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Thermodynamic functions of the system with limiting temperatures

THERMODYNAMIC FUNCTIONS OF THE SYSTEM
WITH LIMITING TEMPERATURES

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In his work J. B. Rumer (1) has explained some fundamental properties of system which is done by the ideal monoatomic gas in external field with the logarithmic asymptote of potencial. To calculate the partition function of one molecule the value of parameter must be selected so that integral in partition function should be convergent. The proper selection of this parameter gives rise to limiting temperature.

In our work the fundamental thermodynamical function and properties with the aid of classical statistical mechanics was derived and the values of free energy and entropy in the neighbourhood of limiting temperature was shown.

I. Partition function of ideal gas in the field with logarithmic asymptote of potencial

Let be done ideal monoatomic gas in the field acting on the boundary of a cylinder with height H and radius a. The potencial has the face

$$U(r) = \begin{cases} 0 & \text{for} \quad r < a \\ 2U_0 \ln r/a & \text{for} \quad r > a. \end{cases} \qquad (I,1)$$

This formulation is due to J. B. Rumer (1).

For describing of the properties of this system it is necessary to derive the partition function $Z(\mu)$, where $\mu = 1/kT$. With the assumption that energetic spectrum is continued we can use the method wichi is described by Schroedinger (2). Hamiltonian of one molecule of gas with mass m is done by

$$H = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + U(x, y, z). \qquad (I,2)$$

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From (I,2) it is shown that we must use the six-dimensional phase space with the coordinates x, y, z, p_x, p_y, p_z. The partition function of one molecule the is

$$Z(\mu) = \iiint\iiint_{-\infty}^{\infty} \exp\left\{-\mu\left[\frac{p_x^2 + p_y^2 + p_z^2}{2m} + U(x, y, z)\right]\right\} dx\, dy\, dz\, dp_x\, dp_y\, dp_z.$$

(I,3)

The integral is composed from two triple integrals. We compute easily the integration with respect to impulses

$$\iiint_{-\infty}^{\infty} \exp\left\{-\frac{\mu}{2m}(p_x^2 + p_y^2 + p_z^2)\right\} dp_x\, dp_y\, dp_z.$$

(I,4)

Each from these integrals may be evaluated separately because they are Laplace's integrals and thus

$$I_x = \int_{-\infty}^{\infty} \exp\left\{-\frac{\mu}{2m} p_x^2\right\} dp_x = \left(\frac{2\pi m}{\mu}\right)^{1/2}.$$

(I,5)

In the some manner we obtain I_y and I_z and after multiplacation the value of triple integral in (I,4) is given by

$$I = \left(\frac{2\pi m}{\mu}\right)^{3/2}$$

(I,6)

With the aid of (I,6) we find for $Z(\mu)$

$$Z(\mu) = \left(\frac{2\pi m}{\mu}\right)^{3/2} \iiint_{-\infty}^{\infty} \exp\left\{-\mu U(x, y, z)\right\} dx\, dy\, dz.$$

(I,7)

In this case it is necessary to use the cylindrical coordinates and the transformation dxdydz shall be worked out by means of functional determinant

$$dx\, dy\, dz = \frac{\partial(x, y, z)}{\partial(r, \varphi, z)} dr\, d\varphi\, dz,$$

(I,8)

where r, z and φ are the cylindrical coordinates. After the computing we see, that the functional determinant is r. From this, after the integration with respect to φ from 0 to 2π and with respect to z from 0 to H, we obtain for $Z(\mu)$

$$Z(\mu) = 2\pi \left(\frac{2m}{\mu}\right)^{3/2} H \int_0^{\infty} \exp\left\{-\mu U(r)\right\} r\, dr.$$

(I,9)

Now, we shall calculate the integral (I,9). With the aid of formula (I,1) this integral may be separated into two and then

$$I' = \int_0^a r \, dr + \int_a^\infty e^{-2\mu U_0 \ln r/a} \, r \, dr. \qquad (I,10)$$

The first integral is $a^2/2$ and the second is computed after the elementary rearrangering

$$e^{-2\mu U_0 \ln r/a} = \left(\frac{r}{a}\right)^{-2\mu U_0}. \qquad (I,11)$$

so

$$I' = \frac{a^2}{2} + \frac{1}{a^{-2\mu U_0}} \left[\frac{r^{2-2\mu U_0}}{2(1 - U_0)}\right]_a^\infty. \qquad (I,12)$$

From the reasons, that this integral must converge, it is necessary to assume, that $\mu U_0 > 1$. Than we find

$$I' = \frac{a^2}{2} \cdot \frac{\mu U_0}{\mu U_0 - 1}. \qquad (I,13)$$

This result we use for to calculate the formula (I,9) and from this follows

$$Z(\mu) = \frac{\pi H (2m)^{3/2} U_0 a^2}{\mu^{1/2}(\mu U_0 - 1)}. \qquad (I,14)$$

The equation was derived at the assumption $\mu U_0 > 1$, in other cases the integral diverges and $Z(\mu)$ should not be calculated. The μU_0 has the limit 1 and thus the system has the limiting temperature $T_{\lim} = U_0/k$, above which it is not possible to heat the system.

The physical meaning of limiting temperature consist in a slow increase of potential at the simultaneous increase of the energy of molecules, so that the distances between the molecules becomes too great and the kinetic energy is negligible as against potential one.

II. The state of system with limiting temperature

The properties of the system with limiting temperature have not been studied in details. We shall show some fundamental thermodynamical functions of this state, that is, free energy F and entropy S. In accordance with the well known expressions from statistical thermodynamics we obtain the expression for F

$$F = -RT \ln Z(\mu), \qquad (II,1)$$

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for one mole of gas. From (I,14) it follows

$$F = -RT \ln \{\pi(2\pi m)^{3/2} H U_0 a^2\} + 1/2 RT \ln \mu + \qquad (II,2)$$
$$+ RT \ln (\mu U_0 - 1).$$

This expression is not generally valid. We may use them for an ideal gas at a heigh temperature or at a small density only. In our assumption the molecules are in great distances, so that the second assumption is fulfiled also in the case when temperature s not too high. We thus find the limit for F for $\mu U_0 \to 1$

$$\lim F = -\infty \qquad (II,3)$$
$$\mu U_0 \to 1,$$

from the reason, that both first terms have the finite limit and the last term has the limit $-\infty$, whereby the limit of free energy F is done. Similarly, we find the limit of entropy for $\mu U_0 \to 1$. We use the expression

$$S = R \{\ln Z(\mu) + \mu\bar{\varepsilon}\} = R \left\{ \ln Z(\mu) - \mu \frac{\partial}{\partial \mu} \ln Z(\mu) \right\} \qquad (II,4)$$

where $\bar{\varepsilon}$ is the mean energy of one molecule, which may be in the system of N molecules expressed

$$\bar{\varepsilon} = \frac{\int\limits_0^\infty \varepsilon \, e^{-\mu\varepsilon} \, d\varepsilon}{\int\limits_0^\infty e^{-\mu\varepsilon} \, d\varepsilon} = -\frac{\partial}{\partial \mu} \ln Z(\mu) \qquad (II,5)$$

where ε is the total energy of the molecule. After the little rearanging and by means of a process of limitation we obtain

$$\lim S = \lim R \left\{ \ln [\pi(2\pi m)^{3/2} H U_0 a^2] - 1/2 \ln \mu - \right.$$
$$\left. - \ln (\mu U_0 - 1) + \frac{1}{2} \frac{\mu U_0}{\mu U_0 - 1} \right\}. \qquad (II,6)$$

All terms have the finite limit with the exception of the term $\ln (\mu U_0 - 1)$ and $\frac{\mu U_0}{\mu U_0 - 1}$, the limit of which is $-\infty$ and thus

$$\lim S = +\infty \qquad (II,7)$$
$$\mu U_0 \to 1.$$

We note, that on the other hand for the limitng case $T \ll T_{\lim}$, also for $\mu U_0 \gg 1$, we get for free energy

$$F = -RT \ln \{\pi(2\pi m)^{3/2} H a^2 + 3/2 \, RT \ln \mu\} \qquad (II, 8)$$

where $\pi H a^2 = V$, the volume of gas and thus

$$F = - RT \ln \{V(2\pi m)^{3/2}\} + 3/2 \, RT \ln \mu \qquad \text{(II, 9)}$$

also the classical case for gas in no-force field.

For entropy in the case $\mu U_0 \gg 1$ we get

$$S = R \{\ln [V(2\pi m)^{3/2}] - 3/2 \ln \mu + 3/2\} \qquad \text{(II, 10)}$$

which is, as in the case for F, the classical expression for ideal gass in noforce field.

For $T \ll T_{\lim}$ the field has the function of unpermeable wals for the molecules.

In this system with limiting temperature it is very interesting that the entropy at $T_{\lim}$ has the limit in infinity. At the present time, the system with limiting temperature has the theoretical meaning only, but after the realisation of this system we may attain interesting results. It it the similar situation as at the discovery of absolute negative temperatures (3).

LITERATURA

[1] *J. B. Rumer*, ŽETF, 38, 1899, (1960).
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Shrnutí

TERMODYNAMICKÉ FUNKCE SYSTÉMU
PŘI LIMITNÍCH TEPLOTÁCH

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V předložené práci byly vypočítány volná energie a entropie systému ideálního plynu ve vnějším poli s logaritmickou asymptotou potenciálu, který byl popsán J. B. Rumerem (I,1). Obě termodynamické veličiny jsou dány vztahy (II,2) a (II,4). Dále jsme ukázali limitní hodnoty obou veličin, protože tento systém má svoji limitní teplotu $T_{\lim} = U_0/k$, nad kterou nemůže být zahřát. Obě tyto veličiny umožňují bližší studium tohoto systému a výpočet dalších thermodynamických veličin.

Zusammenfassung

THERMODYNAMISCHE FUNKTIONEN FÜR SYSTEM
MIT GRENZTEMPERATUREN

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In der vorliegenden Arbeit wurde die freie Energie und Entropie eines Systems des idealen Gases im Feld mit einer logarithmischer Potenzialasymptote berechnet. Die Formulation dieses Potenzials ist von J. B. Rumer gegeben (I,1). Die beiden Grössen sind in den Gleichungen (II,2) und (II,4) angeführt. Weiter wurde die Auswertung der Grenzwert der beiden Grössen in (II,3) und (II,7) gezeigt, da dieses System eine Grenztemperatur besitzt. Die freie Energie und Entropie ermöglichen sowohl ein näheres Studium dieses Systems als auch die Berechnung weiterer thermodynamischer Grössen.