meaning than in the case of macroscopic bodies. Here the limits are established for the applicability of the usual concepts of the law of Archimedes, and the circumstances are determined which one must allow for in the transition to fairly small bodies.

If a liquid (or gas) is located in an external force field, in particular, in a gravitational field, then the pressure inside the liquid (gas) depends on the coordinates. It follows from the condition of mechanical equilibrium that the pressure gradient equals the external force acting on a unit volume of matter:

$$\nabla P = \mathbf{f}_{\text{ext}}. \quad (1.1)$$

Since different points on the surface of a macroscopic body immersed in a liquid or gas are under different pressures, there are acts on the body of the buoyancy

$$\mathbf{F}_{\text{Arch}} = -\oint P d\mathbf{S} = -\int_V \nabla P dV. \quad (1.2)$$

If the volume V of the body is so small that one may neglect the change of the pressure gradient inside it, then

$$\mathbf{F}_{\text{Arch}} = -V(\nabla P) = -V\mathbf{f}_{\text{ext}}. \quad (1.3)$$

In a gravitational field, $\mathbf{f}_{\text{ext}} = \rho\mathbf{g}$, where ρ is the density of matter and \mathbf{g} is the acceleration of gravity.

Let us reduce the volume of the body. It is clear that as long as this volume is still many times larger than the volume of an individual molecule of liquid (gas), the Archimedes force is described by the equation

$$\mathbf{F}_{\text{Arch}} = -\rho V\mathbf{g}, \quad (1.4)$$

which follows from Eq. (1.3). However, it is easy to understand that, if the volume of the body becomes comparable with the volumes of individual molecules or atoms of the medium (in particular, if one discusses a single molecule of matter), then first, the Archimedes force generally remains nonzero, and second, it is already not described by the simple Eq. (1.4). Actually, let us consider an incompressible liquid as an illustration. The atoms of such a liquid do not fall, although the force of gravity acts on them. Consequently, an additional upward directed force, which balances the force of gravity, acts on them. Of course, this is also the Archimedes force, but only with one important stipulation. It is a fact that, besides the atoms or molecules in a liquid, there are still also empty spaces between them, because of which the mean density of a liquid is *less* than the mean density of the matter inside the atoms¹⁾. Therefore, the "weight of liquid" in the volume of an atom is less than the weight of the atom itself, and the requirement for the mutual balance of the lifting force and the force of gravity leads to the need for more precise definition of the law of Archimedes.

In order to understand how the expression for the buoyancy changes as one goes towards microscopic particles, let us consider for simplicity a model of the liquid in which all molecules are hard, impenetrable spheres of radius R . Of course, the presence of a body leads to the occurrence of a volume that is inaccessible to the molecules of the liquid. For $R \neq 0$, this volume includes both the volume of the body and also a certain additional volume adjacent to its surface. If one denotes the indicated additional volume by ΔV , then the total volume which becomes *inaccessible* to atoms of the liquid because of the immersion of a body in it will equal $V + \Delta V$.

Let us show that this total volume specifically enters into the expression for the buoyancy. To demonstrate this, let us imagine that the body is raised by some height z . Then an empty cavity whose volume equals $V + \Delta V$, is also raised by this height, and the space which it occupied earlier is filled by the liquid. If the mean density of the liquid equals ρ , then, upon such a displacement, the potential energy changes by the amount

$$Mgz - (V + \Delta V)\rho gz, \quad (1.5)$$

where M is the mass of the body and g is the acceleration of gravity. From this, it follows immediately that the upward directed Archimedes force is

$$F_{\text{Arch}} = \rho(V + \Delta V)g, \quad (1.6)$$

i.e., the volume of the body V in Eq. (1.4) is replaced by the volume $V + \Delta V$ "inaccessible" to molecules. It is clear that the additional volume ΔV plays no role for macroscopic bodies, but may turn out to be important for sufficiently small bodies²⁾. Specifically, this additional term provides for complete balancing of the force of gravity when one discusses individual atoms of an incompressible liquid. From what has been said, a more precisely defined formulation of the law of Archimedes follows for a model of hard, impenetrable atoms (not necessarily spherical): on a body immersed in a liquid, there acts a buoyancy equal to the weight of the liquid in that volume which became inaccessible to its molecules because of the presence of the body³⁾. Let us note that the energy arguments used in deriving Eq. (1.6) also remain obviously true in the case of a gas, in particular, of a rarefied gas.

If one discusses a sufficiently rarefied gas, then one may easily obtain within the model of impenetrable spherical molecules an explicit expression for the additional volume ΔV . Actually, in this case, each collision of any molecule with the surface of the body occurs independently of collisions where other molecules participate. Then the volume inaccessible to the molecules includes, besides the volume of the body, a layer of thickness R adjacent to its surface. For a sufficiently large body,

$$\Delta V = SR, \quad (1.7)$$

where S is the surface area of the body. For a spherical body of arbitrary radius r , we have

$$\Omega = V + \Delta V = \frac{4\pi}{3}(r + R)^3. \quad (1.8)$$

If the body under consideration is a gas molecule, then $r = R$, and the inaccessible volume is eight times larger than the volume of one molecule (also see Ref. 2). Let us also note

that buoyancy also acts on point particles: at $r = 0$, the inaccessible volume $\Omega = (4\pi/3)R^3$ ⁴⁾

2. THE ARCHIMEDES FORCE AND THE THERMODYNAMIC PROPERTIES OF SLIGHTLY NONIDEAL GASES

a) The fact that an additional force having the meaning of the Archimedes force acts on the molecules of a liquid or gas in an external field is not connected with any definite model; the existence of the Archimedes force by necessity follows from general thermodynamic properties of liquids and gases which are in thermal and mechanical equilibrium.

Let us first consider the simple case of a classical one-component rarefied (slightly nonideal) gas. In the approximation when one may restrict oneself to taking into account only independent pair interactions, the free energy of such a gas has the structure (Ref. 3, Paragraph 74)

$$\mathcal{F} = \mathcal{F}_{\text{id}} + \frac{N^2 kT}{V} b(T); \quad (2.1)$$

here V is the volume occupied by the gas, N is the number of molecules, T is the temperature, k is the Boltzmann constant, \mathcal{F}_{id} is the free energy of an ideal gas with the same values of N , V , and T , and $b(T)$ is the second virial coefficient; the factor N^2 in Eq. (2.1) is connected with calculating the number of possible pairs of molecules ($C_N^2 = \frac{1}{2}N(N-1) \approx \frac{1}{2}N^2$).

The free energy of an ideal gas is described by the expression

$$\mathcal{F}_{\text{id}} = NkT \ln \frac{N}{V} - Nh(T), \quad (2.2)$$

where $h(T)$ is a function of temperature that is unimportant for us (one can find an explicit form of $h(T)$, for example, in Ref. 3, Paragraph 42).

Within the classical theory,

$$b(T) = \frac{1}{2} \int (1 - e^{-U(r)/kT}) dV, \quad (2.3)$$

where $U(r)$ is the potential energy of the interaction of two molecules whose centers are separated by the distance r .⁵⁾

In accordance with Eqs. (2.1) and (2.2), the pressure of the gas is

$$P = - \left(\frac{\partial \mathcal{F}}{\partial V} \right)_{T,N} = nkT + n^2 kT b(T), \quad (2.4)$$

where $n = N/V$ is the molecular concentration. An expression for the chemical potential

$$\mu = \left(\frac{\partial \mathcal{F}}{\partial N} \right)_{T,V} = kT \ln n + 2nkT b(T) - h(T). \quad (2.5)$$

is also necessary for us later on. Let us emphasize that Eqs. (2.1), (2.4), and (2.5) are valid in the rarefied gas approximation when the inequality

$$|b(T)|n \ll 1. \quad (2.6)$$

is fulfilled. If the gas is located in a uniform field of gravity, then the concentration depends on the height z ; in addition, one must add the potential energy of the molecule mgz , where m is the mass of a molecule, to the right hand part of expression (2.5) for the chemical potential.

For thermal equilibrium, the condition

$$\bar{\mu}(z) = \mu + mgz = \text{const.} \quad (2.7)$$

is fulfilled. Differentiating Eq. (2.7) with respect to z , we find

$$\frac{kT}{n} \frac{dn}{dz} = - \left(mg + 2 \frac{dn}{dz} kTb(T) \right). \quad (2.8)$$

Let us represent the dependence of concentration on height z in the form

$$n(z) = n(0) \exp \left(- \frac{A(z)}{kT} \right), \quad (2.9)$$

where $n(0)$ is the molecular concentration at $z = 0$. According to Eq. (2.8), the function $A(z)$ satisfies the equation

$$\frac{dA(z)}{dz} = mg + 2 \frac{dn}{dz} kTb(T). \quad (2.10)$$

In accordance with Boltzmann's general principle, the function $A(z)$ which enters into Eq. (2.9) must have the meaning of the work which the total force F_{tot} acting on a molecule performs as the force displaces it from a height z to the $z = 0$ level. This force is obviously described by the derivative $dA(z)/dz$, i.e., with allowance for Eq. (2.10),

$$F_{\text{tot}} = mg + 2 \frac{dn}{dz} kTb(T) \quad (2.11)$$

(a positive sign for F_{tot} corresponds to a downward directed force). In the case of an ideal gas, when $b(T) = 0$, $F_{\text{tot}} = mg$, and $A(z) = mgz$, we arrive at the well-known barometric equation. But the barometric equation is changed for $b(T) \neq 0$: already the force F_{tot} is not reduced only to the force of gravity mg , and $A(z) \neq mgz$. The additional term in Eq. (2.11) is nothing other than the Archimedes force acting on a molecule. Thus,

$$F_{\text{Arch}} = 2 \frac{dn}{dz} kTb(T). \quad (2.12)$$

Here

$$A(z) = mgz + \int_0^z F_{\text{Arch}}(y) dy = mgz + 2 \left(n(z) - n(0) \right) kTb(T). \quad (2.13)$$

The second term in Eq. (2.13) is the work by the Archimedes force. The work $A(z)$ differs from the work mgz by the external force since, because of the hypothetical interaction between molecules, the displacement of one of them by the height z leads to some change of the configuration of the other molecules. In the case of a classical, ideal gas, the molecules do not interact and there is no such change of configuration.

With the approximation $|b(T)|n \ll 1$, Eq. (2.4) for the pressure gives

$$\frac{dP}{dz} \approx kT \frac{dn}{dz}. \quad (2.14)$$

With allowance for Eq. (2.14),

$$F_{\text{Arch}} = 2b(T) \frac{dP}{dz}, \quad (2.15)$$

or, in vector notation,

$$\mathbf{F}_{\text{Arch}} = -2b(T) \nabla P. \quad (2.16)$$

The corresponding work is proportional to the pressure difference:

$$A_{\text{Arch}} = 2b(T) (P(z) - P(0)). \quad (2.17)$$

According to Eqs. (2.16) and (2.17), for $b(T) > 0$ the Archimedes force is directed upward and its work is negative.

It follows from Eq. (1.1) that, in a gravitational field, $\nabla P = mn\mathbf{g}$; taking this into account, let us rewrite Eq. (2.16) in the form

$$\mathbf{F}_{\text{Arch}} = -2b(T) \rho \mathbf{g}. \quad (2.18)$$

By comparing Eq. (2.18) with Eq. (1.6), we come to the conclusion that one can give the meaning of an effective "inaccessible volume" to the quantity $2b(T)$. In the model of impenetrable spherical molecules of radius R ,

$$U(r) = \begin{cases} \infty, & r \leq 2R, \\ 0, & r > 2R. \end{cases} \quad (2.19)$$

Then it follows from Eq. (2.3) for the second virial coefficient that

$$\Omega = 2b(T) = 8 \left(\frac{4\pi}{3} R^3 \right), \quad (2.20)$$

i.e., that inaccessible volume is eight times larger than the volume of an individual molecule, in complete agreement with the geometric arguments (see Sec. 1). At the same time, in the general case the concept of "inaccessible volume" is conditional; in particular, according to Eq. (2.3), the second virial coefficient can be negative, and then the Archimedes force acting on a molecule is directed not upward, as for a macroscopic body, but downward.

By using an explicit form of the second virial coefficient, we can write

$$\mathbf{F}_{\text{Arch}} = mn \left[\int (e^{-U(r)/kT} - 1) dV \right] \mathbf{g}. \quad (2.21)$$

Relation (2.21) has a simple physical meaning. Interaction between the molecules leads to the situation that their positions in space cease to be independent. In a rarefied gas, the distribution of the distances r from the center of a certain definite molecule to the center of another one is determined by the Boltzmann factor $\exp(-U(r)/kT)$. Therefore, a local departure of the gas density from its value averaged over the entire volume arises near each molecule: a condensation if the molecules attract each other, or a rarefaction for repulsion. The expression $n \int (e^{-U(r)/kT} - 1) dV$ for $U(r) > 0$ has a negative sign and describes a deficiency of molecules in the local region around the molecule under consideration; for $U(r) < 0$, this expression is positive and describes an excess of molecules in the indicated region. It turns out in the end that the work by gravity not only connected with the weight of a single molecule, but also that connected with the deficient (excess) weight corresponding to rarefaction (or condensation) in the vicinity of the molecule, enters into the barometric Eq. (2.9). This additional work is the work of the Archimedes force. We emphasize that the energy approach discussed earlier also leads to the result of Eq. (2.21) if one applies it to the case of a nonideal gas. What has been said elucidates the true meaning of the Archimedes force; the appearance of this force is determined by simple geometrical arguments only in the particular case of impenetrable, hard bodies.

b) Let us now go from a one-component gas to a mix-

ture of two rarefied gases (the absence of chemical transformations of molecules is assumed here and from now on). Let N_1 molecules of one type and N_2 molecules of another type be located in a volume V at temperature T . In the general case, the interaction between the molecules is characterized by three different potentials $U_{11}(r)$, $U_{22}(r)$, and $U_{12}(r)$. Here the free energy is

$$\mathcal{F} = \mathcal{F}_{id}^{(1)} + \mathcal{F}_{id}^{(2)} + \frac{kT}{V}(N_1^2 b_{12}(T) + N_2^2 b_{22}(T) + 2N_1 N_2 b_{12}(T)), \quad (2.22)$$

where $\mathcal{F}_{id}^{(1)}$ and $\mathcal{F}_{id}^{(2)}$ are terms which coincide with the free energies of an ideal gas for each of the components (see Eq. (2.2)), and $b_{11}(T)$, $b_{22}(T)$, and $b_{12}(T)$ are the second virial coefficients:

$$\begin{aligned} b_{11}(T) &= \frac{1}{2} \int (1 - e^{-U_{11}(r)/kT}) dV, \\ b_{22}(T) &= \frac{1}{2} \int (1 - e^{-U_{22}(r)/kT}) dV, \\ b_{12}(T) &= \frac{1}{2} \int (1 - e^{-U_{12}(r)/kT}) dV. \end{aligned} \quad (2.23)$$

We emphasize that the free energy of a mixture of non-ideal gases is not equal to the sum of the free energies of its components; an additional term, proportional to $2N_1 N_2 b_{12}(T)$, is determined by the interaction between molecules of different types and by the number of pair combinations for such molecules.

According to Eq. (2.22), the pressure of a mixture of gases and the chemical potentials corresponding to the first and second components, are described by the equations

$$\begin{aligned} P &= - \left(\frac{\partial \mathcal{F}}{\partial V} \right)_{N_1, N_2, T} \\ &= (n_1 + n_2)kT + (n_1^2 b_{11}(T) + n_2^2 b_{22}(T) + 2n_1 n_2 b_{12}(T))kT, \end{aligned} \quad (2.24)$$

$$\begin{aligned} \mu_1 &= \left(\frac{\partial \mathcal{F}}{\partial N_1} \right)_{N_2, V, T} \\ &= kT \ln n_1 + kT - h_1(T) + 2(n_1 b_{11}(T) + n_2 b_{12}(T))kT, \end{aligned} \quad (2.25)$$

$$\begin{aligned} \mu_2 &= \left(\frac{\partial \mathcal{F}}{\partial N_2} \right)_{N_1, V, T} \\ &= kT \ln n_2 + kT - h_2(T) + 2(n_2 b_{22}(T) + n_1 b_{12}(T))kT. \end{aligned} \quad (2.26)$$

For thermal equilibrium in a gravity field, the equations

$$\mu_1 + m_1 g z = \text{const}, \quad \mu_2 + m_2 g z = \text{const}, \quad (2.27)$$

must be fulfilled, where m_1 and m_2 are the masses of molecules of the first and second kind.

Differentiating Eqs. (2.27) with respect to z , we arrive at the system of equations

$$kT \frac{dn_1}{dz} = - \left(m_1 g + 2kT \frac{dn_1}{dz} b_{11}(T) + 2kT \frac{dn_2}{dz} b_{12}(T) \right), \quad (2.28)$$

$$kT \frac{dn_2}{dz} = - \left(m_2 g + 2kT \frac{dn_2}{dz} b_{22}(T) + 2kT \frac{dn_1}{dz} b_{12}(T) \right). \quad (2.29)$$

Just as in the one-component case, we represent the dependence of the concentration on height in the form

$$n_1(z) = n_1(0) \exp\left(-\frac{A_1(z)}{kT}\right), \quad n_2(z) = n_2(0) \exp\left(-\frac{A_2(z)}{kT}\right); \quad (2.30)$$

here, in accordance with Boltzmann's principle, the function $A_{1(2)}(z)$ denotes the work which the force acting on a molecule of the first (second) type performs as the force displaces it from a height z to the $z = 0$ level. From Eqs. (2.28) and (2.29), it follows that the total forces $F_1(z)$ and $F_2(z)$ acting on molecules of the first and second type equal:

$$F_1(z) = \frac{dA_1(z)}{dz} = m_1 g + 2kT \left(\frac{dn_1}{dz} b_{11}(T) + \frac{dn_2}{dz} b_{12}(T) \right), \quad (2.31)$$

$$F_2(z) = \frac{dA_2(z)}{dz} = m_2 g + 2kT \left(\frac{dn_2}{dz} b_{22}(T) + \frac{dn_1}{dz} b_{12}(T) \right).$$

We see that the forces F_1 and F_2 match the weights of the corresponding molecules only in the case of a mixture of ideal gases. The additional terms in Eqs. (2.31) describe the Archimedes forces. Considering the relative smallness of the terms in Eqs. (2.28) and (2.29) that are proportional to the virial coefficients, we can substitute into Eqs. (2.31) the approximate relations:

$$kT \frac{dn_1}{dz} \approx -m_1 n_1 g, \quad kT \frac{dn_2}{dz} \approx -m_2 n_2 g.$$

Then

$$F_{\text{Arch}}^{(1)} = F_1 - m_1 g = -2(\rho_1 b_{11}(T) + \rho_2 b_{12}(T))g, \quad (2.32)$$

$$F_{\text{Arch}}^{(2)} = F_2 - m_2 g = -2(\rho_2 b_{22}(T) + \rho_1 b_{12}(T))g,$$

where $\rho_1 = m_1 n_1$ and $\rho_2 = m_2 n_2$ are the partial densities. In the same approximation

$$\begin{aligned} A_1(z) &= m_1 g z + 2(P_1(z) - P_1(0))b_{11}(T) \\ &\quad + 2(P_2(z) - P_2(0))b_{12}(T), \end{aligned} \quad (2.33)$$

$$\begin{aligned} A_2(z) &= m_2 g z + 2(P_2(z) - P_2(0))b_{22}(T) \\ &\quad + 2(P_1(z) - P_1(0))b_{12}(T), \end{aligned}$$

where $P_1 = n_1 kT$ and $P_2 = n_2 kT$ are the partial pressure values without allowance for interactions between the molecules. It follows from relations (2.30) and (2.33) that the presence of molecules of the second type affects the distribution in height of molecules of the first type, and vice versa.

The results obtained are easily generalized to the case of a mixture which consists of any number of components. The Archimedes force acting on a molecule of the i th type is described by the expression (compare it with Eqs. (2.32))

$$F_{\text{Arch}}^{(i)} = -2 \left(\sum_{l=1}^s \rho_l b_{il} \right) g, \quad (2.34)$$

where s is the number of components, and ρ_l are the partial densities of the components,

$$b_{il} = \frac{1}{2} \int (1 - e^{-U_{il}(r)/kT}) dV, \quad (2.35)$$

and $U_{il}(r)$ is the interaction potential between molecules of the i th and l th types. In the model of impenetrable spheres,

$$2b_{il} = \frac{4\pi}{3} (R_i + R_l)^3.$$

Thus, in the case of an arbitrary mixture of rarefied (weakly nonideal) gases, the force $\mathbf{F}_{\text{Arch}}^{(i)}$ is made up of the Archimedes forces which refer to the components of the mixture, to each of which its own effective "inaccessible volume" $2b_{il}$ corresponds. We emphasize that if the second virial coefficients do not equal each other, the Archimedes force is already not proportional to the pressure gradient, as it is in the one-component case (see Sec. 5b for more detail).

3. BOLTZMANN'S PRINCIPLE AND THE THERMODYNAMIC EQUATIONS FOR THE ARCHIMEDES FORCE

As we convinced ourselves for the example of rarefied gases, the Archimedes force acting on a molecule may be introduced on the basis of the Boltzmann principle. Let us now discard any kind of limitations of the type of inequality (2.6) that are imposed on the gas density. If a one-component gas or liquid is located in an external force field (not necessarily gravitational!), then, according to Boltzmann's principle, the equation

$$\frac{kT}{n} \nabla n = \mathbf{F}_{\text{tot}}, \quad (3.1)$$

must be fulfilled (compare it with Eqs. (2.8) and (2.11)), where \mathbf{F}_{tot} is the total static force acting on a molecule. This force matches the external force only in the limiting case where the molecules do not interact with each other (an ideal gas). With allowance for interaction, $\mathbf{F}_{\text{tot}} \neq \mathbf{F}_{\text{ext}}$; we define the additional term as the Archimedes force:

$$\mathbf{F}_{\text{Arch}} = \mathbf{F}_{\text{tot}} - \mathbf{F}_{\text{ext}} = \frac{kT}{n} \nabla n - \mathbf{F}_{\text{ext}}. \quad (3.2)$$

From the condition of thermal equilibrium in an external field (see Eq. (2.7)), it also follows that the external force acting on a molecule equals the gradient of the chemical potential:

$$\mathbf{F}_{\text{ext}} = \nabla \mu = \left(\frac{\partial \mu}{\partial n} \right)_T \nabla n. \quad (3.3)$$

From this, the concentration gradient $\nabla n = \mathbf{F}_{\text{ext}} / (\partial \mu / \partial n)_T$. Substituting this expression into Eq. (3.2), we find

$$\mathbf{F}_{\text{Arch}} = \left(\frac{kT}{n(\partial \mu / \partial n)_T} - 1 \right) \mathbf{F}_{\text{ext}}. \quad (3.4)$$

One can also obtain one more expression for the Archimedes force. Actually, according to relation (1.1), in the case of a one-component gas or liquid, the external force \mathbf{F}_{ext} is proportional to the pressure gradient:

$$\mathbf{F}_{\text{ext}} = \frac{1}{n} \nabla P = \left(\frac{\partial P}{\partial n} \right)_T \frac{\nabla n}{n}. \quad (3.5)$$

Comparing Eqs. (3.5) and (3.2), we have

$$\mathbf{F}_{\text{Arch}} = \left(\frac{kT}{(\partial P / \partial n)_T} - 1 \right) \mathbf{F}_{\text{ext}}. \quad (3.6)$$

In a gravity field, $\mathbf{F}_{\text{ext}} = mg$ and

$$\mathbf{F}_{\text{Arch}} = \left(\frac{kT}{(\partial P / \partial n)_T} - 1 \right) mg. \quad (3.7)$$

Eqs. (3.4) and (3.6) are not independent; by virtue of the well-known thermodynamic equation $(\partial \mu / \partial P)_T = 1/n$ (see Ref. 3, Sec. 24), they are completely equivalent. With allowance for expression (2.4) for the pressure of a rarefied gas and condition (2.6), Eq. (3.7) leads to relation (2.18). In the limit of a cold, incompressible liquid, when $kT / (\partial P / \partial n)_T \ll 1$,

$$\mathbf{F}_{\text{Arch}} = -mg,$$

i.e., the buoyancy acting on a molecule almost completely balances the force of gravity (see Sec. 1). For a classical ideal gas, $(\partial P / \partial n)_T = kT$, and Eq. (3.7) leads to the natural result $\mathbf{F}_{\text{Arch}} = 0$. In the general case, the value of $(\partial P / \partial n)_T$ can be both larger and also smaller than kT . Therefore, the force acting on a molecule can be directed not only upward, but also down. At the same time, the force

$$\mathbf{F}_{\text{tot}} = \mathbf{F}_{\text{Arch}} + mg = mg \frac{kT}{(\partial P / \partial n)_T} \quad (3.8)$$

must be directed down (since the thermodynamic inequality $(\partial P / \partial n)_T > 0$ is fulfilled). One must keep in mind, however, that this result applies only to the one-component case.

4. THE ARCHIMEDES FORCE AND THE EINSTEIN EQUATION

In connection with relations (3.1) and (3.2), which express Boltzmann's principle in differential form, let us consider the meaning of the well-known Einstein equation

$$D = \alpha kT \quad (4.1)$$

under conditions when the ideal gas approximation is inapplicable (here D is the diffusion coefficient and α is the mobility; see, for example, Ref. 4, Sec. 60). Since the concentration gradient is non-zero in an external field (it equals zero only in the limiting case of an incompressible liquid, when $(\partial P / \partial n)_T \rightarrow \infty$), there arises a diffusion flux

$$\mathbf{J}_{\text{dif}} = -D \nabla n. \quad (4.2)$$

However, in thermodynamic equilibrium, the diffusion flux must be balanced by a drift flux,

$$\mathbf{J}_{\text{dr}} = n \mathbf{v}_{\text{dr}}, \quad (4.3)$$

where \mathbf{v}_{dr} is the drift velocity. Thus,

$$D \nabla n = n \mathbf{v}_{\text{dr}}. \quad (4.4)$$

On the other hand, according to Boltzmann's principle (see Eqs. (3.1) and (3.2)), one can express the quantity ∇n in terms of the total force $\mathbf{F}_{\text{tot}} = \mathbf{F}_{\text{ext}} + \mathbf{F}_{\text{Arch}}$. This gives

$$D \nabla n = n \frac{D}{kT} (\mathbf{F}_{\text{ext}} + \mathbf{F}_{\text{Arch}}). \quad (4.5)$$

From this, with allowance for the Einstein Eq. (4.1), the drift velocity is

$$\mathbf{v}_{\text{dr}} = \alpha (\mathbf{F}_{\text{ext}} + \mathbf{F}_{\text{Arch}}). \quad (4.6)$$

Thus, the universal character of the Einstein relation in combination with Boltzmann's principle by necessity lead to the conclusion that, along with the external force, the Archi-

medes force also enters into the expression for drift velocity. And this is understandable; in a steady state, the drag force

$$\mathbf{F}_{\text{drg}} = -\frac{1}{\alpha} \mathbf{v}_{\text{dr}}, \quad (4.7)$$

which is proportional to velocity, must balance out the total static force acting on the molecule: $\mathbf{F}_{\text{drg}} = -\mathbf{F}_{\text{tot}} = -(\mathbf{F}_{\text{ext}} + \mathbf{F}_{\text{Arch}})$.

5. THE ARCHIMEDES FORCES IN MULTI-COMPONENT MEDIA

a) For a mixture of several gases or liquids, Boltzmann's principle gives

$$\frac{kT}{n_i} \nabla n_i = \mathbf{F}_{\text{tot}}^{(i)}, \quad (5.1)$$

where $\mathbf{F}_{\text{tot}}^{(i)}$ is the total static force acting on a molecule of the i th type, which includes both the external force $\mathbf{F}_{\text{ext}}^{(i)}$, and also the Archimedes force. Then the Archimedes force acting on the same molecule is

$$\mathbf{F}_{\text{Arch}}^{(i)} = \mathbf{F}_{\text{tot}}^{(i)} - \mathbf{F}_{\text{ext}}^{(i)} = \frac{kT}{n_i} \nabla n_i - \mathbf{F}_{\text{ext}}^{(i)}. \quad (5.2)$$

The condition of thermodynamic equilibrium of the mixture under consideration will have in an external field the form $\nabla \mu_i = \mathbf{F}_{\text{ext}}^{(i)}$, $i = 1, 2, \dots, s$, or

$$\sum_{i=1}^s \frac{\partial \mu_i(n_1, n_2, \dots, n_s, T)}{\partial n_i} \nabla n_i = \mathbf{F}_{\text{ext}}^{(i)}, \quad (5.3)$$

where μ_i is the chemical potential for the i th component⁶⁾. One may consider relation (5.3) as a system of algebraic equations for the concentration gradients. Let us introduce a symmetric matrix with the elements $A_{il} = (\partial \mu_i / \partial n_l)_T$; $i, l = 1, 2, 3, \dots, s$ ⁷⁾. From relations (5.3), there follows

$$\nabla n_i = \sum_{l=1}^s (\hat{A}^{-1})_{il} \mathbf{F}_{\text{ext}}^{(l)}, \quad (5.4)$$

where \hat{A}^{-1} is the inverse matrix of \hat{A} . It is easy to see that

$$(\hat{A}^{-1})_{il} = \frac{\partial n_i(\mu_1, \mu_2, \dots, \mu_s, T)}{\partial \mu_l}, \quad (5.5)$$

where the concentrations n_i are considered as functions of the chemical potentials and temperature. Substituting Eqs. (5.4) and (5.5) into Eq. (5.2), we find for the Archimedes force acting on a molecule of the i th type

$$\mathbf{F}_{\text{Arch}}^{(i)} = \sum_{l=1}^s \left[\frac{kT}{n_i} \left(\frac{\partial n_i}{\partial \mu_l} \right)_T - \delta_{il} \right] \mathbf{F}_{\text{ext}}^{(l)}. \quad (5.6)$$

In a gravity field,

$$\mathbf{F}_{\text{Arch}}^{(i)} = \sum_{l=1}^s \left[\frac{kT}{n_i} \left(\frac{\partial n_i}{\partial \mu_l} \right)_T - \delta_{il} \right] m_l \mathbf{g}. \quad (5.7)$$

In the one-component case, $(\partial n / \partial \mu)_T = 1 / (\partial \mu / \partial n)_T$, and expressions (5.6) and (5.7) transform into Eqs. (3.4), (3.6), and (3.7), respectively.

b) Let the interaction potentials be independent of the type of molecules. Then, within the classical theory, even for

unequal masses of the molecules which make up the mixture, those terms in the thermodynamic functions which are connected with interaction must have the same structure as for one-component matter with the number of molecules $N = \sum_i N_i$ and concentration $n = (N/V) = \sum_i n_i$. For the free energy, we can write the expression

$$\mathcal{F} = \sum_i \mathcal{F}_{\text{id}}^{(i)} + NQ(n, T). \quad (5.8)$$

Then the pressure is

$$P = - \left(\frac{\partial \mathcal{F}}{\partial V} \right)_T = nkT + P_{\text{int}}(n, T), \quad P_{\text{int}} = n^2 \frac{\partial Q(n, T)}{\partial n}, \quad (5.9)$$

and the chemical potentials are

$$\mu_i = \left(\frac{\partial \mathcal{F}}{\partial N_i} \right)_{V, T} = \mu_{\text{id}}^{(i)} + \mu_{\text{int}}(n, T),$$

$$\mu_{\text{id}}^{(i)} = kT \ln n_i + kT - h_i(T),$$

$$\mu_{\text{int}}(n, T) = Q(n, T) + n \frac{\partial Q(n, T)}{\partial n}, \quad (5.10)$$

where $h_i(T)$ are functions of temperature (see Eq. (2.2)).

From Eqs. (5.9) and (5.10), there follows the equation

$$n \frac{\partial \mu_{\text{int}}(n, T)}{\partial n} = \frac{\partial P_{\text{int}}(n, T)}{\partial n} = \left(\frac{\partial P}{\partial n} \right)_T - kT. \quad (5.11)$$

In the case under consideration, to calculate the Archimedes forces it is simpler to start not from Eq. (5.7), but directly from relations (5.2) and (5.3). It is easy to see that here the Archimedes force is independent of the kinds of molecules (although their masses may not be the same!), and is proportional to the pressure gradient. Actually, Eqs. (5.2) and (5.3), together with Eqs. (5.10) and (5.11), give

$$\mathbf{F}_{\text{Arch}} = - \frac{\partial \mu_{\text{int}}(n, T)}{\partial n} \nabla n = \left(\frac{kT}{(\partial P / \partial n)_T} - 1 \right) \frac{\nabla P}{n}, \quad (5.12)$$

where $\nabla P = \sum_i m_i n_i \mathbf{g}$. If, for this same equation, the masses of all the molecules are the same ($m_i = m$), Eq. (5.12) transforms, as was to be expected, into relation (3.7) for one-component matter.⁸⁾

6. THE RELATIONSHIP OF THE ARCHIMEDES FORCE WITH FLUCTUATIONS OF THE NUMBER OF MOLECULES AND WITH CORRELATION FUNCTIONS

a) Let us show that, in the general case, the Archimedes force acting on a molecule of gas or liquid is directly expressed by the fluctuations of the number of molecules, or by functions which describe the pair correlations of their positions. Here the thermodynamic equations lead to the same results as the energy approach described in Section 1.

Let us first consider a one-component gas (liquid). It is easy to be convinced that, for a number N of particles in any macroscopic volume V which is a small part of the total volume V_0 , the simple equation

$$\frac{kT}{n(\partial \mu / \partial n)_T} = \frac{(\Delta N)^2}{N}. \quad (6.1)$$

is fulfilled. To prove it, let us use the Gibbs distribution with a variable number of particles (see Ref. 3, Sec. 35):

$$W_{\{\alpha\}N} = \exp\left(\frac{\mu N - PV - E_{\{\alpha\}N}}{kT}\right), \quad \sum_{\{\alpha\}} \sum_N W_{\{\alpha\}N} = 1; \quad (6.2)$$

here P is the pressure, μ is the chemical potential, and $\{\alpha\}$ are the quantum numbers which correspond to the possible states of the system. The average number of molecules is

$$\bar{N} = e^{-PV/kT} \sum_{\{\alpha\}} \sum_N N \exp\left(\frac{\mu N - E_{\{\alpha\}N}}{kT}\right). \quad (6.3)$$

Differentiating this expression with respect to μ with constant V and T , we find

$$\left(\frac{\partial \bar{N}}{\partial \mu}\right)_{V,T} = \frac{e^{-PV/kT}}{kT} \sum_{\{\alpha\}} \sum_N \left(N^2 + N \frac{\partial(-PV)}{\partial \mu}\right) \times \exp\left(\frac{\mu N - E_{\{\alpha\}N}}{kT}\right). \quad (6.4)$$

Let us now consider the well-known thermodynamic equation (see Ref. 3, Sec. 24)

$$-d(PV) = SdT - \bar{N}d\mu, \quad (6.5)$$

from which it follows that $(\partial(PV)/\partial\mu)_T = \bar{N}$. Then

$$\left(\frac{\partial \bar{N}}{\partial \mu}\right)_{V,T} = \frac{1}{kT} (\bar{N}^2 - \overline{N^2}) = \frac{(\overline{\Delta N})^2}{kT}. \quad (6.6)$$

It is clear that

$$\left(\frac{\partial \bar{N}}{\partial \mu}\right)_{V,T} = \frac{1}{(\partial\mu/\partial\bar{N})_{V,T}} = \frac{V}{(\partial\mu/\partial n)_T}, \quad (6.7)$$

where $n = (\bar{N}/V)$. From this,

$$\frac{V}{\bar{N}} = \frac{1}{(\partial\mu/\partial n)_T} = \frac{1}{n(\partial\mu/\partial n)_T} = \frac{(\overline{\Delta N})^2}{kT\bar{N}}. \quad (6.8)$$

By virtue of the equation $n(\partial\mu/\partial n)_T = (\partial P/\partial n)_T$, we can also write

$$\frac{1}{(\partial P/\partial n)_T} = \frac{(\overline{\Delta N})^2}{kT\bar{N}}. \quad (6.9)$$

Substituting Eq. (6.8) into the thermodynamic Eq. (3.4) for the Archimedes force (or substituting Eq. (6.9) into Eq. (3.6)), we find

$$F_{\text{Arch}} = \left(\frac{(\overline{\Delta N})^2}{\bar{N}} - 1\right) F_{\text{ext}}. \quad (6.10)$$

In a gravity field,⁹⁾

$$F_{\text{Arch}} = \left(\frac{(\overline{\Delta N})^2}{\bar{N}} - 1\right) mg. \quad (6.11)$$

For an incompressible liquid, fluctuations of the number of particles are lacking; consequently, we again obtain $F_{\text{Arch}} = -mg$. In the case of an ideal classical gas, $(\overline{\Delta N})^2 = \bar{N}$, and the Archimedes force equals zero. Let us emphasize that, for a quantum ideal gas, $(\overline{\Delta N})^2 \neq \bar{N}$, i.e., in accordance with Eq. (6.11), in a gravity field the additional force F_{Arch} acts on the atoms of such a gas. The thermodynamic relation (3.7) also leads to the same result if one considers that $P \neq nkT$ for an ideal quantum gas. Here an up-

ward directed force F_{Arch} acts on an atom of an ideal Fermi gas, but the force is directed down for a Bose gas.

b) As is well known, the concentration of other molecules in the vicinity of a specified molecule inside the matter differs from the mean concentration n and depends on the distance to the molecule under consideration. This dependence shows up only at distances less than or of the order of the so-called effective correlation radius r_{corr} .

Let us denote the concentration of molecules in the vicinity of the specified molecule by $n(r)$. At distances $r \gg r_{\text{corr}}$, the concentration $n(r)$ equals the mean concentration n . We can represent $n(r)$ in the form $n(r) = n\omega(r)$, where $\omega(r)$ is a function proportional to the probability of finding two molecules at a distance r from each other.

The average number of pairs of molecules in the two small volumes dV_1 and dV_2 is (see Ref. 3, Sec. 116)

$$dN_{12} = n^2\omega(r)dV_1dV_2. \quad (6.12)$$

Integrating Eq. (6.12) over dV_1 and dV_2 within the finite volume V , we obtain an expression for the total number of pairs

$$\frac{N(N-1)}{2} = \frac{1}{2}n^2 \int_V \int_V \omega(r)dV_1dV_2, \quad (6.13)$$

or

$$\overline{N^2} - \bar{N} - \bar{N}^2 = n^2 \int_V \int_V (\omega(r) - 1)dV_1dV_2, \quad (6.14)$$

where $N = nV$. Let the volume V inside the matter and its parts ΔV_i have linear dimensions many times larger than a correlation radius between the positions of the molecules. Then the variances of the number of particles in different parts of the volume are combined additively. Thus, if $V = \sum_i \Delta V_i$, then $(\overline{\Delta N})^2 = \sum_i (\overline{\Delta N_i})^2 \sim V$. Consequently, under these conditions the quantity $(\overline{\Delta N})^2/\bar{N}$ must depend not on volume, but only on the concentration $n = \bar{N}/V$. And actually, by converting in Eq. (6.14) from integration over dV_1dV_2 to integration over a coordinate of one of the particles and over the relative coordinate $r = r_1 - r_2$, and allowing for the rapid convergence of the integral, we obtain

$$\overline{N^2} - \bar{N} - \bar{N}^2 = \bar{N}n \int (\omega(r) - 1)d^3r. \quad (6.15)$$

Since $\overline{N^2} - \bar{N}^2 = (\overline{\Delta N})^2$, we have

$$\frac{(\overline{\Delta N})^2}{\bar{N}} - 1 = n \int (\omega(r) - 1)d^3r. \quad (6.16)$$

One can rewrite the last equation in the form

$$\frac{(\overline{\Delta N})^2}{\bar{N}} - 1 = 4\pi n \int_0^\infty (\omega(r) - 1)r^2dr. \quad (6.17)$$

From relations (6.11), (6.16), and (6.17), it follows that the Archimedes force is¹⁰⁾

$$F_{\text{Arch}} = mng \int (\omega(r) - 1)d^3r = 4\pi mng \int_0^\infty (\omega(r) - 1)r^2dr. \quad (6.18)$$

For rarefied gases, $\omega(r) = \exp(-U(r)/kT)$, and Eq. (6.18) is the same as Eq. (2.21).

We see that, in the general case, the Archimedes force is connected with the action of the force of gravity on an additional "cloud" which arises in the vicinity of the molecule under consideration. In accordance with this, one can obtain Eq. (6.18) directly from energy arguments by considering the work which one must perform in raising this "cloud" by a definite height (see the discussion of relation (2.21)).

c) Let us now go to a mixture of several components. On the basis of a Gibbs distribution with a variable number of particles (see Ref. 3, Sec. 85), it is easy to be convinced that the relations which generalize Eq. (6.1) are valid:

$$\frac{kT}{n_i} \left(\frac{\partial n_i}{\partial \mu_i} \right)_T = \frac{\overline{N_i N_i} - \overline{N_i} \overline{N_i}}{\overline{N_i}} = \frac{\overline{\Delta N_i \cdot \Delta N_i}}{\overline{N_i}}, \quad (6.19)$$

where N_i and N_l are the number of molecules of the i th and l th kinds in a volume $V \gg r_{\text{corr}}^3$, and ΔN_i and ΔN_l are the corresponding fluctuations. If one substitutes Eq. (6.19) into the thermodynamic relation (5.6), we shall find the following expression for the Archimedes force acting on a molecule of the i th kind:

$$F_{\text{Arch}}^{(i)} = \sum_{l=1}^s \left(\frac{\overline{\Delta N_i \cdot \Delta N_l}}{\overline{N_l}} - \delta_{il} \right) F_{\text{ext}}^{(l)}, \quad (6.20)$$

which generalizes the result of Eq. (6.10). Here s is the number of components in the mixture. In a gravity field⁽¹¹⁾

$$F_{\text{Arch}}^{(i)} = \sum_{l=1}^s m_l \left(\frac{\overline{\Delta N_i \cdot \Delta N_l}}{\overline{N_l}} - \delta_{il} \right) \mathbf{g}, \quad (6.21)$$

d) Let the concentration of molecules of the l th kind in the vicinity of a given molecule of the i th kind be described by the function $n_{il}(r) = n_l \omega_{il}(r)$. The average number of (li) pairs in the two small volumes dV_1 and dV_2 situated at a distance r from each other is

$$dN_{1,2}^{(li)} = n_l n_i \omega_{il}(r) dV_1 dV_2 = n_l n_i \omega_{il}(r) dV_1 dV_2. \quad (6.22)$$

It is obvious that the function ω_{il} is symmetric with respect to transposition of the indices.

Let us now find the average number of pairs of molecules in a finite volume V whose linear dimensions are considerably larger than the effective correlation radii. For this, let us integrate Eq. (6.22). If one discusses molecules of one kind ($i \equiv l$), then the average number of pairs is (see Eq. (6.13))

$$\overline{N^{(ii)}} = \frac{\overline{N_i(N_i - 1)}}{2} = \frac{1}{2} n_i^2 \int \int \omega_{ii}(r) dV_1 dV_2. \quad (6.23)$$

Thus,

$$\overline{N_i^2} - \overline{N_i}^2 = n_i^2 \int \int (\omega_{ii}(r) - 1) dV_1 dV_2, \quad (6.24)$$

where $N_i = n_i V$. From this (compare with Eqs. (6.14) and (6.15))

$$\frac{\overline{N_i^2} - \overline{N_i}^2}{\overline{N_i}} - \overline{N_i} = \frac{\overline{(\Delta N_i)^2}}{\overline{N_i}} - 1 = n_i \int (\omega_{ii}(r) - 1) d^3r. \quad (6.25)$$

But if one discusses molecules of a different kind ($i \neq l$), then the average number of pairs is

$$N^{(li)} = \overline{N_i N_l} = n_i n_l \int \int \omega_{il}(r) dV_1 dV_2, \quad (6.26)$$

or

$$\overline{N_i N_l} - \overline{N_i} \overline{N_l} = n_i n_l \int \int (\omega_{il}(r) - 1) dV_1 dV_2. \quad (6.27)$$

It follows from Eq. (6.27) that, for $i \neq l$,

$$\overline{N_i N_l} - \overline{N_i} \overline{N_l} = n_i n_l \int (\omega_{il}(r) - 1) d^3r. \quad (6.28)$$

Consequently,

$$\frac{\overline{\Delta N_i \cdot \Delta N_l}}{\overline{N_l}} = n_l \int (\omega_{il}(r) - 1) d^3r. \quad (6.29)$$

Combining Eqs. (6.25) and (6.29), we find

$$\frac{\overline{\Delta N_i \cdot \Delta N_l}}{\overline{N_l}} - \delta_{il} = n_l \int (\omega_{il}(r) - 1) d^3r. \quad (6.30)$$

Taking Eq. (6.30) into account, the expression for the Archimedes force acting on a molecule of the i th kind takes the form

$$F_{\text{Arch}}^{(i)} = 4\pi \left(\sum_{l=1}^s m_l n_l \int_0^\infty (\omega_{il}(r) - 1) r^2 dr \right) \mathbf{g}, \quad (6.31)$$

where m_l is the mass of a molecule of the l th kind. Just as in the one-component case, the results of Eq. (6.31) can also be obtained within the energy approach.

Let us emphasize that, in the general case, the correlation functions $\omega_{il}(r)$ depend on the concentrations of all components. At the same time, if the concentration of one of the components (for example, the i th) is sufficiently small, then the term with $l = i$ drops out of Eq. (6.31) for the Archimedes force acting on particles of the i type, and the correlation functions $\omega_{il}(r)$ cease to depend on the concentration n_i for $l \neq i$. It is clear that the same result completely applies also to any single particle. In particular, if a single particle of type 1 is located in a medium formed by molecules of type 2, then

$$F_{\text{Arch}} = 4\pi m_2 n_2 \left(\int_0^\infty (\omega_{12}(r) - 1) r^2 dr \right) \mathbf{g} \quad (6.32)$$

7. THE ARCHIMEDES FORCE IN A WEAK SOLUTION

If one discusses a mixture of two components with the concentrations $n_1 \ll n_2 = n$, and one can neglect interaction between the molecules of the dissolved matter (the so-called "weak solution"; see Ref. 3, Sec. 87), then the free energy has the structure

$$\mathcal{F} = \mathcal{F}_0(N, V, T) + \mathcal{F}_{\text{id}}^{(i)} + N_1 G(n, T), \quad (7.1)$$

where $\mathcal{F}_0(N, V, T)$ is the free energy of the pure solvent, and $G(n, T)$ is some function whose form is determined by the specific properties of the solution.

Here the pressure in the solution is

$$P = P_0(n, T) + n_1 \left(kT + n \frac{\partial G(n, T)}{\partial n} \right), \quad (7.2)$$

and the chemical potentials of the dissolved matter and of the solvent are

$$\mu_1 = G(n, T) + kT \ln n_1 + kT - h_1(T), \quad (7.3)$$

$$\mu = \mu_0(n, T) + n_1 \frac{\partial G(n, T)}{\partial n}.$$

Here P_0 and μ_0 are the pressure and chemical potential of pure solvent which satisfy the thermodynamic equation $(\partial\mu_0/\partial P_0)_T = 1/n$. According to Eqs. (5.2) and (5.3), the Archimedes force acting on a molecule of dissolved matter is

$$F_{\text{Arch}} = - \frac{\partial G(n, T)}{\partial n} \nabla n. \quad (7.4)$$

With an accuracy to small terms of the order of n_1/n , the condition of mechanical equilibrium (Eq. (1.1)) gives

$$\nabla P \approx \nabla P_0 = \left(\frac{\partial P_0}{\partial n} \right)_T \nabla n = mn\mathbf{g},$$

where m is the mass of a molecule of solvent.

From this,

$$F_{\text{Arch}} = -\rho\Omega\mathbf{g}, \quad \Omega = \frac{\partial G(n, T)}{\partial n} \left(\frac{\partial P_0(n, T)}{\partial n} \right)^{-1}, \quad (7.5)$$

here $\rho = mn$ is the density of the solution. A comparison of Eqs. (7.5) with Eq. (1.6) shows that the quantity Ω has the meaning of the effective volume that is "inaccessible" to molecules of the solvent (calculated per molecule of the dissolved matter). Thus, in accordance with Eqs. (5.2) and (7.5), the dependence of the molecular concentration of the dissolved matter on the height z is described by the equation

$$\frac{kT}{n_1} \frac{dn_1}{dz} = -(Mg - mn\Omega g), \quad (7.6)$$

where M is the mass of a molecule of dissolved matter. If one can consider the values of Ω and n to be independent of z (the approximation of an "incompressible" solution), then, from Eq. (7.6), there follows the barometric equation

$$n_1(z) = n_1(0) \exp \left[- \frac{gz}{kT} (M - mn\Omega) \right], \quad (7.7)$$

which takes into account the law of Archimedes (see Ref. 3, p. 389).¹²⁾

Let us suppose that one discusses such large molecules of dissolved matter (or macroscopic particles) that one can neglect the surface effects and dimensions of the solvent molecules. Then, in agreement with the usual law of Archimedes, the "inaccessible volume" Ω must coincide with the volume v_0 of a particle. Of course, this is also evident from Eq. (6.32) for the Archimedes force acting on a single particle, if one considers that, in the case under consideration, the correlation function ω_{12} equals zero inside the volume of the particle, and outside its volume v_0 , the function equals one.

The same result also follows from Eqs. (7.5). Actually, a combination of Eqs. (7.5) and (7.2) leads to the expression

$$\Omega = \frac{(\partial P/\partial n_1)_{n, T} - kT}{n \partial P_0(n, T)/\partial n}. \quad (7.8)$$

For the pressure of a solution in the limiting case under discussion, one can write

$$P = n_1 kT + P_0(\tilde{n}, T). \quad (7.9)$$

Here $n_1 kT$ is the pressure connected with the motions of the particles of the dissolved matter (the same as for an ideal gas with the same concentration n_1), and $P_0(\tilde{n}, T)$ is the pressure of the solvent molecules, which is taken, however, not for the concentration $n = (N/V)$, but for another concentration $\tilde{n} = (N/\tilde{V})$ corresponding to the volume \tilde{V} into which the solvent molecules are "crowded out." The total volume of the macromolecules that are located in the volume V which the solution occupies amounts to

$$\Delta V = n_1 V v_0. \quad (7.10)$$

Consequently,

$$\tilde{V} = V - \Delta V = V(1 - n_1 v_0). \quad (7.11)$$

From this, it is easy to obtain the relation between \tilde{n} and n :

$$\tilde{n} = \frac{n}{1 - n_1 v_0} \approx n + n n_1 v_0. \quad (7.12)$$

Allowing for the smallness of n_1 , we have

$$P_0(\tilde{n}, T) = P_0(n, T) + \frac{\partial P_0(n, T)}{\partial n} n n_1 v_0. \quad (7.13)$$

Substituting Eq. (7.13) into expression (7.9), we find

$$P = P_0(n, T) + n_1 \left(kT + n \frac{\partial P_0(n, T)}{\partial n} v_0 \right). \quad (7.14)$$

From Eqs. (7.8) and (7.14), there follows the equation sought

$$\Omega = v_0. \quad (7.15)$$

As has already been said, the explicit form of the function $G(n, T)$ which enters into expression (7.1) is determined both by the specific properties of the solvent, and also by the properties of the molecules of the dissolved matter. In particular, by comparing Eqs. (7.14) and (7.2), we arrive at the conclusion that, in the limiting case of macroscopic impurity molecules, the function $G(n, T)$ is determined by the relation

$$\frac{\partial G(n, T)}{\partial n} = v_0 \frac{\partial P_0(n, T)}{\partial n}. \quad (7.16)$$

It is easy to see that a closer connection is also valid:

$$G(n, T) = v_0 P_0(n, T). \quad (7.17)$$

The result of Eq. (7.17) follows directly from Eq. (7.16) and the obvious condition

$$\lim_{n \rightarrow 0} G(n, T) = 0.$$

One more example of calculating the values of Ω and G will be considered in the next section.

8. THE LAW OF ARCHIMEDES FOR NEUTRONS

In connection with a comment at the end of Sec. 6d, it is clear that the result of Eqs. (7.5) is valid for any foreign particles suspended in a uniform gas or liquid, in particular, for neutrons.

As is well known, the average energy of interaction of a thermal neutron with the molecules of a medium is determined from the equation (see Ref. 6, Secs. 142 and 151; Ref. 7, Sec. 90)

$$U(n) = 2\pi\hbar^2 n \sum_i \frac{r_i a_i}{M_i}, \quad (8.1)$$

where n is the number of molecules in a unit volume, r_i is the number of nuclei of the i th type in a molecule, a_i is the neutron scattering length for a nucleus of the i th type, and $M_i = m_n m_i / (m_n + m_i)$ is the reduced mass of a neutron and a nucleus. For the condition $|U(n)| \ll kT$ (which certainly is fulfilled at temperatures $T > 0.001$ K), one can use thermodynamic perturbation theory (Ref. 3, Sec. 32), within which the chemical potential of neutrons with the concentration n_1 is determined from the first equation of Eqs. (7.3) with the function

$$G(n, T) = U(n). \quad (8.2)$$

From this, according to Eqs. (7.5), the Archimedes force acting on a neutron is

$$F_{\text{Arch}} = -\rho\Omega\mathbf{g},$$

where $\rho = n\sum_i m_i$, and

$$\Omega = 2\pi\hbar^2 \frac{\sum_i (r_i a_i / M_i)}{(\partial P / \partial n)_T} = \frac{U(n)}{n(\partial P / \partial n)_T}. \quad (8.3)$$

The question of the Archimedes force acting on a neutron was considered earlier in a report by Pokotilovskii⁸ by invoking arguments⁹ based on the theory of wave propagation in an elastic medium (Ref. 10, Sec. 22). Within such an approach, the effective "inaccessible volume" is determined by the vector of the medium deformation u in the vicinity of the neutron from the equation $\Omega = \int \text{div } u dV$. The final result has the form

$$\Omega = \frac{U}{\rho v_{\text{sd}}^2}, \quad (8.4)$$

where v_{sd} is the speed of sound in the medium. Which speed of sound is discussed, the usual adiabatic one v_{ad} or the isothermal one v_{iso} , is not precisely defined in Ref. 8. However, it is well known that deformations have an isothermal nature in the static case (Ref. 10, Sec. 3). Therefore, the isothermal speed of sound $v_{\text{iso}} = (\partial P / \partial \rho)_T^{1/2}$ must go into the equation for Ω . With allowance for this comment, the results, Eqs. (8.3) and (8.4), are completely consistent.

9. CONCLUSION

We have been convinced that the concept of an Archimedes force acting on microscopic objects (atoms and molecules) is directly relevant to various problems of macroscopic and microscopic physics. To the connections with Boltzmann's principle, the Einstein relation, the fluctuations and correlations of the molecules of matter, and to the properties of mixtures and solutions that have been considered above, one might have also added other questions (in particular, one must note the role of the Archimedes force in the operation of so-called semi-permeable barriers, which are extensively used in the justification of thermodynamics). It seems to be interesting and unexpected that a very old

problem, and one that, at first glance, has been exhaustively worked out long ago, turned out to be profoundly and organically connected with the structure and fundamental principles of thermodynamics and statistical physics.

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¹⁾ For the densest packing of a large number of identical spheres, empty space takes up approximately 0.26 of the total volume.¹

²⁾ The additional force acting on a microscopic body whose dimensions are comparable with those of the atoms of the medium fluctuates in time; for such a body, Eq. (1.6) and all subsequent analogous equations determine only an average value of this force.

³⁾ In connection with the law of Archimedes, one usually speaks either of the weight of liquid in the volume of a body, or of the weight of the extruded liquid. Both statements are equivalent for macroscopic bodies; they are different for sufficiently small bodies. Only the second statement is valid in the model of spherical atoms, but it will become clear below that, in the general case, it also is in need of further precise definition.

⁴⁾ In the case of a dense medium, expressions (1.7) and (1.8) are, strictly speaking, incorrect, but they are probably suitable for approximate estimates of the Archimedes force based on Eq. (1.6). It is not impossible that such estimates can prove to be useful in the centrifugal separation of solutions of organic molecules, the complicated structures of which lead to the appearance of a large additional volume inaccessible to molecules of the solvent.

⁵⁾ Expression (2.3) also applies to asymmetric molecules if one carries out additional averaging over all possible orientations of their axes (see Ref. 3, Sec. 74).

⁶⁾ In the case of a mixture, the condition of mechanical equilibrium (Eq. (1.1)) reads $\nabla P = \sum_i n_i F_{\text{ext}}^{(i)}$. Let us emphasize that, in the general case, the pressure is not reduced to the sum of the independent partial pressures of the individual components.

⁷⁾ The equation $A_{ii} = A_{ii}$ is a consequence of the definition of the chemical potential

$$\mu_i = \left(\frac{\partial \mathcal{F}}{\partial N_i} \right)_{T, V} = \frac{1}{V} \left(\frac{\partial \mathcal{F}}{\partial n_i} \right)_{T, V}.$$

⁸⁾ Strictly speaking, this is true when one neglects the quantum exchange interaction between identical molecules (see Ref. 5, Ch. 4).

⁹⁾ We note that, in the hard sphere model, the quantity $\overline{(\Delta N)^2}$ is not directly connected with thermodynamic ideas and can be calculated by means of purely combinatorial arguments, as this, in particular, has been done in Ref. 2. On the other hand, $\overline{(\Delta N)^2}$ enters into the thermodynamic relations (6.1), (6.9), (6.10), and (6.11). In accordance with Ref. 2, for a set of spheres of radius R randomly distributed in space with a low concentration,

$$\overline{(\Delta N)^2} = \left(1 - \frac{32\pi}{3} n R^3\right) \overline{N}.$$

A thermodynamic approach (for example, a comparison of the expressions (2.18), (2.20), and (6.11)) leads to the same result.

¹⁰⁾ We note that, in an external field, the concentration n itself is a function of the coordinates. It is significant that all the thermodynamic equations containing gradients of concentration and pressure that have been shown earlier have meaning only for the condition $|\nabla n| r_{\text{corr}} \ll 1$; thereby, the external fields are assumed to be fairly weak.

¹¹⁾ A comparison of Eqs. (2.34) and (6.21) enables one to find easily the correlations $\overline{\Delta N_i \Delta N_j}$ for a mixture of rarefied gases. In particular, in a model of several types of hard spheres, we shall have

$$\frac{\overline{\Delta N_i \Delta N_j}}{\overline{N_i}} = \delta_{ij} - \frac{4\pi}{3} n_i (R_i + R_j)^3.$$

¹²⁾ Often the chemical potentials of dissolved matter and solvent are considered as functions of pressure, temperature, and of the relative concentration $c_i = (n_i/n)$ (Ref. 3, Sec. 87):

$$\mu_i = kT \ln c_i + \Psi(P, T), \quad \mu = \bar{\mu}_0(P, T) - kT c_i.$$

The connection of $\Psi(P, T)$ and $\bar{\mu}_0(P, T)$ with the functions $G(n, T)$ and $\mu_0(n, T)$ is given by the relations

$$\Psi(P, T) = G(n, T) + kT - h_1(T) + kT \ln n,$$

$$\tilde{\mu}_0(P, T) = \tilde{\mu}_0(P_0, T) + \frac{1}{n}(P - P_0) = \mu_0(n, T) + \frac{n_1}{n}kT + n_1 \frac{\partial G(n, T)}{\partial n}.$$

Here, with an accuracy to terms of the order of (n_1/n) ,

$$\Omega = \frac{\partial \Psi(P, T)}{\partial P} - \frac{kT}{n(\partial P / \partial n)_T}.$$

For an incompressible solution

$$\Omega = -\frac{\partial \Psi(P, T)}{\partial P}.$$

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