

Distribution of Molecules by Kinetic Energy Revisited

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Abstract. The distribution of the molecules by their kinetic energy is treated from statistical point of view. Boltzmann's formula for the distribution of the molecules by energy was found as a limit case of digamma function. Maxwell's formula for the ideal monoatomic gas was derived directly from Boltzmann's main result without employing other sketch formulas. The analytical formulas for two speeds - one real and the other virtual - of molecules were obtained for the case when the molecules carry the kinetic energy in more than three independent components, like in polyatomic molecules. Analysis of the generalized distribution function of the molecules by their virtual speeds indicated that certain molecular states the reach a highest mode in the distribution of the molecules by their virtual speed for a deterministic value of the energy components.

Keywords: kinetic theory, distribution of the molecules by kinetic energy, virtual speed.

DISTRIBUTION OF THE MOLECULES BY ENERGY AND ITS LIMIT APPROXIMATION

For a system with N undistinguishable particles and K energy states, the chance (or probability, p_j) of any molecule to fall in a certain ($1 \leq j \leq K$) energy state (Boltzmann, 1868) leads, at observational level, to a multinomial distribution. Thus the chance to see a certain distribution (N_1, \dots, N_K) is (eq.1):

$$\text{PMF}(N_1, \dots, N_K) = \frac{N!}{\prod_{j=1}^K N_j!} \cdot \prod_{j=1}^K p_j^{N_j} \quad (1)$$

At equilibrium, the observation of the system with the arrangement (N_1, \dots, N_K) should come from maximum likelihood (Fisher, 1912) and thus the maximum likelihood estimation is applied (Eq.2):

$$\text{MLE} = \ln(\text{PMF}(N_1, \dots, N_K)) = \ln(N!) - \sum_{j=1}^K \ln(N_j!) + \sum_{j=1}^K \ln(p_j^{N_j}) = \max. \quad (2)$$

For a closed system, the Eq.2 is under two constrains ($N = \sum_{1 \leq j \leq K} N_j$ and $E = \sum_{1 \leq j \leq K} \epsilon_j N_j$, where ϵ_j is the distinct kinetic energy of the j state) and the solutions of Eq.2 are solutions of eq.3. Eq.3 is according to Lagrange multiplier's method (Lagrange, 1811) an associated unconstrained equation (with two more unknowns):

$$\text{MLEI}(N_1, \dots, N_K) = \ln(N!) + \sum_{j=1}^K N_j \cdot \ln(p_j) - \sum_{j=1}^K \ln(N_j!) + \alpha \left(N - \sum_{j=1}^K N_j \right) + \beta \left(E - \sum_{j=1}^K N_j \cdot \epsilon_j \right) \quad (3)$$

The derivatives of MLEI function - Eq.3 - provide the relationships between the energy of a certain level and its population (Eq.4):

$$\frac{\partial \text{MLEI}(N_1, \dots, N_K)}{\partial N_i} = 0 + 1 \cdot \ln(p_i) - \frac{\partial}{\partial N_i} \ln(N_i!) + \alpha(0 - 1) + \beta(0 - \epsilon_i) \equiv 0 \quad (4)$$

The obtained equations are not simple at all, involving the digamma (Ψ) function (Eq.5):

$$\frac{\Gamma'(N_i + 1)}{\Gamma(N_i + 1)} = \Psi(N_i + 1) = \ln(p_i) - \alpha - \beta \varepsilon_i \quad (5)$$

In (Eq.5) two unknown are present due to constraining of the system to be closed: α and β , but these values are common for any value of i ($1 \leq i \leq K$).

By using the Euler's famous relationship (Euler, 1781) for large numbers of molecules ($N_i \gg 1$) a convergence relationship between digamma function and logarithm can be written (Eq.6):

$$\ln(N_i) - \Psi(N_i + 1) \xrightarrow{N_i \rightarrow \infty} \Psi(1) \quad (6)$$

and an analytical solution can be extracted. Thus if (Eq.6) is used as approximation, then by embedding the $\Psi(1)$ into α , the Eq.5 becomes:

$$\ln(N_i) \cong \ln(p_i) - \alpha - \beta \varepsilon_i, \text{ or } N_i \cong p_i \cdot e^{-\alpha - \beta \varepsilon_i} \rightarrow N = e^{-\alpha} \cdot \sum_{j=1}^K p_j \cdot e^{-\beta \varepsilon_j} \quad (7)$$

It should be noted that using the approximation for large numbers, the expression for the proportion (N_i/N) of the particles possessing certain kinetic energy (ε_i) depend only in one unknown (Eq.8):

$$\frac{N_i}{N} = \frac{p_i \cdot e^{-\alpha - \beta \varepsilon_i}}{\sum_{j=1}^K p_j \cdot e^{-\alpha - \beta \varepsilon_j}} = \frac{p_i \cdot e^{-\beta \varepsilon_i}}{\sum_{j=1}^K p_j \cdot e^{-\beta \varepsilon_j}} \rightarrow p_i = (N_i e^{\beta \varepsilon_i}) \frac{1}{N} \sum_{j=1}^K p_j \cdot e^{-\beta \varepsilon_j} \quad (8)$$

The formula from Eq.8 was derived in the assumption that each energy state does not possess any internal structure, which may influence the random falling of the molecule in the state.

By replacing p_i from Eq.8 and N from Eq.7 in Eq.1 (replacing in Eq.2 or Eq.3 provides the same result):

$$\begin{aligned} \ln(\text{PMF}) - \ln(N!) &= \sum_{i=1}^K \ln \left(\frac{p_i^{N_i}}{N_i!} \right) = \sum_{j=1}^K \ln \left(\frac{1}{N} \sum_{k=1}^K p_k e^{-\beta \varepsilon_k} \right)^{N_j} + \sum_{j=1}^K \ln \left(\frac{(N_j e^{\beta \varepsilon_j})^{N_j}}{N_j!} \right) = \\ &= \sum_{j=1}^K \ln \left(\frac{1}{N} \frac{N}{e^{-\alpha}} \right)^{N_j} + \sum_{j=1}^K \ln \left(\frac{N_j^{N_j}}{N_j!} \right) + \sum_{j=1}^K \ln \left(e^{\beta N_j \varepsilon_j} \right) \cong \alpha N + \sum_{j=1}^K \ln \left(e^{N_j} \right) + \beta \sum_{j=1}^K N_j \varepsilon_j \\ \ln(\text{PMF}) - \ln(N!) - \ln(e^N) &= N \cdot \alpha + \beta \cdot E \rightarrow \ln \frac{p_1^{N_1} \dots p_K^{N_K}}{N_1! \dots N_K!} e^N = \alpha \cdot N + \beta \cdot E \end{aligned} \quad (9)$$

$$N_j! \cong \frac{N_j^{N_j}}{e^{N_j}} \rightarrow \sum_{j=1}^K N_j \ln \frac{p_j}{N_j} = \alpha \cdot N + \beta \cdot E; \quad \frac{N_j}{N} = f_j \rightarrow -N \sum_{j=1}^K f_j \ln N p_j f_j = \alpha \cdot N + \beta \cdot E \rightarrow$$

$$E = -\frac{\alpha}{\beta} \cdot N - \frac{N}{\beta} \sum_{j=1}^K f_j \ln f_j p_j N; \quad q_j = p_j N \rightarrow E = -\frac{\alpha}{\beta} \cdot N - \frac{N}{\beta} \sum_{j=1}^K f_j \ln f_j - \frac{N}{\beta} \sum_{j=1}^K f_j \ln q_j$$

Experiments with ideal gas allow identification of the constant β while experiments with mixing of pure substances allow the identification of the constant α (Gibbs, 1902): $k_B T = -1/\beta$, $k_B T = -\mu/\alpha$, μ being the chemical potential.

By making $N = ct.$ and $T = ct.$ in the last expression of Eq.9, the change in the energy is:

$$dE \Big|_{T=ct}^{N=ct} = k_B \cdot T \cdot N \cdot d \left(\sum_{j=1}^K f_j \ln f_j \right) - k_B \cdot T \cdot N \cdot d \left(\sum_{j=1}^K f_j \ln q_j \right) \quad (9a)$$

By constraining even more the system with $V = ct.$ the last term vanishes (is an extensive property volume dependent) and allows extraction of the entropy:

$$dE_{T=ct, V=ct}^{N=ct} = k_B \cdot T \cdot N \cdot d \left(\sum_{j=1}^K f_j \ln f_j \right); S(f) \stackrel{\text{def}}{=} N \cdot k_B \cdot \sum_{j=1}^K f_j \ln f_j \rightarrow dE_{T=ct, V=ct}^{N=ct} = T \cdot dS \quad (9b)$$

Similarly, for $S = ct.$ along with $V = ct.$ and $T = ct.$ gives the chemical potential (μ):

$$dE_{T=ct, V=ct}^{S=ct} = -\frac{\alpha}{\beta} \cdot dN; \mu \stackrel{\text{def}}{=} -\frac{\alpha}{\beta} \rightarrow dE_{T=ct, V=ct}^{S=ct} = \mu \cdot dN \quad (9c)$$

Definition of the entropy from reversible processes and the first principle allows finally giving a more convenient expression for a change in energy:

$$dE = T \cdot dS - p \cdot dV + \mu_N \cdot dN \quad (9d)$$

IDEAL GAS

For an ideal gas, the total internal energy has three components, corresponding each to a translation in one direction in space. Even more, the p_j/p_i ratio is not significantly different from 1, and thus for each of its components the assumptions used to derive (eq.8) holds as a limit case - the value of a speed component (for instance v_x) takes any value from $(-\infty, \infty)$ interval, and fraction of the molecules possessing a certain speed is the probability for the speed. In the (Eq.10) are one unknown constant (β) and one non-evaluated integral, which are constant too, which allows rewriting with two unknown constants:

$$f(v_x) = \frac{e^{-\frac{\beta m}{2} v_x^2}}{\int_{-\infty}^{\infty} e^{-\frac{\beta m}{2} v_x^2} dv_x} \rightarrow f(v_x) = a e^{-b v_x^2} \quad (10)$$

One constant from the expression of f in Eq.10 results from the condition that f is a probability density function (Eq.11):

$$1 = \int_{-\infty}^{\infty} f(v_x) dv_x = \int_{-\infty}^{\infty} a e^{-b v_x^2} dv_x = a \int_{-\infty}^{\infty} e^{-b v_x^2} dv_x = \frac{a \sqrt{\pi}}{\sqrt{b}} \rightarrow b = \pi a^2 \rightarrow f(v_x) = a e^{-\pi a^2 v_x^2} \quad (11)$$

From Eq.11, an expression for the mean of one component of the energy can be obtained (Eq.12):

$$M(\varepsilon_x) = \frac{m}{2} M(v_x^2) = \frac{m}{2} \int_{-\infty}^{\infty} v_x^2 f(v_x) dv_x = \frac{m a}{2} \int_{-\infty}^{\infty} v_x^2 e^{-\pi a^2 v_x^2} dv_x = \frac{m a}{2} \cdot \frac{\sqrt{\pi}}{2(a\sqrt{\pi})^3} = \frac{m}{4\pi a^2} \quad (12)$$

For the identification of the constant a , a relationship between the energy and state parameters must be derived. In the ideal gas, all energy is from translation of the molecules and has three components, corresponding to the degrees of freedom ($\varepsilon = \varepsilon_x + \varepsilon_y + \varepsilon_z$). Even more, for each arbitrary value, of an energy component (such as $\varepsilon_x = m \cdot v_x^2/2$), the molecules possessing a speed of v_x and the molecules possessing a speed of $-v_x$ are in equal number.

Considering a box of volume V and a wall of the box of surface S parallel to yOz plane in a timeframe of δt , the molecules that may hit the wall are at a distance of $v_x \cdot \delta t$ by the wall. Their density ($\delta N_x/\delta V$) in this volume ($S \cdot v_x \cdot \delta t$) is equal to the density (N/V) from the entire box (V). Considering that only half of them ($\delta N_x/2 = (S \cdot v_x \cdot \delta t) \cdot (N/V)/2$) have the orientation of the speed component v_x to the wall, the impulse transferred to the wall (Eq.13) is calculated as the sum of the impulses transferred by every molecule ($2 \cdot m \cdot v_x$). This impulses create an instantaneous force acting on the wall ($\delta F_x = \delta P_x/\delta t$) as well as an instantaneous pressure ($\delta p_x = \delta F_x/S$). Since Eq.13 stands for any arbitrary value of the speed component v_x it is also stands when the averages are applied in both parts of the equality (Eq.14). But $M(p_x)$ is in fact the observed pressure on the wall ($p = M(p_x)$).

$$\begin{aligned} \delta P_x &= (2 \cdot m \cdot v_x) \cdot (\delta N_x/2) = m \cdot S \cdot N \cdot v_x^2 \cdot \delta t / V \\ \delta F_x &= \delta P_x / \delta t = m \cdot S \cdot N \cdot v_x^2 / V \end{aligned} \quad (13)$$

$$\begin{aligned}\delta p_x &= N \cdot m \cdot v_x^2 / V \\ p &= M(\delta p_x) = 2 \cdot N \cdot M(m \cdot v_x^2 / 2) / V = 2 \cdot N \cdot M(\varepsilon_x) / V \rightarrow M(\varepsilon_x) = p \cdot V / (2 \cdot N)\end{aligned}\quad (14)$$

By using relations given by Eq.12 and Eq.14, results the expression for the constant a (Eq.15):

$$\frac{m}{4\pi a^2} = \frac{pV}{2N} \rightarrow \pi a^2 = \frac{mN}{2pV}, \quad a = \frac{1}{\sqrt{\pi}} \sqrt{\frac{mN}{2pV}} \quad (15)$$

In order to obtain the distribution of the molecules by its value of the speed it should recall first the Eq.12:

$$v = \sqrt{v_x^2 + v_y^2 + v_z^2} \quad (16)$$

To simplify the formula, the constant expressed as a it will be kept. As given in Eq.16, in every moment of time, speed on the direction of the translation is related with its components by $v^2 = v_x^2 + v_y^2 + v_z^2$. There are no constrictions regarding the value of one component of the speed (v_x) in relation with the value of the others (v_y and v_z), which it means that these three components acts independently one vs. each other. The event to see a particle with the v value for the speed in the direction of the translation (φ and θ give the direction of the translation) is a dependent event, depending by the independent events for the components of speed possessing the values $|v_x|$, $|v_y|$ and $|v_z|$ and (Eq.17):

$$g(v, \varphi, \theta) dv d\varphi d\theta = \left(2ae^{-\pi a^2 v_x^2}\right) \cdot \left(2ae^{-\pi a^2 v_y^2}\right) \cdot \left(2ae^{-\pi a^2 v_z^2}\right) dv_x dv_y dv_z = 8a^3 e^{-\pi a^2 v^2} dv_x dv_y dv_z \quad (17)$$

Using the Jacobian (1841) for $v_x = v \sin(\theta) \cos(\varphi)$, $v_y = v \sin(\theta) \sin(\varphi)$, $v_z = v \cos(\theta)$, the function $g(v, \varphi, \theta)$ can be obtained (Eq.18) from Eq.11:

$$g(v, \varphi, \theta) = 8a^3 e^{-\pi a^2 v^2} \frac{dv_x dv_y dv_z}{dv d\varphi d\theta} = 8a^3 e^{-\pi a^2 v^2} \cdot v^2 \sin(\theta) \quad (18)$$

The event to see a particle with the v value in any direction of the translation (Eq.18) results from integration of g for all directions (Eq.19). Please note that if v_x , v_y and v_z takes only positive values (as takes $|v_x|$, $|v_y|$ and $|v_z|$) then the angles φ and θ takes values in $[0, \pi/2]$ interval:

$$\begin{aligned}h(v) dv &= \left(\int_0^{\pi/2} \int_0^{\pi/2} g(v, \varphi, \theta) d\varphi d\theta \right) dv \\ h(v) &= \int_0^{\pi/2} \int_0^{\pi/2} g(v, \varphi, \theta) d\varphi d\theta = 8a^3 e^{-\pi a^2 v^2} \cdot v^2 \int_0^{\pi/2} \int_0^{\pi/2} \sin(\theta) d\varphi d\theta = 8a^3 e^{-\pi a^2 v^2} \cdot v^2 \cdot \frac{\pi}{2} \cdot 1\end{aligned}\quad (19)$$

$$h(v) = 4\pi a^3 v^2 e^{-\pi a^2 v^2}$$

An expression for the mean of the kinetic energy can be obtained (Eq.20) from Eq.19:

$$\begin{aligned}M(\varepsilon) &= \frac{m}{2} M(v^2) = \frac{m}{2} \int_0^\infty v^2 h(v) dv = \frac{m}{2} \int_0^\infty 4\pi a^3 v^4 e^{-\pi a^2 v^2} dv = 2\pi a^3 m \int_0^\infty v^4 e^{-\pi a^2 v^2} dv \\ M(\varepsilon) &= 2\pi a^3 m \frac{3\sqrt{\pi}}{8(a\sqrt{\pi})^5} = \frac{3m}{4\pi a^2}\end{aligned}\quad (20)$$

Turning back to Eq.12, through Eq.20, it could be shown that (Eq.21):

$$M(\varepsilon) = \frac{3m}{4\pi a^2} = 3 \frac{m}{4\pi a^2} = 3M(\varepsilon_x) \quad (21)$$

The Eq.21 is a proof for the ehipartition of the kinetic energy on its components (Eq.22) since the chosen component (ε_x) was arbitrary:

$$M(\varepsilon)/3 = M(\varepsilon_x) = M(\varepsilon_y) = M(\varepsilon_z) \quad (22)$$

KINETIC ENERGY OF GAS MOLECULES WITH AN ARBITRARY NUMBER OF ENERGY COMPONENTS

It has already been proof that one component of the energy for the ideal monoatomic gas is given by Eq.11 with the constants identified in Eq.15:

$$f(v_x) = ae^{-\pi a^2 v_x^2}, \quad a = \pi^{-1/2} (mN/2pV)^{1/2} \quad (23)$$

For an unknown gas with J components of the total energy, 3 of these components come from translation movement, as come for the ideal monoatomic gas. The other components of the energy may be stored in rotation and vibration of the molecules whenever the molecule is build from more than one atom.

However, the real speed of the molecules, as can be recorded from translation, it can be decomposed in its three Cartesian components ($v^2 = v_x^2 + v_y^2 + v_z^2$), still have only three degrees of freedom, and is computed from averaging the velocity from three of its components (the translation ones). Therefore, this speed is with disregard to the number of energy components and is defined by Eq.24:

$$M(v) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \sqrt{v_x^2 + v_y^2 + v_z^2} \cdot f(v_x) \cdot f(v_y) \cdot f(v_z) dv_x dv_y dv_z = \int_0^{\infty} v \cdot h(v) dv \quad (24)$$

$$M(v) = 4\pi a^3 \int_0^{\infty} v^3 e^{-\pi a^2 v^2} dv = 4\pi a^3 \cdot \frac{1}{2(a\sqrt{\pi})^4} = \frac{2}{\pi} \frac{1}{a} = \frac{2}{\pi} \frac{\sqrt{\pi}}{1} \sqrt{\frac{2pV}{mN}} = \sqrt{\frac{8pV}{\pi mN}}$$

In the next, it could be noted that the decomposition of the kinetic energy in J components (more than three) also defines other speed (let's label with s), a virtual speed, as energetic equivalent of all types of movement (including rotation and translation) (Eq.25).

$$E = E_1 + E_2 + \dots + E_J = N \cdot m \cdot M(s^2)_{\text{formal}} / 2 \quad (25)$$

For an arbitrary gas with J components of the kinetic energy, there is no reason to suspect that the energy are distributed different on other energy components than is on the three components of translation (a part of the energy is stored in the rotation and possibly in the vibration as well). Even more, for some types of movement (such as rotation and translation) an instantaneous speed has sense. If Eq.23 express the distribution of one component of the energy then the mean energy can be computed from Eq.26:

$$M(s^2) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} (s_1^2 + s_2^2 + \dots + s_J^2) \cdot f(s_1) \cdot f(s_2) \cdot \dots \cdot f(s_J) ds_1 ds_2 \dots ds_J = \frac{J}{2a^2} = J \cdot \frac{pV}{mN} \quad (26)$$

Furthermore, the virtual speed (Eq.27) is harder to compute:

$$M(s) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} \sqrt{s_1^2 + s_2^2 + \dots + s_J^2} \cdot f(s_1) \cdot f(s_2) \cdot \dots \cdot f(s_J) ds_1 ds_2 \dots ds_J \quad (27)$$

As is defined by (Eq.25) $M(s)$ defines a virtual speed (s) because it has no sense to use more than three independent directions of movement of a body in a physical space.

VIRTUAL SPEED OF GAS MOLECULES WITH AN ARBITRARY NUMBER OF KINETIC ENERGY COMPONENTS

In order to compute the integral defined by Eq.27, the variables must be change in a multidimensional sphere. This transformation can be conducted similarly with the transformation of the three-dimensional case (Eq.17-18). Thus, changing of the integrals limits from $(-\infty, \infty)$ to $[0, \infty)$ in Eq.27, will multiply by 3 each kinetic energy component (Eq.28):

$$M(s) = 2^J \cdot \int_0^\infty \int_0^\infty \dots \int_0^\infty \sqrt{s_1^2 + s_2^2 + \dots + s_J^2} \cdot f(s_1) \cdot f(s_2) \cdot \dots \cdot f(s_J) ds_1 ds_2 \dots ds_J \quad (28)$$

The proper method to change the variable must be applied first. Like in both 2- and 3-dimensional cases, the positive values of all virtual speed components will determine that the integration domain for angular variables to be $[0, \pi/2]$.

An iterative (with increasing of J) changing of the variables can be defined as is given in Tab. 1. If the variables are changed accordingly, then the Jacobian is easily computable and reveals an iterative formula too (see Tab.1).

Tab.1

Change of the variables from Cartesian to polar and the Jacobian of the change

J	Changing of the variables	Jacobian
2	$s_1 = q_0 \cdot \cos(q_1)$ $s_2 = q_0 \cdot \sin(q_1)$	$\frac{ds_1 ds_2}{dq_0 dq_1} = q_0$
3	$s_1 = q_0 \cdot \cos(q_1)$ $s_2 = q_0 \cdot \sin(q_1) \cdot \cos(q_2)$ $s_3 = q_0 \cdot \sin(q_1) \cdot \sin(q_2)$	$\frac{ds_1 ds_2 ds_3}{dq_0 dq_1 dq_2} = q_0^2 \cdot \sin(q_1)$
4	$s_1 = q_0 \cdot \cos(q_1)$ $s_2 = q_0 \cdot \sin(q_1) \cdot \cos(q_2)$ $s_3 = q_0 \cdot \sin(q_1) \cdot \sin(q_2) \cdot \cos(q_3)$ $s_4 = q_0 \cdot \sin(q_1) \cdot \sin(q_2) \cdot \sin(q_3)$	$\frac{ds_1 ds_2 ds_3 ds_4}{dq_0 dq_1 dq_2 dq_3} = q_0^3 \cdot \sin^2(q_1) \cdot \sin(q_2)$
5	$s_1 = q_0 \cdot \cos(q_1)$ $s_2 = q_0 \cdot \sin(q_1) \cdot \cos(q_2)$ $s_3 = q_0 \cdot \sin(q_1) \cdot \sin(q_2) \cdot \cos(q_3)$ $s_4 = q_0 \cdot \sin(q_1) \cdot \sin(q_2) \cdot \sin(q_3) \cdot \cos(q_4)$ $s_5 = q_0 \cdot \sin(q_1) \cdot \sin(q_2) \cdot \sin(q_3) \cdot \sin(q_4)$	$\frac{ds_1 ds_2 ds_3 ds_4 ds_5}{dq_0 dq_1 dq_2 dq_3 dq_4} = q_0^4 \cdot \sin^3(q_1) \cdot \sin^2(q_2) \cdot \sin(q_3)$
J	$s_1 = q_0 \cdot \cos(q_1)$... $s_{J-1} = q_0 \cdot \sin(q_1) \cdot \dots \cdot \sin(q_{J-2}) \cdot \cos(q_{J-1})$ $s_J = q_0 \cdot \sin(q_1) \cdot \dots \cdot \sin(q_{J-2}) \cdot \sin(q_{J-1})$	$\frac{ds_1 \dots ds_J}{dq_0 \dots dq_{J-1}} = q_0^{J-1} \cdot \prod_{k=1}^{J-2} \sin^{J-k-1}(q_k)$

The second task is to evaluate the integrals of the angular coordinates (q_1, \dots, q_{J-1}) and this procedure is illustrated in Tab.2. For simplification, the variables from q_1 to q_{J-1} are renamed in the expression of the Jacobian in a reversed order, and the integrals are given only for the new occurring expressions.

The distribution of the molecules by its virtual speeds (Eq.29) could be written as:

$$PDF(s) = \frac{\pi^{J/2}}{2^{J-1} \Gamma(J/2)} \cdot s^{J-1} \cdot a^J e^{-\pi a^2 s^2} \quad (29)$$

To evaluate the integrals given in Eq.26 and Eq.27 is the last task (Eq.30):

$$M(s^2) = 2^J \cdot \int_0^\infty s^2 \cdot PDF(s) ds = \frac{2\pi^{J/2} a^J}{\Gamma(J/2)} \int_0^\infty s^{J+1} \cdot e^{-\pi a^2 s^2} ds \quad (30)$$

$$M(s) = 2^J \cdot \int_0^\infty s \cdot PDF(s) ds = \frac{2\pi^{J/2} a^J}{\Gamma(J/2)} \int_0^\infty s^J \cdot e^{-\pi a^2 s^2} ds$$

To accomplish this last task, the formula presented in Eq.31 should be used:

$$\int_0^\infty s^n \cdot e^{-q^2 s^2} ds = \frac{\Gamma(n/2 + 1/2)}{2q^{n+1}} \text{ with } q = a\sqrt{\pi} \quad (31)$$

and the expressions of mean square ($M(s^2)$) and mean ($M(s)$) virtual speeds becomes (Eq.32):

$$a = \frac{1}{\sqrt{\pi}} \sqrt{\frac{mN}{2pV}}$$

$$M(s^2) = \frac{2\pi^{J/2} a^J}{\Gamma(J/2)} \frac{\Gamma(J/2+1)}{2a^{J+2} \pi^{J/2+1}} = \frac{\Gamma(J/2+1)}{\Gamma(J/2)} \frac{1}{\pi a^2} = J \frac{pV}{mN} \quad (32)$$

$$M(s) = \frac{2\pi^{J/2} a^J}{\Gamma(J/2)} \frac{\Gamma(J/2+1/2)}{2a^{J+1} \pi^{J/2+1/2}} = \frac{\Gamma(J/2+1/2)}{\Gamma(J/2)} \frac{1}{\pi^{1/2} a} = \frac{\Gamma(J/2+1/2)}{\Gamma(J/2)} \sqrt{\frac{2pV}{mN}}$$

Tab.2

Integrals on $[0, \pi/2]$ for all angles for the Jacobian of changed coordinates

J	Jacobian	Integrals on $[0, \pi/2]$ for all angles
2	q_0	$\int_0^{\pi/2} 1 dq_1 = \frac{\pi}{2}$
3	$q_0^2 \cdot \sin(q_2)$	$\int_0^{\pi/2} \sin(q_2) dq_2 = 1$
4	$q_0^3 \cdot \sin^2(q_3) \cdot \sin(q_2)$	$\int_0^{\pi/2} \sin^2(q_3) dq_3 = \frac{\pi}{4}$
5	$q_0^4 \cdot \sin^3(q_4) \cdot \sin^2(q_3) \cdot \sin(q_2)$	$\int_0^{\pi/2} \sin^3(q_4) dq_4 = \frac{2}{3}$
J	$q_0^{J-1} \cdot \prod_{k=1}^{J-2} \sin^k(q_{k+1})$	$\int_0^{\pi/2} \sin^k(q_{k+1}) dq_{k+1} = \frac{\Gamma(1/2) \cdot \Gamma(1/2 + k/2)}{2 \cdot \Gamma(1 + k/2)}$
J	Generalized formula	$\prod_{k=0}^{J-2} \int_0^{\pi/2} \sin^k(q_{k+1}) dq_{k+1} = \frac{\pi}{2} \cdot \frac{\pi^{J/2-1}}{2^{J-2} \Gamma(J/2)}$

A remark can be made about the obtained result (Eq.33):

$$\lim_{J \rightarrow \infty} (M(s) - \sqrt{M(s^2)}) = \sqrt{\frac{pV}{mN}} \lim_{J \rightarrow \infty} \left(\sqrt{J} - \frac{\Gamma(J/2+1/2)\sqrt{2}}{\Gamma(J/2)} \right) = 0 \quad (33)$$

and thus with the increasing of the number of the components of the energy (at very high temperatures or for very large molecules) both measures of virtual speed become equal.

Tab.3 exemplifies the values of the squared root of mean square virtual speed ($M(s^2)$) and mean virtual speed ($M(s)$) for some values of J .

If we turn back (Eq.29) to the distribution of the molecules by their virtual speed (Eq.34):

$$PDF(s, a, J) = \frac{\pi^{J/2}}{2^{J-1} \Gamma(J/2)} \cdot s^{J-1} \cdot a^J e^{-\pi a^2 s^2} \quad (34)$$

the above equation indicate that for certain states (a in Eq.34) the distribution of the molecules by their virtual speeds have a high mode (Eq.35):

$$0 = \frac{\partial}{\partial s} PDF(s, a, J) \rightarrow s = \frac{\sqrt{J-1}}{a}, \quad PDF\left(\frac{\sqrt{J-1}}{a}, a, J\right) = \frac{e^{1-J/2} (J-1)^{J/2-1/2}}{2^{3J/2-1} \Gamma(J/2)} a^{-J/2} \text{ to max.} \quad (35)$$

and if it exists, we should call these states as 'preferred state'.

Differences between virtual speeds for different number of kinetic energy components

J	$\sqrt{M(s^2)}$	M(s)
2	$\sqrt{2} \cdot \sqrt{\frac{pV}{mN}} ; \sqrt{2} \approx 1.414$	$\frac{\Gamma(3/2)\sqrt{2}}{\Gamma(1/2)} \sqrt{\frac{pV}{mN}} ; \frac{\Gamma(3/2)\sqrt{2}}{\Gamma(1/2)} \approx 1.253$
3	$\sqrt{3} \cdot \sqrt{\frac{pV}{mN}} ; \sqrt{3} \approx 1.732$	$\frac{\Gamma(2)\sqrt{2}}{\Gamma(3/2)} \sqrt{\frac{pV}{mN}} ; \frac{\Gamma(2)\sqrt{2}}{\Gamma(3/2)} \approx 1.596$
4	$\sqrt{4} \cdot \sqrt{\frac{pV}{mN}} ; \sqrt{4} = 2.000$	$\frac{\Gamma(5/2)\sqrt{2}}{\Gamma(2)} \sqrt{\frac{pV}{mN}} ; \frac{\Gamma(5/2)\sqrt{2}}{\Gamma(2)} \approx 1.880$
5	$\sqrt{5} \cdot \sqrt{\frac{pV}{mN}} ; \sqrt{5} \approx 2.236$	$\frac{\Gamma(3)\sqrt{2}}{\Gamma(5/2)} \sqrt{\frac{pV}{mN}} ; \frac{\Gamma(3)\sqrt{2}}{\Gamma(5/2)} \approx 2.128$
6	$\sqrt{6} \cdot \sqrt{\frac{pV}{mN}} ; \sqrt{6} \approx 2.449$	$\frac{\Gamma(7/2)\sqrt{2}}{\Gamma(3)} \sqrt{\frac{pV}{mN}} ; \frac{\Gamma(7/2)\sqrt{2}}{\Gamma(3)} \approx 2.350$
7	$\sqrt{7} \cdot \sqrt{\frac{pV}{mN}} ; \sqrt{7} \approx 2.646$	$\frac{\Gamma(4)\sqrt{2}}{\Gamma(7/2)} \sqrt{\frac{pV}{mN}} ; \frac{\Gamma(4)\sqrt{2}}{\Gamma(7/2)} \approx 2.553$

THE NUMBER OF ENERGY COMPONENTS FOR HYDROGEN MOLECULES

The advantage of introducing the number of energy components for which Eq.29 provides the distribution of the virtual speeds of the molecules is obvious when we go back to the experimental data. By using the experimental data from (Debye, 1912; Johnson *et al.*, 1950; Smith *et al.*, 1954; Chase, 1998), as well as the definition of the constant-pressure heat capacity ($C_p = (\partial H/\partial T)_{p=ct}$, $H = E + p \cdot V$) the number of the energy components (J) for hydrogen can be derived from the experimental data ($C_{p,m} = (J+2) \cdot R/2$) as a smooth curve, as it is depicted in Fig. 1.

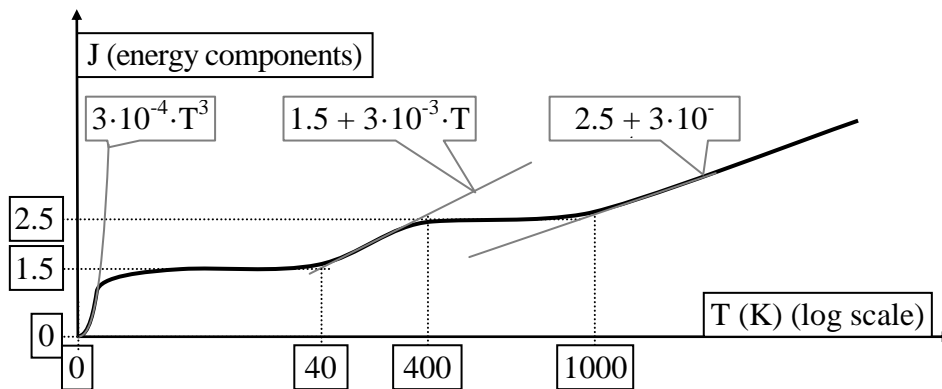


Fig. 1. Energy components for hydrogen

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