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Density matrix and temperature of an isolated body

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The density matrix for an isolated body is defined as the Laplace transform of the density matrix of the Gibbs statistical ensemble. On this basis, the temperature of an isolated body is determined as a function of its energy. The temperature of an isolated ensemble of harmonic oscillators is determined, which is in accordance with the law of equipartition of energy. The thermoelastic effect under mechanical loading of anharmonic oscillators is considered as a consequence of their parametric excitation using adiabatic invariants..

Keywords: energy, quantization, density matrix, anharmonic oscillator, thermoelastic effect

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1. Introduction

The Gibbs distribution cannot be used without isolated body corrections because it predicts non-zero energy fluctuations, while the isolated body energy is constant by default [1]. Certainly, in equilibrium for small subsystems of a large body, this distribution is implemented to a high degree of accuracy. Nevertheless, searching for an adequate replacement for the Gibbs distribution is a matter of principle. This search will be based on close coupling between the nonrelativistic quantum mechanics and statistical Gibbs distribution. It implies that the parabolic equation for statistical operator (density matrix) is

$$-\frac{\partial \rho}{\partial \beta} = \hat{H}\hat{\rho}, \tag{1}$$

where $\beta = 1/(k_{\mathrm{B}}T)$ is derived from the Schrödinger non-steady-state equation through transition to imaginary time [2]:

$$t = -i\hbar\beta. \tag{2}$$

Therefore, possible distribution modification can be also seen. Modification of statistical partition for the isolated body by transition to a covariant quantum theory formalism was proposed in [3]. Covariance is based on the fact that there is no concept of thermostat-defined external temperature or external time for the isolated body. However, the transition to covariant formalism was performed with excessive details that hindered calculations. Unlike [3], this work addresses equation

$$C(p, q) \equiv H(p, q) - E = 0 \tag{3}$$

as the main, rather than supplementary, dynamic equation of constraints or covariant mechanics.

2. Covariant quantum mechanics of the isolated body

Stationary Schrödinger equation is the main equation of „motion“ in the quantum mechanics of isolated body

$$\hat{H}\Psi = E\Psi, \tag{4}$$

and will be addressed herein as the equation of constraints in the covariant quantum theory. For this, we will start from a covariant form of classical mechanics, whose canonical action is written as

$$I = \int_0^1 d\tau \left[p(\tau), \dot{q}(\tau) - N(\tau)C\big(p(\tau), q(\tau)\big)\right], \tag{5}$$

where $N(\tau)$ is an arbitrary Lagrange multiplier; a point indicates a derivative with respect to τ. Selection of path parameterization here is arbitrary and therefore quantization shall be covariant. Transition to the covariant quantum theory is now feasible by writing the propagator for the Schrödinger equation (4) as an invariant functional integral. This theory is generally formulated in the Batalin–Fradkin–Vilkovyssky (BFV) theorem [4,5]. However, in the simplest case of the reparametrization-invariant theory when (5) is applicable, the resulting expression for invariant propagator is derived in the same easy way [6]: solution of the equation

$$-\frac{\partial \hat{\rho}}{\partial \beta} = (\hat{H} - E)\hat{\rho} \tag{6}$$

— density matrix $\rho(q, q'; \beta, E)$, satisfying the initial condition $\rho(q, q'; \beta, E) = \delta(q - q')$ shall be integrated with respect to $\beta \in [0, \infty]$:

$$D(q, q'; E) = \int_0^\infty d\beta \rho(q, q'; \beta, E). \tag{7}$$

The obtained result may be formulated otherwise: $D(q, q';E)$ is the Laplace transform [7] of the density matrix $\rho(q, q';\beta)$ — solution of equation (1) corresponding to the Gibbs distribution, or the operator resolvent $\hat{H}$ [8]. This quantity depending on E, is assumed as the density matrix of the isolated body. Elaborating the form of the initial Lagrange function of the body,

$$L = \frac{1}{2} m_{lk} \dot{q}_l \dot{q}_k - V(q), \tag{8}$$

$\rho(q, q';\beta)$ is written as a functional Feynman integral [9]:

$$\rho(q, q';\beta) = \int Dq \exp\left\{ - \int_0^\beta d\tau \left[\frac{1}{2} m_{lk} \dot{q}_l \dot{q}_k + V \right] \right\}. \tag{9}$$

As for the initial density matrix, $D(q, q;E)$ is supposed to be equal to the density of probability that the system will be identified in the vicinity of point q of the configuration space, and

$$Z(E) = \int dq D(q, q;E) \tag{10}$$

is the partition function for the isolated body. Now, the isolated body temperature is defined as [10]:

$$\frac{1}{k_B T} = \frac{\partial \ln Z(E)}{\partial E}. \tag{11}$$

We are based here on the fact that statistical partition for the isolated body doesn't differ a lot from the Gibbs distribution that is a function of dimensionless ratio $E/(k_{/B}T)$.

3. Temperature of an isolated ensemble of harmonic oscillators

It should be clarified here that, as we assume, thermodynamic equilibrium in the isolated ensemble is established by means of weak anharmonic oscillator interaction that will be neglected in calculations. We use a density matrix for harmonic oscillator in the Gibbs distribution case [2]:

$$\rho_1(q, q';\beta) = \sqrt{\frac{m\omega}{2\pi\hbar \operatorname{sh}(2f)}} \times \exp\left\{ -\frac{m\omega}{2\hbar \operatorname{sh}(2f)} \left[(q + q') \operatorname{ch}(2f) - 2qq' \right] \right\}, \tag{12}$$

where $f = \hbar\omega\beta/2$. Partition function of the oscillator ensemble:

$$Z_N(\beta) = \int \prod_k dq_k \rho_1(q_k, q_k;\beta) = (\operatorname{sh} f)^{-N}. \tag{13}$$

Partition function of the isolated ensemble is found using the Laplace transform:

$$Z_N(E) = \int_0^\infty d\beta Z_N(\beta) \exp(E\beta) = \int_0^\infty d\beta \exp(-N \ln \operatorname{sh} f + E\beta). \tag{14}$$

Integral is calculated approximately in (14) by the saddle-point method [11]:

$$Z_N(E) \approx \sqrt{\frac{2\pi}{N}} \frac{2}{\hbar\omega} \operatorname{sh} f_0 \exp(-N \ln \operatorname{sh} f_0 + E\beta_0), \tag{15}$$

where f_0 is defined as follows

$$\operatorname{cth} f_0 = \frac{2E}{\hbar\omega N}. \tag{16}$$

Note that this relation associates the ensemble temperature with the mean oscillator energy in the statistical Gibbs mechanics assuming that $E/N = \langle E_{\text{osc}} \rangle$ [2]. This is exactly the desired definition of temperature for a large isolated oscillator ensemble. However, we find a correction to the ensemble's intrinsic temperature associated with the ensemble finitrness. According to equation (11), the isolated ensemble temperature with the pe-defined full energy is equal to

$$k_B T = \left(\beta_0 - \frac{\operatorname{ch}^2 f_0}{E} \right)^{-1}. \tag{17}$$

With high oscillator excitation energy

$$k_B T \propto \frac{E}{N - 1}, \tag{18}$$

which corresponds to the law of equipartition of energy at high N. Note that for low N such definition of temperature deviates from the law of equipartition of energy, and is not applicable at all to one oscillator. This is explained by the fact that the intrinsic temperature of the body (ensemble) is set by energy partitioning within the body, rather than in equilibrium with a thermostat.

4. Thermoelastic effect

The initial target of search for statistical partition for the isolated body was a thermoelastic effect [12] meaning that the body temperature varies a little when adiabatic mechanical loading is applied. It is clear that body isolation is an important precondition here. Anharmonic nature of this effect is also obvious. If we limit ourselves to the first order perturbation theory with respect to cubic anharmonicity, adiabatic approximation , where the system energy varies parametrically, will be sufficient to explain the thermoelastic effect (see [13]). In a classical high excitation (temperature) region, the law of equipartition of energy (18) and mechanical adiabatic invariant will be used [14]:

$$J = E/\omega, \tag{19}$$

where the oscillator frequency depends on the external force F —

$$\omega = \omega_0 \sqrt{1 - \frac{2gF}{k}}, \tag{20}$$

and k, g are harmonic and anharmonic constants of potential. Hence, for the isolated oscillator ensemble in adiabatic mechanical loading, we get [13]:

$$\frac{\Delta T}{T} = \frac{\Delta\omega}{\omega_0} = \frac{gF}{k}. \tag{21}$$

In the low excitation (temperature) region, adiabatic invariant should be considered as a medium degree of oscillator excitation $\langle J\rangle$ because quantum transition probability in adiabatic loading tends to zero [15]. Substituting

$$E = N\hbar\omega\left(\langle J\rangle + \frac{1}{2}\right) \tag{22}$$

to (17) and taking into account also that according to (16)

$$\beta_0 = \frac{2}{\hbar\omega}\,\mathrm{arccth}(2\langle J\rangle + 1), \tag{23}$$

we find the temperature of the isolated ensemble of harmonic oscillators at low excitations $\langle J\rangle$:

$$k_{\mathrm{B}}T = \frac{\hbar\omega}{2}\left[\mathrm{arccth}(2\langle J\rangle + 1) - \frac{(2\langle J\rangle + 1)}{(2\langle J\rangle + 1)^2 - 1}\right]^{-1}. \tag{24}$$

Note that at zero oscillator excitation ($\langle J\rangle = 0$), the ensemble temperature is equal to zero as for the Gibbs ensemble. Dependence of temperature on loading is fully defined by the frequency dependence (20), so classical equation (21) is maintained also at low temperatures. This result differs from that in [16], where thermoelastic effect at low temperatures is discussed using the Gibbs distribution.

Here, we discussed the thermoelastic effect in the first order perturbation theory with respect to cubic anharmonicity, where adiabatic approximation was sufficient. High order anharmonicity and perturbation theory should be considered by expanding the power exponent into power series in (9).

5. Conclusion

As expected initially, the isolated body temperature determined using equation (11) is „not much“ different from the Gibbs ensemble temperature. For the harmonic oscillator ensemble, this difference is defined by the second term in square brackets in (24). In the classical high excitation region, this difference disappears, but is considerable at low temperatures:

How to measure the isolated body temperature? Traditional thermometry methods may be used in the classical region. At low excitations according to (24), some macroscopic properties of a thermometric body shall explicitly depend on the degree of body excitation $\langle J\rangle$.

Another question — what energy is the isolated body temperature associated with? If this body is in the force field F, it is deformed and has statistical potential energy $V(q_0)$, where q_0 is the static equilibrium atom configuration. This energy is obviously not associated with the isolated body temperature and shall be subtracted from the full internal energy. Moreover, if the anharmonic body is excited (heated), it is also deformed, and there is a corresponding contribution to energy. However, these continuous contributions to energy occur automatically when integrals (9) and (10) are calculated by the saddle-point method, and for the Laplace transform (7), they are also automatically subtracted from the full energy E. This justifies separation of macroscopic deformation potential energy from the full body energy [17] and simultaneously makes it superfluous in the proposed formalism.

Conflict of interest

The authors declare that they have no conflict of interest.

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