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Dynamic statistical sum and temperature of an isolated body

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Analysis of the thermoelastic Joule–Thomson effect indicates the need to separate the total energy of an isolated body into two components — the quasi-static energy of elastic deformation, which includes thermal expansion, and the energy of atomic vibrations. A dynamic statistical sum is proposed as an analysis tool, which allows one to calculate the average values of observed values over a long period of time, including in the presence of external time-dependent forces. Based on the fact that, in accordance with the ergodic hypothesis, the limit of the dynamic statistical distribution for an isolated body is the microcanonical distribution, and for its subsystems the canonical Gibbs distribution, a definition of the temperature of an isolated body is proposed. The energy balance in the thermoelastic effect is in full accordance with the first law of thermodynamics for an isolated body.

Keywords: anharmonicity, stochasticity, deformation, energy, temperature.

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1. Introduction

Thermoelastic effect was detected and discussed in classical studies performed by Joule and Thomson [1,2]. Having a long history, it is currently of interest [3–8]. The effect is defined by low temperature variation of an adiabatically isolated body in uniaxial mechanical deformation and is described by the following empirical equation

$$\frac{\Delta T}{T} = -\frac{\alpha\sigma}{c\rho}, \tag{1}$$

where α is the linear thermal expansion coefficient, c is the specific heat capacity, ρ is the density of the body, σ is the mechanical stress. It shall be primarily emphasized that in tension ($\sigma > 0$) the absolute temperature decreases ($\Delta T < 0$ for most of the bodies). It should be also noted that the effect itself is obviously a sign of nonlinearity of interatomic forces (anharmonicity) which is shown by the thermal axpansion coefficient in (1) (see [9]).

In [10], for the simplest anharmonic solid body model — anharmonic oscillator, dynamic explanation is proposed for the thermoelastic effect that is based on the adiabatic invariant in the oscillator dynamics [11]:

$$I = \frac{E}{\omega} \tag{2}$$

with its slow deformation. Oscillation frequency variation ω in this case is a result of anharmonicity [10]:

$$\frac{\Delta\omega}{\omega} \approx -\frac{gF}{f^2}. \tag{3}$$

Here f and g are elastic and anharmonic constants of the oscillator potential, F is the external force. It is shown that empiric equation (1) may be explained by relation (3), if it is naturally assumed that temperature T is proportional to oscillation energy E. Thus, in tension ($F > 0$), the oscillation energy (temperature) decreases. In this case, the mean potential energy (and full energy) of oscillator grows at any sign of the external force F. This ensures fulfilment of the law of conservation of energy when it seems to be violated in case of tension. This suggests that the temperature of body is associated only with that part of the total energy that may be called the oscillation energy W_{osc}. The second part of the total energy is the elastic strain energy of the body U_{o} that, as a consequence of anharmonicity, is non-zero even in the absence of external forces (thermal pressure, [12]). A general definition of these energy components and temperature of the anharmonic solid body will be proposed herein. Since the thermoelastic effect has a dynamic nature [10], a dynamic partition function will serve as the main analysis tool.

2. Dynamic statistical sum

For simplicity, the analysis will be limited by a one-dimensional solid body model — atomic chain with the Hamilton function

$$H(p, x) = \sum_{n=1}^{N} \frac{p_n^2}{2m_n} + U(x) - \sum_{n=1}^{N} F_n x_n, \tag{4}$$

$$U(x) = \frac{1}{2}\sum_{l,n=1}^{N} f_{nl} x_n x_l - \frac{1}{3}\sum_{knl}^{N} g_{knl} x_k x_n x_l, \tag{5}$$

where f_{nl}, g_{knl} are symmetrical matrices of force constants, F_n is the force applied to the n-th atom (force field component). For simplicity, we are limited by the cubic anharmonicity. The way how to consider higher orders of expansion of potential energy will be described below. f_{nl}, g_{knl} matrices are such that $U(x)$ depends only on the difference of coordinates, thus, the potential energy is invariant with respect to shift along the $0x$ axis. The resultant force applied to the chain is considered to be equal to zero and its center of mass is at rest. Our purely dynamic consideration allows dependence of forces on time, but within a limited range or with a limited period. In this case, it is possible to determine the any average value of $A(t)$ within a long time period

$$\langle A\rangle \equiv \frac{1}{t}\int\limits_0^t A(\tau)d\tau. \quad (6)$$

We will be primarily interested in average coordinates and atom pulses for which we will introduce a generating function

$$Z(\alpha,\beta) = \frac{1}{t}\int\limits_0^t \exp\left\{\sum_{n=1}^N [\alpha_n x_n(\tau) + \beta_n p_n(\tau)]\right\} d\tau. \quad (7)$$

Coordinates obey the equations of motion

$$m_n\ddot{x}_n + \sum_{l=1}^N f_{nl}x_l - \sum_{kl}^N g_{knl}x_k x_l - F_n \equiv X_n(\tau) = 0. \quad (8)$$

This will be explicitly considered in generating function (7) using the additional functional integration of δ-function

$$Z(\alpha,\beta) = \frac{1}{t}\int\limits_0^t d\tau \int \prod_{\tau'} d^N x(\tau')\delta\big(X(\tau')\big)$$

$$\times \exp\left\{\sum_{n=1}^N \big[\alpha_T x_n(\tau) + \beta_n p_n(\tau)\big]\right\}, \quad (9)$$

where $p_n = m_n\dot{x}_n$. This function is the sought-for dynamic partition function of chain. We can advance in functional integration using the integral representation of δ-function

$$\delta\big(X(\tau)\big) = \int\limits_{-\infty}^{\infty} \prod_{\tau'} \frac{1}{2\pi} d^N\lambda(\tau')$$

$$\times \exp\left[i\int\limits_0^\tau \sum_n^N \lambda_n(\tau')X_n(\tau')d\tau'\right]. \quad (10)$$

Integrating by parts in the exponent in (10), we obtain

$$I_n \equiv \int\limits_0^\tau \lambda_n(\tau')X_n(\tau')d\tau' = m_n\lambda_n\dot{x}_n\,\big|_0^\tau - m_n\dot{\lambda}_n x_n\big|_0^\tau$$

$$+ \int\limits_0^\tau d\tau'\left(\ddot{\lambda}_n x_n + \lambda_n\sum_{l=1}^N f_{nl}x_l - \lambda_n\sum_{kl}^N g_{knl}x_k x_l - \lambda_n F_n\right). \quad (11)$$

After this transformation, we will be able to take the functional integral over$x_n(\tau)$ in (9):

$$\int \prod_{\tau'} d^N x(\tau')\delta(X(\tau')) = \int \prod_{\tau'} d^N\lambda(\tau')\,\frac{1}{\sqrt{\det G}}\,\exp(\Delta)$$

$$\times \exp\left\{i\sum_n^N \big[m_n\left(\dot{\lambda}_n(0)x_n(0) - \lambda_n(0)\dot{x}_n(0)\right)\big]\right\}$$

$$\times \delta^N(\alpha - im\lambda(\tau))\delta^N\big(\beta + i\lambda(\tau)\big), \quad (12)$$

where

$$\Delta = \frac{i}{4}\int\limits_0^\tau d\tau' \sum_{nk}^N G_{nk}^{-1}\Lambda_n\Lambda_k - \sum_n^N F_n(\tau)\lambda_n(\tau), \quad (13)$$

$$G_{kn} \equiv \sum_l^N \lambda_l g_{lkn}, \quad (14)$$

$$\Lambda_n \equiv \ddot{\lambda}_n + \sum_{l=1}^N \lambda_l f_{nl}. \quad (15)$$

We omitted constant multipliers in expression (12) that are insignificant for determination of the partition function. The initial conditions $x_n(0)$, $\dot{x}_n(0)$ define the initial energy W_{o} of the body. Thus, relation between the dynamic variables $x_n(\tau)$, $p_n(\tau)$ and their initial values was established. It is contained in δ-functions in (12) $(i\lambda(\tau), mi\lambda(\tau))$. It can be easily seen that the Wick rotation $\lambda \to -i\lambda$ makes the last functional integral in (12) well converging and explicitly real. If the examined system is ergodic [13], partition function (9) does not depend on initial conditions on the initial energy surface $W_{\text{o}} = \text{const}$. Here, the dynamic partition function calculation has also approached the place where the role of anharmonicity in the system ergodicity is clearly seen. representation (12) of dynamic part of the partition function (9) makes sense if matrix (14) formed from the cubic anharmonicity coefficients g_{nlk} has a nonzero determinant. It this matrix is degenerate, a part of degrees of freedom is harmonic and does not satisfy the Birkhoff theorem conditions [14] for ergodic systems. To consider the higher orders of anharmonicity in this representation, the perturbation theory rules shall be used by expanding the exponent under the integral sign (10) as a power series in higher order constnats. The next step in the dynamic partition function calculation may be the use of a stationary phase for evaluation of the integral over λ in (12). To define the concept of temperature, it id sufficient here to assume that anharmonicity ensures system ergodicity.

3. Temperature of an isolated body

Since we correlate the temperature of the body with the atom vibration energy W_{osc}, this quantity will be defined in general. For this, quasistatic potential energy of elastic strain of the body U_o will be defined. Recall that this strain in the anharmonic system is also present when there are no external forces (thermal expansion [9]). Let us first find average coordinates of atoms within a long time period using generating function (9):

$$\langle x_n \rangle \equiv \left. \frac{\partial \ln Z(\alpha\beta)}{\partial a_n} \right|_{\alpha,\beta=0}. \tag{16}$$

We substitute these average values into the potential energy of the body and obtain

$$U_\text{o} = U(\langle x_n \rangle). \tag{17}$$

This quantity obviously depends on the total energy of the body and on external forces: $U_\text{o} = U_\text{o}(W, F)$. The remaining part of the total energy falls on the oscillation energy

$$W_\text{osc} = W - U_\text{o}(W, F), \tag{18}$$

this part also depends on the (initial) total energy and external force field: $W_\text{osc} = W_\text{osc}(W_\text{o}, F)$. This dependence constitutes justification of the thermoelastic effect. It is only left to find the correlation between temperature and oscillation energy. The isolated body temperature initially bears the stamp of uncertainty because the concepts of „warm“ and „cold“ make sense only when the bodies are in contact. If the anharmonicity is neglected, we can use the law of equipartition of energy according to which energy $k_\text{B}T$ corresponds „on average“ to one oscillation degree of freedom. This law was formulated and proved using the Gibbs distribution for the harmonic oscillator assembly that are in contact with the thermostat. Such definition of temperature is assumed in [10] and it appears to be quite sufficient for explanation of the thermoelastic effect. It is, however, assumed that the contact between the body and thermostat avoids any thermomechanical effects and an alternative explanation shall be sough for in the thermomechanics of an isolated body. Here, as we have seen, the anharmonicity is a significant factor that ensures ergodicity of the system. According to the ergodic hypothesis, dynamic partition function (9) at $t \to \infty$ coincides with the microcanonical Gibbs distribution (see also [15]). In this case, for any small subsystem of a large isolated body the Boltzmann distribution is fulfilled with high accuracy [16]:

$$p(W') \propto \exp\left(-\frac{w'}{k_\text{B}T}\right), \tag{19}$$

where W' is the subsystem (vibration) energy. In other words, the large isolated body is a thermostat with a particular temperature for its subsystems. To determine the total temperature of the body, we use equation (19) as reference for its parts. Considering the microcanonical distribution to be valid for the body vibration energy individually,

$$\rho = \text{const} \cdot \delta\left(W_\text{osc} - \sum W'\right), \tag{20}$$

we derive equation [15]:

$$\frac{1}{k_\text{B}T} = \left. \frac{\partial \ln Z}{\partial W_\text{osc}} \right|_{\alpha,\beta=0} \tag{21}$$

The use of this equation in case of microcanonical distribution for the harmonic oscillator assembly gives the expected result — vibration energy distribution law: $k_\text{B}T = W_\text{osc}/N$.

4. Conclusion

Finally, we will draw the energy balance in the Joule–Thomson thermoelastic effect. According to the first onset for the isolated body, the work of external force is fully expended on the augmentation of its (full) internal energy. More precisely, according to our construction, the quasistatic potential energy (elastic strain energy) of the body U_o increases. In tension, it is supplemented by (with plus sign) by the work of thermal pressure forces, so the increase of U_o is a little higher than the purely mechanical work. The energy balance is restored exactly due to the thermoelastic effect — decrease of the vibration energy W_osc and the related temperature. Thus, the work of thermal pressure forces is a dynamic effect that restores the energy balance in the parametric reduction of the anharmonic ocsillator energy that is discussed in [10].

Conflict of interest

The authors declare that they have no conflict of interest.

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