SOME FEATURES OF THE THERMODYNAMICS OF NONLINEAR CLASSICAL SYSTEMS

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We derive the thermodynamic characteristics of an ideal gas of diatomic molecules with a nonlinear interatomic interaction, solving the problem for a wide class of potentials on the classical level, which is permissible for relatively high temperatures. The nonlinearity of the interaction can yield some characteristic properties of the gas.

1. Introduction

The thermodynamic properties of various physical systems depend on inter- and intramolecular interactions in these systems. The departure of the potential from the harmonic one and the need for taking additional intermolecular forces into account sometimes result in essential modifications of the thermodynamic characteristics such as the heat capacity, chemical potential, and thermodynamic mean size of a molecule (the bond length). In addition, the number of excited degrees of freedom at different temperatures, a possibility for a semiclassical description of the interparticle interaction in the system, and some other properties can be easily inferred from these characteristics [1, 2].

In this paper, we consider the properties of classical thermodynamic systems with essentially anharmonic interactions. The nonlinear interactions are taken into account exactly, not perturbatively, which allows deducing a number of interesting properties of the nonlinear systems in the intermediate-temperature region.

The best known example of the anharmonic interaction is the potential

\[ U(x) = U_0 \left[ \left( \frac{x}{a} \right)^2 - 1 \right]^2, \]  

which is used, for example, in the hydrogen bond theory of water. This potential allows considering not only the nonlinearity of the interaction but also (when solving the problem on the quantum level) the proton transport processes [3, 4]. The quantum mechanical treatment of this problem reveals the fine-structure splitting of the energy levels of the tunneling proton because of degeneracy of the spectrum for such a potential, which involves certain difficulties in constructing the thermodynamic theory of this effect. At the same time, the contribution of such effects is essential in only a narrow region of low temperatures and is not taken into account here.

In what follows, we consider the thermodynamic properties of an “ideal gas” of pairwise-bonded atoms with an interatomic interaction of type (1) (the analogue of the hydrogen bond of water molecules). We disregard the interaction of pairs with each other, as well as the effects of dissociation and ionization of

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molecules, assuming that the considered temperature interval is below the typical dissociation temperatures. We also assume that the interaction of the constituents of a pair can be considered on the classical level using the standard Boltzmann distribution. We study only the contribution corresponding to the interaction of the constituents of a pair assuming that the rotational degrees of freedom and the translations of the pair as a whole can be taken into account in the standard way [1].

2. One-dimensional problem

For the first step, we consider the one-dimensional problem with the Hamiltonian \( H_r(p, x) = p^2 + U_r(x) \) in dimensionless variables, where the potential

\[
U_r(x) = (x^r - a^r)^2
\]

has two minimums at the points \( \pm a \) for even \( r \) and one minimum at the point \( a > 0 \) for odd \( r \), \( U_{\text{min}} = 0 \). For \( r = 1 \), the potential describes the standard harmonic interaction with the displaced mean \( \langle x \rangle = a \), and for \( r = 2 \), it is a potential of type (1).

The contribution of the pairwise interaction to the partition function is determined by the statistical integral

\[
Z = \text{Sp} e^{-\beta H(p, x)} = \int \int \frac{dx \, dp}{2\pi} e^{-\beta H(p, x)},
\]

where \( \beta = 1/T \) is the inverse temperature and \( H(p, x) \) is the Hamiltonian of a pair. In particular, evaluating the corresponding integral (3) for potential (2), we obtain

\[
Z_r = C_r^{(0)} b^{-(r+1)/(2r)} e^{-b} \Phi(b),
\]

where

\[
\Phi(b) = C_r^{(1)} M\left(\frac{1}{2r}; \frac{1}{2}; b\right) + 2\sqrt{b} C_r^{(2)} M\left(\frac{r + 1}{2r}; \frac{1}{2}; b\right)
\]

and \( M \) is a confluent hypergeometric function (the Kummer function) in the notation in [5] (see also [6]). For \( r > 1 \), the constants are

\[
C_r^{(0)} = \frac{a^{r+1}}{\pi 2^{1/r} \Gamma\left(\frac{r+1}{r}\right)},
\]

\[
C_r^{(1)} = 2 \cos \frac{\pi}{2r} \Gamma\left(\frac{r-1}{2r}\right),
\]

\[
C_r^{(2)} = \left[1 + (-1)^r\right] \sin \frac{\pi}{2r} \Gamma\left(\frac{2r-1}{2r}\right),
\]

and the variable \( b = \beta a^{2r} \) is related to the temperature. For odd \( r \), we have the coefficient \( C_r^{(2)} = 0 \), and for \( r = 1 \), the constant \( C_r^{(1)} \) is not defined but can be replaced by the corresponding limit value. For \( r = 2 \), the partition function can be obtained using the partial value of the Kummer function and has the simpler form

\[
Z_2 = \frac{a^3}{4} \sqrt{\frac{\pi}{b}} e^{-b/2} \left[I_{-1/4}\left(\frac{b}{2}\right) + I_{1/4}\left(\frac{b}{2}\right)\right].
\]