

Statistical Thermodynamics

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Molecular theory of ideal gases

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I. PREFACE

Molecular theory can be considered as a preliminary to statistical physics. While the latter employs a more sophisticated formalism encompassing quantum-mechanical systems, the former operates with a classical ideal gas. Molecular theory studies the relation between the temperature of the gas and the kinetic energy of the molecules, pressure on the walls due to the impact of the molecules, distribution of molecules over velocities etc. All these results can be obtained in a more formal way in statistical physics. However, it is convenient to first study molecular theory at a more elementary level. On the other hand, molecular theory includes *kinetics* of classical gases that studies nonequilibrium phenomena such as *heat conduction* and *diffusion* (not a part of this course)

II. BASIC ASSUMPTIONS OF THE MOLECULAR THEORY

1. Motion of atoms and molecules is described by classical mechanics
2. The number of particles in a considered macroscopic volume is very large. As there are about 10^{19} molecules in 1 cm^3 at normal conditions, this assumption holds down to high vacuums. Because of the large number of particles, the impacts of individual particles on the walls merge into time-independent pressure.
3. The characteristic distance between the molecules largely exceeds the molecular size and the typical radius of intermolecular forces. This assumption allows to consider the gas as ideal, with the internal energy dominated by the kinetic energy of the molecules. In describing equilibrium properties of the ideal gas collisions between the molecules can be neglected. If pressure is increased and/or temperature is decreased, this assumption becomes violated and the gas becomes non-ideal and then condenses into a liquid or solid.
4. The molecules are uniformly distributed within the container. In most cases this is true. In the case of strong enough potential fields, this condition may be violated. For instance, the density (concentration) of molecules in the atmosphere decreases with the height. This decrease is slow, however, so that in a laboratory-size container the gas is still approximately uniform.
5. Directions of velocities of the molecules are uniformly distributed. This is the hypothesis of the *molecular chaos* that is always true.

An important independent consideration is that motion of molecules along different perpendicular directions such as x , y , and z is independent. Indeed, if a molecule experiences a force impulse (e.g., because of a collision) in the direction x , it does not change its velocity components v_y and v_z . This leads to the postulate of factorization of their distribution function into parts depending on the velocity components v_x , v_y , and v_z . The latter allows to find this distribution function that turns out to be exponentially dependent on molecule's kinetic energy.

III. CHARACTERISTIC LENGTHS OF THE GAS

The concentration of molecules n is defined by

$$n \equiv \frac{N}{V}, \quad (1)$$

where V is the volume of the container and N is the total number of molecules. If the concentration is non-uniform, one has to modify this formula by considering a small volume around a particular point in the space that contains a macroscopic number of molecules.

The characteristic distance r_0 between the molecules can be estimated as

$$r_0 = \frac{1}{n^{1/3}}. \quad (2)$$

Note that one cannot introduce a meaningful average distance between the molecules as the latter will be dominated by the molecules far apart.

Let a be the radius of the molecule or an atom. (For simplicity, we consider them as spheres.) Then the third assumption requires $a \ll r_0$. There are also long-range attractive forces between the molecules but they are weak and do not essentially deviate molecular trajectories from straight lines if the temperature is high enough.

One can define the mean free path l of the molecules as the distance they typically travel before colliding with another molecule. As the molecule is moving straight, it will hit any molecule whose center is located at the distance less than $2a$ from the molecule's trajectory, that is, any molecule within a cylinder of the radius $2a$. The cross-section of this cylinder is $\sigma = \pi(2a)^2$. The free path ends, on average, when the height l of the cylinder reaches such a value when there is one molecule within the cylinder: $l\sigma n = 1$. Thus one obtains the expression for l and important inequalities:

$$l = \frac{1}{\sigma n} \sim \frac{1}{a^2 n} = \left(\frac{r_0}{a}\right)^2 r_0 \gg r_0 \gg a. \quad (3)$$

Although the numerical factor in l can be calculated more accurately, one can already see that l is very large in the ideal gas, so that one can neglect collisions on the way to the wall in calculating the pressure and other quantities.

IV. VELOCITY AND SPEED DISTRIBUTION FUNCTIONS OF MOLECULES

Whereas the distribution of molecules in space is practically uniform, their distribution in the space of velocities (v_x, v_y, v_z) is nontrivial. One can introduce the distribution function $G(v_x, v_y, v_z)$ via

$$dN = NG(v_x, v_y, v_z) dv_x dv_y dv_z, \quad (4)$$

where dN is the number of molecules with the velocities within the elementary volume

$$dv_x dv_y dv_z \equiv d^3v \equiv d\mathbf{v} \quad (5)$$

around the velocity vector specified by its components (v_x, v_y, v_z) . Integration over the whole velocity space gives the total number of molecules N , thus $G(v_x, v_y, v_z)$ satisfies the normalization condition

$$1 = \int \int \int_{-\infty}^{\infty} dv_x dv_y dv_z G(v_x, v_y, v_z). \quad (6)$$

As the directions of the molecular velocities are distributed uniformly, $G(v_x, v_y, v_z)$ in fact depends only on the absolute value of the velocity, the speed

$$v = \sqrt{v_x^2 + v_y^2 + v_z^2}. \quad (7)$$

Using the expression for the elementary volume in the spherical coordinates

$$d^3v = dv \times v d\theta \times v \sin \theta d\varphi = v^2 dv \sin \theta d\theta d\varphi, \quad (8)$$

one can rewrite Eq. (4) as

$$dN = NG(v)v^2 dv d\Omega, \quad (9)$$

where

$$d\Omega \equiv \sin \theta d\theta d\varphi \quad (10)$$

is the elementary body angle. The number of molecules within the spherical shell of width dv can be obtained by integration over irrelevant directions. Since for the area of a sphere of unit radius one has

$$\int_{\text{sphere}} d\Omega = \int_0^\pi d\theta \sin \theta \int_0^{2\pi} d\varphi = 2\pi \int_{-1}^1 dx = 4\pi \quad (11)$$

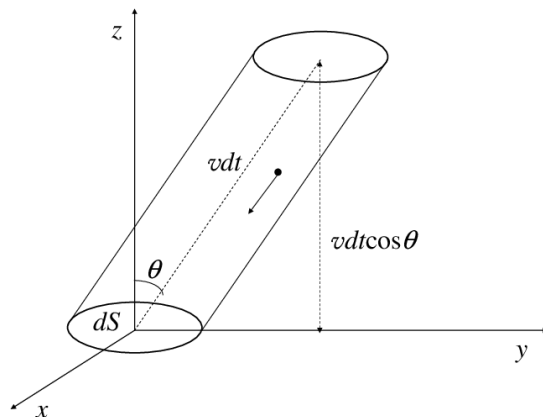


FIG. 1: Slant cylinder used in the calculation of the molecular flux. Here $\varphi = \pi/2$.

($x \equiv \cos \theta$), the number of molecules within the spherical shell becomes

$$dN = NG(v)4\pi v^2 dv = Nf(v)dv. \quad (12)$$

Here we have introduced the distribution function over molecular speeds

$$f(v) = 4\pi v^2 G(v) \quad (13)$$

that is also normalized by 1:

$$1 = \int_0^\infty dv f(v). \quad (14)$$

Now Eq. (9) can be rewritten in terms of $f(v)$ as

$$dN = Nf(v)dv \frac{d\Omega}{4\pi}. \quad (15)$$

It is remarkable that the functional form of $G(v)$ or $f(v)$ can be found from symmetry arguments only. This will be done later. Here we introduce the *average* speed

$$\bar{v} = \int_0^\infty dv v f(v) \quad (16)$$

and the *mean square* speed

$$\overline{v^2} = \int_0^\infty dv v^2 f(v). \quad (17)$$

The *root mean square* or *rms* speed is defined by

$$v_{\text{rms}} = \sqrt{\overline{v^2}}. \quad (18)$$

The two characteristic speeds, \bar{v} and v_{rms} , are of the same order of magnitude and differ only by a numerical factor of order 1. We will see that the molecular flux is proportional to \bar{v} while the pressure on the walls is proportional to $\overline{v^2}$.

V. MOLECULAR FLUX

Molecular flux Φ is defined as the number of molecules dN crossing a unit surface in one direction during a unit of time. For instance, molecular flux determines the rate of molecules striking the wall or exiting the container through a small orifice in the wall (effusion). The expression for the flux reads

$$\Phi = \frac{dN}{dS dt}, \quad (19)$$

where dS is the elementary surface. As the molecules are approaching the surface dS from all directions θ, φ of a hemisphere, one should first consider the number of molecules $dN_{\theta, \varphi}$ coming from a particular direction θ, φ within the body angle $d\Omega$ around it. From these molecules we single out molecules with the speeds in the interval dv around v , thus obtaining $dN_{v, \theta, \varphi}$. The latter is the number of molecules within the slant cylinder with the base area dS and height $v \cos \theta dt$, see Fig. V. The volume of this cylinder is $dV = dS v \cos \theta dt$ and the total number of molecules in it is $dN_V = n dV$, where the concentration n is defined by Eq. (1). From this total number of molecules dN_V one has to pick those within the given velocity interval specified by v, θ, φ . With the help of Eq. (15) with $N \Rightarrow dN_V$ this yields

$$dN_{v, \theta, \varphi} = dN_V f(v) dv \frac{d\Omega}{4\pi} = n dS v \cos \theta dt f(v) dv \frac{\sin \theta d\theta d\varphi}{4\pi}. \quad (20)$$

Integrating over v, θ, φ and using Eqs. (19) and (16) one obtains the flux

$$\begin{aligned} \Phi &= \int \frac{dN_{v, \theta, \varphi}}{dS dt} = n \int_0^\infty dv v f(v) \frac{1}{4\pi} \int_0^{\pi/2} d\theta \sin \theta \cos \theta \int_0^{2\pi} d\varphi \\ &= n \times \bar{v} \times \frac{1}{4\pi} \int_0^1 dx x \times 2\pi. \end{aligned} \quad (21)$$

Note that the molecules are approaching the wall only from inside of the container, $0 \leq \theta \leq \pi/2$. After calculating the integral over x , one obtains

$$\Phi = \frac{1}{4} n \bar{v}. \quad (22)$$

If, instead of the wall, one considers the flux through a flat region on the area dS inside the container, the molecules will approach this area from both directions, so that one has to integrate over the interval $0 \leq \theta \leq \pi$ that results in a zero flux (the numbers of molecules crossing in both directions are the same).

VI. GAS PRESSURE ON THE WALLS

As said above, the gas pressure is due to the impact of molecules on the walls. Considering the elementary surface dS as above one can define pressure as $P = dF/dS$, where dF is the force acting upon the surface dS from the molecules. The force can be obtained from the Newton's second law in the form $dp/dt = F$, where p is the momentum of the molecules that changes in time due to the rebound from the wall. Adopting this to our case yields the formula

$$P = \frac{dp}{dS dt}, \quad (23)$$

where dp is the change of the momentum of the molecules within the slant cylinder considered in the preceding section.

The change of the momentum of a single molecule in the collision with the wall is, strictly speaking, not well defined. The problem is that at the atomic level walls are rough and the incident molecule can rebound in different directions. On the other hand, one can consider the realistic rough wall as built of small plates oriented at different angles. Since the pressure will not depend on the orientation of the elementary surfaces (similarly to Pascal's law), one can dismiss the effect of the wall roughness. Another effect that can make the calculation more involved is the inelasticity of the molecule-wall collision due to the exchange of energy between the molecules and the atoms of the wall. As a result, some molecules rebound stronger and some rebound weaker, relative to the elastic collision. A detailed analysis shows that the molecule-wall collisions average out to the elastic collision if the walls and the gas have the same temperatures and thus are at equilibrium. Thus here we will consider the collisions of molecules with the wall as elastic collisions with a flat surface.

As the change of the momentum of an individual molecule in an elastic collision is given by $mv \cos \theta - (-mv \cos \theta) = 2mv \cos \theta$, m being the mass of a molecule, similarly to Eq. (21) one obtains

$$\begin{aligned} P &= \int 2mv \cos \theta \frac{dN_{v, \theta, \varphi}}{dS dt} = 2nm \int_0^\infty dv v^2 f(v) \frac{1}{4\pi} \int_0^{\pi/2} d\theta \sin \theta \cos^2 \theta \int_0^{2\pi} d\varphi \\ &= 2nm \times \bar{v}^2 \times \frac{1}{4\pi} \int_0^1 dx x^2 \times 2\pi \end{aligned} \quad (24)$$

that results in

$$P = \frac{1}{3} nm \bar{v}^2. \quad (25)$$

VII. MOLECULAR INTERPRETATION OF TEMPERATURE AND EQUIPARTITION OF ENERGY

Rewriting Eq. (25) as $PV = (1/3)Nm\overline{v^2}$ and comparing this with the equation of state in the form $PV = Nk_B T$ one obtains

$$k_B T = \frac{1}{3}m\overline{v^2}, \quad (26)$$

the fundamental relation between the temperature and average kinetic energy of the molecule $\bar{\varepsilon}$. This relation can be rewritten in the form

$$\bar{\varepsilon} = \frac{1}{2}m\overline{v^2} = \frac{3}{2}k_B T. \quad (27)$$

Since $\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}$ and by symmetry $\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} = \overline{v^2}/3$, for the kinetic energies corresponding to the three *degrees of freedom* x, y, z one obtains

$$\bar{\varepsilon}_x = \bar{\varepsilon}_y = \bar{\varepsilon}_z = \frac{1}{2}k_B T. \quad (28)$$

That is, the thermal energy per degree of freedom is $(1/2)k_B T$.

This is a particular case of the equipartition of energy valid for classical systems: There is thermal energy $(1/2)k_B T$ per each degree of freedom. In addition to the three translational degrees of freedom there are rotational and vibrational degrees of freedom if the molecules of the gas consist of more than one atom. Vibrational degrees of freedom are counted twice since there are both kinetic and potential energies involved.

For instance, for diatomic molecules there are two rotational degrees of freedom corresponding to rotations around the two axes perpendicular to the axis connecting the two molecules. Also there is one vibrational degree of freedom that is counted twice. The total number of degrees of freedom is

$$f = 3 + 2 + 2 = 7 \quad (29)$$

for diatomic molecules.

For multi-atomic molecules with $\mathcal{N} > 2$ atoms that are not aligned, there are 3 translational and 3 rotational degrees of freedom. The number of vibrational degrees of freedom is difficult to calculate directly. However, this number can be easily calculated by subtracting $3 + 3$ non-vibrational degrees of freedom from the total $3\mathcal{N}$ degrees of freedom. Thus one obtains $3\mathcal{N} - 6$ vibrational degrees of freedom that should be counted twice. The total number of degrees of freedom for multi-atomic molecules is thus

$$f = 3 + 3 + 2(3\mathcal{N} - 6) = 6(\mathcal{N} - 1) \quad (30)$$

that yields $f = 12$ for $\mathcal{N} = 3$.

VIII. HEAT CAPACITY OF THE IDEAL GAS

For the monoatomic gas the average energy per particle is given by Eq. (27). Since there is no potential energy, the internal energy of the system is given by

$$U = \frac{3}{2}Nk_B T. \quad (31)$$

This the heat capacity at constant volume is

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{3}{2}Nk_B. \quad (32)$$

Now with the use of the Mayer's formula one obtains

$$C_P = C_V + Nk_B = \frac{5}{2}Nk_B \quad (33)$$

that yields $\gamma = C_P/C_V = 5/3$. For multi-atomic molecules assuming equipartition results in $U = (f/2)Nk_B T$ and

$$C_V = \frac{f}{2}Nk_B, \quad C_P = \frac{f+2}{2}Nk_B, \quad \gamma = 1 + \frac{2}{f}. \quad (34)$$

In all these cases the heat capacity is a constant, so that the ideal gas is perfect gas. However, it turns out that vibrational degrees of freedom for multi-atomic gases are affected by quantum effects. As a result, these degrees of freedom are fully or partially frozen out so that there is less thermal energy in them than the equipartition would suggest. Quantum effects are strongly pronounced at low temperatures, whereas at high temperatures the vibrational modes behave classically. As a result, heat capacities increase with temperature making the ideal gas not a perfect gas.

IX. MAXWELL-BOLTZMANN DISTRIBUTION FUNCTION

In this section the functional form of $G(v)$ will be found from symmetry arguments. First, motion of molecules of an ideal gas along different axes x, y, z is completely independent that implies statistical independence of different velocity components. Thus $G(v)$ factorizes:

$$G(v) = G\left(\sqrt{v_x^2 + v_y^2 + v_z^2}\right) = g(v_x)g(v_y)g(v_z), \quad (35)$$

the function g being normalized by 1:

$$1 = \int_{-\infty}^{\infty} dv_x g(v_x). \quad (36)$$

This means that each velocity component has its own distribution function g . Indeed, the number of molecules within the shell dv_x around v_x is obtained by integrating Eq. (4) over irrelevant v_y, v_z :

$$dN = N \left[\int \int_{-\infty}^{\infty} dv_y dv_z G(v) \right] dv_x. \quad (37)$$

With the help of Eqs. (35) and (36) this becomes

$$dN = N g(v_x) dv_x, \quad (38)$$

that is, $g(v_x)$ is the distribution function of v_x .

Factorization of G and its spherical symmetry implemented in Eq. (35) already allow to find its functional form. Taking the logarithm of this equation,

$$\ln G(v) = \ln g(v_x) + \ln g(v_y) + \ln g(v_z), \quad (39)$$

and differentiating it with respect to v_x yields

$$\frac{G'(v)}{G} \frac{\partial v}{\partial v_x} = \frac{G'(v)}{G} \frac{v_x}{v} = \frac{g'(v_x)}{g(v_x)}. \quad (40)$$

Rearranging and adding similar results for other components one obtains

$$\frac{1}{v} \frac{G'(v)}{G} = \frac{1}{v_x} \frac{g'(v_x)}{g(v_x)} = \frac{1}{v_y} \frac{g'(v_y)}{g(v_y)} = \frac{1}{v_z} \frac{g'(v_z)}{g(v_z)}. \quad (41)$$

Since different terms of these equations depend on different independent arguments, the only possibility to satisfy these equations is all terms being equal to the same constant:

$$\frac{1}{v} \frac{G'(v)}{G} = -2k, \quad \frac{1}{v_x} \frac{g'(v_x)}{g(v_x)} = -2k, \quad (42)$$

etc. Integrating these differential equations one obtains

$$G(v) = A e^{-kv^2}, \quad (43)$$

where A is the integration constant. One can see that indeed $G(v)$ factorizes and

$$g(v_x) = A^{1/3} e^{-kv_x^2}. \quad (44)$$

In fact, the derivation starting with Eq. (39) is probably unnecessary because Eq. (43) is the only factorizable function depending on v . One can persuade oneself in it by a long contemplation of Eq. (35).

Now the two constants, k and A , can be found from the normalization condition, Eq. (14) and the condition for the mean square speed, Eq. (17), taking into account Eq. (26). As $f(v)$ is related to $G(v)$ by Eq. (13),

$$f(v) = 4\pi v^2 A e^{-kv^2}, \quad (45)$$

we will use the values of two Gaussian integrals

$$\begin{aligned} \int_0^\infty dx x^2 e^{-kx^2} &= \frac{\sqrt{\pi}}{4} k^{-3/2} \\ \int_0^\infty dx x^4 e^{-kx^2} &= \frac{3\sqrt{\pi}}{8} k^{-5/2} \end{aligned} \quad (46)$$

that can be obtained by successive differentiation of the generic integral

$$\int_0^\infty dx e^{-kx^2} = \frac{\sqrt{\pi}}{2} k^{-1/2} \quad (47)$$

with respect to k . The normalization condition, Eq. (14), works out as

$$1 = \int_0^\infty dv f(v) = 4\pi A \int_0^\infty dv v^2 e^{-kv^2} = \pi^{3/2} A k^{-3/2}. \quad (48)$$

The condition for the mean square speed becomes

$$\frac{3k_B T}{m} = \overline{v^2} = \int_0^\infty dv v^2 f(v) = 4\pi A \int_0^\infty dv v^4 e^{-kv^2} = \frac{3\pi^{3/2}}{2} A k^{-5/2}. \quad (49)$$

From these two equations one finds

$$k = \frac{m}{2k_B T}, \quad A = \left(\frac{k}{\pi}\right)^{3/2} = \left(\frac{m}{2\pi k_B T}\right)^{3/2}. \quad (50)$$

Let us now write down the final results for the distribution functions. Eq. (45) becomes

$$f(v) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} 4\pi v^2 \exp\left(-\frac{\varepsilon}{k_B T}\right), \quad \varepsilon = \frac{mv^2}{2} \quad (51)$$

and Eq. (44) becomes

$$g(v_x) = \left(\frac{m}{2\pi k_B T}\right)^{1/2} \exp\left(-\frac{\varepsilon_x}{k_B T}\right), \quad \varepsilon_x = \frac{mv_x^2}{2}. \quad (52)$$

X. CHARACTERISTIC SPEEDS OF GAS MOLECULES

Let us calculate characteristic speeds for the ideal gas, two of which are the rms and average speed, Eqs. (18) and (16). The rms speed can be immediately obtained from Eq. (49):

$$v_{\text{rms}} = \sqrt{\overline{v^2}} = \sqrt{\frac{3k_B T}{m}} \simeq 1.732 \sqrt{\frac{k_B T}{m}}. \quad (53)$$

To calculate the average speed, one makes use of the Gaussian integral

$$\int_0^\infty dx x^{2n+1} e^{-kx^2} = \frac{n!}{2k^{n+1}}, \quad n = 0, 1, 2, \dots \quad (54)$$

with $n = 1$. From Eq. 16) one obtains

$$\bar{v} = \int_0^\infty dv v f(v) = 4\pi A \int_0^\infty dv v^3 e^{-kv^2} = 4\pi A \frac{1}{2k^2} = \frac{2\pi}{k^2} \left(\frac{k}{\pi}\right)^{3/2} = \frac{2}{\sqrt{\pi k}} = \sqrt{\frac{8k_B T}{\pi m}} \simeq 1.596 \sqrt{\frac{k_B T}{m}}. \quad (55)$$

The third characteristic speed is the most probable speed v_m corresponding to the maximum of $f(v)$. From

$$0 = \frac{d}{dv^2} v^2 e^{-kv^2} = e^{-kv^2} - v^2 k e^{-kv^2} \quad (56)$$

one obtains

$$v_m = \frac{1}{\sqrt{k}} = \sqrt{\frac{2k_B T}{m}} \simeq 1.414 \sqrt{\frac{k_B T}{m}}, \quad (57)$$

the smallest of the three characteristic speeds.

XI. EFFUSION

In Sec. V we have calculated the molecular flux Φ , the number of molecules hitting the unit area during the unit of time. If there is a small hole in the wall of the container, the molecules will escape through this hole, the process called effusion. If the hole is small enough, it does not disturb the gas in the container close to the hole and the result for the molecular flux given by Eq. (22) remains valid. Then the number of molecules leaving the container per second is given by $\Phi \Delta S$, where ΔS is the area of the hole.

One can ask what is the speed distribution of escaping molecules. Certainly this is not the Maxwell-Boltzmann distribution, already by the fact that the effusing molecules are moving all away from the container. Moreover, it turns out that the characteristic speeds of the effusing molecules are higher than the speeds of the molecules in the container. The reason is that faster molecules are approaching the hole from inside the container and exit at a higher rate than the slow molecules. There are quite a few very slow molecules in the flux through the hole.

One can obtain the speed distribution of the effusing molecules by removing the integration over v in Eq. (21). One can write

$$\Phi = \int_0^\infty dv \Phi_v, \quad (58)$$

where

$$\Phi_v = \frac{1}{4} n v f(v) \quad (59)$$

is the molecular flux corresponding to the speed interval dv around the value v . This is Φ_v , that defines the speed distribution of the effusing molecules. Because of the additional v , this distribution is shifted to higher speeds. For instance, the most probable speed of the effusing molecules corresponds to the maximum of Φ_v and is defined as

$$0 = \frac{d}{dv} v^3 e^{-kv^2} = 3v^2 e^{-kv^2} - v^3 2k v e^{-kv^2}, \quad (60)$$

so that

$$v_{e,m} = \sqrt{\frac{3}{2k}} = \sqrt{\frac{3k_B T}{m}}. \quad (61)$$

One can see that $v_{e,m} > v_m$ given by Eq. (57). Similarly $v_{e,rms} > v_{rms}$ and $\bar{v}_e > \bar{v}$.