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THE THERMODYNAMICAL PROPERTIES OF AN IDEAL GAS IN A PERIODICAL POTENTIAL FIELD

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I. The partition function of an ideal gas in a periodical potential field

Let be done an ideal gas with a given volume influenced by a periodical potential field of a sine-wave. For reason of simplicity let us limit on calculating the μ-phase space where the outer potential periodical field is given by means of the relation

$$U(x) = U_0 \sin \frac{2\pi}{a} x \qquad 0 \leqq x \leqq a, \tag{I,1}$$

where a is the period of the potential field. In this case we may write the Hamiltonian in the following form

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

The partition function $z(\beta)$, where $\beta = \frac{1}{kT}$, will be given μ-space

$$z(\beta) = \int\int\int\int\int\int_{-\infty}^{+\infty} \mathrm{e}^{-\frac{\beta}{2m} p^2} \mathrm{e}^{-\beta U(x)} \, \mathrm{d}p_x \, \mathrm{d}p_y \, \mathrm{d}p_z \, \mathrm{d}x \, \mathrm{d}y \, \mathrm{d}z. \tag{I,3}$$

The integral on the right side of the preceding relation consists of two triple integrals. These integrals regards to the impulses are Laplacian integrals.

Denoting the integrals over $\mathrm{d}p_x$ by means of the symbol I_x, it follows

$$I_x = \int_{-\infty}^{+\infty} \exp\left\{-\frac{\beta}{2m} p_x^2\right\} \mathrm{d}p_x = \left(\frac{2\pi m}{\beta}\right)^{\frac{1}{2}}. \tag{I,4}$$

The analogical relations are valid also for integrals I_y and I_z, so that the first of the triple integrals in (I,3) has the following value

$$I = \left(\frac{2\pi m}{\beta}\right)^{\frac{3}{2}} \tag{I,5}$$

after substituting in (I,3) it follows then

$$z(\beta) = \left(\frac{2\pi m}{\beta}\right)^{\frac{3}{2}} \int_0^a \int\int_{-\infty}^{+\infty} \exp\left\{-\beta\, U_0 \sin\frac{2\pi}{a} x\right\} \mathrm{d}x\, \mathrm{d}y\, \mathrm{d}z. \tag{I,6}$$

Let us define now the value of a triple integral relation (I,7). With respect to the fact that the integrand is a function of coordinates only, we can write

$$K = \int_0^a \exp\left\{-\beta\, U_0 \sin\frac{2\pi}{a} x\right\} \mathrm{d}x \int_{-\infty}^{+\infty} \mathrm{d}y \int_{-\infty}^{+\infty} \mathrm{d}z \tag{I,7}$$

$$\int_{-\infty}^{+\infty} \mathrm{d}y \int_{-\infty}^{+\infty} \mathrm{d}z = y \,.\, z$$

represents the surface P, so that

$$K = P \int_0^a \exp\left\{-\beta U_0 \sin\frac{2\pi}{a} x\right\} \mathrm{d}x\,. \tag{I,8}$$

To evaluate this integral we can use the analysis of the function e^x in a power series. Limiting ourselves in such a series on the terms of the third — order, we get

$$\int_0^a \exp\left\{-\beta U_0 \sin\frac{2\pi}{a} x\right\} \mathrm{d}x =$$

$$= \int_0^a \left[1 - \frac{\beta U_0 \sin\frac{2\pi}{a} x}{1!} + \frac{\beta^2 U_0^2 \sin^2\frac{2\pi}{a} x}{2!} - \frac{\beta^3 U_0^3 \sin^3\frac{2\pi}{a} x}{3!}\right] \mathrm{d}x =$$

$$= x\Big|_0^a + \frac{\beta U_0 a}{2\pi} \cos\frac{2\pi}{a} x\Big|_0^a + \frac{\beta^2 U_0^2}{4}\left(x - \frac{a}{4\pi}\sin\frac{4\pi}{a} x\right)\Big|_0^a -$$

$$- \frac{\beta^3 U_0^3}{6}\left(-\frac{a}{2\pi}\cos\frac{2\pi}{a} x + \frac{a}{6\pi}\cos^3\frac{2\pi}{a} x\right)\Big|_0^a. \tag{I,9}$$

The integral (I,9) may be written after modification in the following form

$$\frac{a}{4}(\beta^2 U_0^2 + 4).$$

After substituting this value in (I,6) we obtain

$$z(\beta) = \left(\frac{2\pi m}{\beta}\right)^{\frac{3}{2}} \frac{P \cdot a}{4} (\beta^2 U_0^2 + 4) = \left(\frac{2\pi m}{\beta}\right)^{\frac{3}{2}} \frac{V}{4} (\beta^2 U_0^2 + 4). \qquad \text{(I,10)}$$

Such a partition function however doesn't give a clear idea about the influence a potential field on the properties of the system, while the integration over the whole period of a sine — field compensate the field effects in both half periods.

From the more detailed evaluations it is going out that the partition function of a system is a function of the volume. In a fact making successively the integration of an expression (I,9) in the limit $0 \div \frac{a}{2}$, $0 \div \frac{a}{4}$, $0 \div \frac{a}{6}$, and commonly $0 \div \frac{a}{2n}$ where $n = 1, 2, 3, \ldots$, we obtain for a partition function $z(\beta)$ the following expressions

$$\begin{aligned} z(\beta)_{\frac{a}{2}} &= \left(\frac{2\pi m}{\beta}\right)^{\frac{3}{2}} \left(\frac{1}{2} a - \frac{1}{\pi} \beta U_0 a + \frac{1}{8} \beta^2 U_0^2 a - \frac{1}{9\pi} \beta^3 U_0^3 a\right) \\ z(\beta)_{\frac{a}{4}} &= \left(\frac{2\pi m}{\beta}\right)^{\frac{3}{2}} \left(\frac{1}{4} a - \frac{1}{2\pi} \beta U_0 a + \frac{1}{16} \beta^2 U_0^2 a - \frac{1}{18\pi} \beta^3 U_0^3 a\right) \qquad \text{(I,11)} \\ z(\beta)_{\frac{a}{6}} &= \left(\frac{2\pi m}{\beta}\right)^{\frac{3}{2}} \left(\frac{1}{6} a - \frac{1}{4\pi} \beta U_0 a + \left(24 - \frac{3\sqrt{3}}{96\pi}\right) \beta^2 U_0^2 a - \frac{5}{288\pi} \beta^3 U_0^3 a\right) \end{aligned}$$

In what follows let us limit on the positive half period $(0 \div \pi)$ as so as on the linear terms βU_0 in the expression (I,11). We can express then the partition function $z(\beta)$ for the even parts of a half period $0 \div \pi$, that is $0 \div \frac{a}{2}$, $0 \div \frac{a}{4}$ a.s. o by means of a recurrent relation

$$z(\beta) = \left(\frac{2\pi m}{\beta}\right)^{\frac{3}{2}} V \left(\frac{1}{2n} - \frac{n^{n-1}}{n\, 2^{n-1}\pi} \beta U_0\right) \qquad n = 1, 2, 3, \ldots \qquad \text{(I,12)}$$

II. The thermodynamical function of an ideal gas in a periodical potential field

First let us define the mean value of the gas energy. We use for evaluation statistical relation

$$\bar{\varepsilon} = -\frac{\partial}{\partial \beta} \ln z(\beta). \qquad \text{(II,1)}$$

Using the relation (I,12) we obtain successively

$$\ln z(\beta) = \frac{3}{2} \ln (2\pi m) + \ln V - \frac{3}{2} \ln \beta + \ln \left(\frac{1}{2n} - \frac{n^{n-1}}{n\, 2^{n-1}\pi} \beta U_0\right) \qquad \text{(II,2)}$$

$$\frac{\partial}{\partial \beta} \ln z(\beta) = -\frac{3}{2\beta} - \frac{U_0}{(2^n n^{1-n}\pi - \beta U_0)} \qquad \text{(II,3)}$$

and then
$$\bar{\varepsilon} = -\frac{\partial}{\partial \beta} \ln z(\beta) = \frac{3}{2\beta} - \frac{U_0}{(\beta U_0 - 2^n n^{1-n}\pi)}. \tag{II,4}$$

This relation is valid for $\beta U_0 \neq 2^n n^{1-n}\pi$. If the field is absent, this expression satisfies the equation for the ideal gas in a powerless field.

For a free energy defined by means of the relation
$$F = -\frac{1}{\beta} \ln z(\beta)$$
we obtain the expression
$$F = -\frac{3}{2\beta} \ln (2\pi m) - \frac{1}{\beta} \ln V + \frac{3}{2\beta} \ln \beta - \frac{1}{\beta} \ln \left(\frac{1}{2n} - \frac{n^{n-1}\beta U_0}{n\, 2^{n-1}\pi} \right). \tag{II,5}$$

While in what follows it is valid $p = -\frac{\partial F}{\partial V}$, the state equation of a system will be given by means of the expression
$$p = \frac{1}{\beta} \cdot \frac{1}{V} = \frac{kT}{V}$$
or
$$pV = kT, \tag{II,6}$$
from this we see that the presence of a periodical potential field does not influence the partition function of the system while the expression (II,6) is the partition function of the ideal gas in a powerless field.

The entropy of a system S may be given as follows
$$S = -\left(\frac{\partial F}{\partial T}\right)_v = k[\ln z(\beta) + \beta \bar{\varepsilon}]. \tag{II,7}$$

Using the relation (II,2) and (II,4) we obtain
$$S = k\left[\frac{3}{2} \ln (2\pi m) + \ln V - \frac{3}{2} \ln \beta + \ln \left(\frac{1}{2n} - \frac{n^{n-1}\beta U_0}{n 2^{n-1}\pi}\right) + \right.$$
$$\left. + \frac{3}{2} - \frac{\beta U_0}{(\beta U_0 - 2^n n^{1-n}\pi)}\right]. \tag{II,8}$$

The heat capacity of a system has a special meaning while studying the thermodynamical properties of a system. We shall give it in our case with the aid of the relation
$$C = k\beta^2 \frac{\partial^2}{\partial \beta^2} \ln z(\beta). \tag{II,9}$$

Using the relation (II,2) respectively (II,4) we obtain
$$\frac{\partial^2}{\partial \beta^2} \ln z(\beta) = \frac{3}{2\beta^2} - \frac{U_0^2}{(\beta U_0 - 2^n n^{1-n}\pi)^2}$$
$$C = k\beta^2 \frac{\partial^2}{\partial \beta^2} \ln z(\beta) = k\left[\frac{3}{2} - \frac{\beta^2 U_0^2}{(\beta U_0 - 2^n n^{1-n}\pi)^2}\right]. \tag{II,10}$$

From the expression (II,10) it follows that the field contributes to the heat capacity by the value $\frac{k\beta^2 U_0^2}{(\beta U_0 - 2^n n^{1-n}\pi)^2}$. Plotting away the field, we get again for the heat capacity the value $\frac{3}{2}k$, which corresponds to the ideal gas in a powerless field.

Let us notice now the energy fluctuations in our system. The mean quadratic energy fluctuation will be given from the relation

$$\overline{\Delta\varepsilon^2} = \frac{\partial^2}{\partial\beta^2} \ln z(\beta). \tag{II,11}$$

After evaluating we obtain

$$\overline{\Delta\varepsilon^2} = \frac{3}{2\beta^2} - \frac{U_0^2}{(\beta U_0 - 2^n n^{1-n}\pi)^2} \tag{II,12}$$

from what follows that under the action of the periodical field the energy fluctuations are falling and they correspond to the second power of an absolute temperature.

Even in this case getting away the outer field we get for the mean energy fluctuation the expression for an ideal gas in a powerless field. It should be mentioned that we have made in ale ovaluations certain simplifications.

Deducing the partition function $z(\beta)$ of a given system we have limited consciously on the first approximation. In this case all the deduced relations for the fundamental thermodynamical quantities are valid only in the range of this first approximation.

The dependance of various thermodynamical quantities on the field will be in a fact evidently more complex. But with the respect to the expressions (I,11) where the influence of the field goes out as a series of expression with growing powers of the expression βU_0, the terms having higher powers βU_0 will have the negligible value of the sufficiently high temperature and from thus the influence of the field on the properties of an ideal gas may be neglected.

In the part II we have deduced some relations for evaluating of the thermodynamical quantities of the system. With regars to the recurrent partition function the properties of the system may be studies always in a certain region of a positive half period of a potential field which equals the even part of a half period. With respect to the fact that the outer fields has a periodical and complex potential course the thermodynamical properties of a system with in a period a will evidently change continuously.

We have shown what influence (under given circumstances) has an outer periodically changing potential field of a sine course on the thermodynamical properties of a system.

While the similar problems appear also by the processus in clystrons, it is possible to consider this work as a certain zero-approximation of a statistical solution of these processus.

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SHRNUTÍ

TERMODYNAMICKÉ VLASTNOSTI IDEÁLNÍHO PLYNU V PERIODICKÉM POTENCIÁLOVÉM POLI

VLADIMÍR JANKŮ

V předložené práci je ukázán výpočet statistické sumy ideálního plynu, který se nachází v periodickém potenciálovém poli sinusového průběhu. Pomocí statistické sumy jsou pak odvozeny vztahy pro výpočet nejdůležitějších termodynamických veličin zkoumaného systému.