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A second generalized equipartition theorem[a)]

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It is a truism of classical statistical mechanics that each independent degree of freedom (each separate co-ordinate) contributes to the average thermal energy $\langle E \rangle$ an amount $k_B T/2$. Many texts exhibit this result for the one-dimensional kinetic energy $(E = P_x^2/2m)$, the har-monic oscillator $(E = P_x^2/2m + \frac{1}{2}ax^2)$, or the symmetric linear top $(E = \frac{1}{2}I(\dot\omega_1^2 + \dot\omega_2^2))$. The more general result, that any coordinate q which contributes quadratically to the energy of a system (i.e., $E = aq^2 + F$, F being inde-pendent of q) contributes $k_B T/2$ to the average thermal energy, is found in Gibbs' monograph.[1] This result was generalized substantially by Tolman.[2] Using the usual notation for the canonical ensemble average of a vari-able A,

$$\langle A \rangle = Q^{-1} \int dq_1 \, dq_2 \cdots dq_N \, A(q_1, \ldots, q_N)$$
$$\times \exp[-\beta E(q_1, \ldots, q_N)] \,, \tag{1a}$$

$$Q^{-1} = \int dq_1 \, dq_2 \cdots dq_N \, \exp[-\beta E(q_1, \ldots, q_N)] \,, \tag{1b}$$

where $\beta = (k_B T)^{-1}$, Tolman demonstrated

$$\left\langle q_A \frac{\partial E}{\partial q_A} \right\rangle = k_B T \,. \tag{2}$$

Here q_A is an arbitrary coordinate. To obtain Eq. (2), it was assumed that (i) the q_i are canonical conjugate coordinates in the sense of Hamiltonian mechanics, and (ii) as q_A goes to either of its limiting values, the total energy of the system diverges to $+\infty$.

A useful extension of Eq. (2) is here obtained. Equa-tion (2) was originally derived by an integration of parts of Eq. (1b), with respect to an arbitrary variable q_A. A second integration by parts of Eq. (1b), with respect to a second variable q_B, leads to a second generalized equipartition theorem

$$\left\langle q_A q_B \frac{\partial E}{\partial q_A} \frac{\partial E}{\partial q_B} \right\rangle$$
$$= (k_B T)^2 + k_B T \left(\left\langle q_A q_B \frac{\partial^2 E}{\partial q_A \partial q_B} \right\rangle + \left\langle q_B \frac{\partial q_A}{\partial q_B} \frac{\partial E}{\partial q_A} \right\rangle \right) . \tag{4}$$

As q_A and q_B could refer to the same variable, $(\partial q_A/\partial q_B)$ need not necessarily vanish. Equation (4) gives the mean-square energy in the same sense that Eq. (2) gives the mean-thermal energy. For example, for the clas-sical example in which $E = aq^2$, the classical result

$$\langle E^2 \rangle = \tfrac{1}{4}[(k_B T)^2 + 4k_B T \langle E \rangle] = \frac{3(k_B T)^2}{4} \tag{5}$$

follows immediately.

A less familiar case is the mixed quadratic-quartic oscillator for which $E = aq^2 + bq^4$ where $a, b \geq 0$. Morita and Frood[3] and Booth[4] have discussed the importance of this potential in the treatment of ferroelectric crystals, and methods for its application. For this potential, Eqs. (2) and (4) indicate

$$\langle E \rangle = \tfrac{1}{2}k_B T - \langle bq^4 \rangle \,, \tag{6a}$$

$$\langle E^2 \rangle = \tfrac{3}{4}(k_B T)^2 + 2k_B T \langle bq^4 \rangle - 3\langle b^2 q^8 \rangle) - 2\langle abq^6 \rangle \,. \tag{6b}$$

The effect of the anharmonicity is to reduce the average energy. The average displacements $\langle q^4 \rangle$, $\langle q^6 \rangle$, and $\langle q^8 \rangle$ may be obtained by expanding the quadratic part of the statistical weight as a power series in aq^2[3,4] showing

$$\langle q^n \rangle = \frac{1}{(\beta b)^{n/4}} \frac{\sum_{j=0}^{\infty} \Gamma\left(\frac{2j+n+1}{4}\right)(-1)^j \left(\frac{\beta a^2}{b}\right)^{j/2} [j!]^{-1}}{\sum_{j=0}^{\infty} \Gamma\left(\frac{2j+1}{4}\right)(-1)^j \left(\frac{\beta a^2}{b}\right)^{j/2} [j!]^{-1}} \,. \tag{7}$$

Given the lamentations over the disappearance of classical Hamiltonian mechanics from the modern theo-retical curriculum, it seems worthwhile to extend Eqs. (2) and (4) to an arbitrary set of coordinates. Gibbs demonstrates that if the phase space integral in Carte-sian coordinates is $\int dx \, dy \, dz \, dp_x \, dp_y \, dp_z \exp(-\beta E)$, the Jacobian of the transformation to any other set of canon-ically conjugate coordinates is unity. Therefore, if one goes to, e.g., spherical polar coordinates, the phase space integral becomes $\int dr \, d\theta \, d\phi \, dp_r \, dp_\theta \, dp_\phi \exp(-\beta E)$ where p_r, p_θ, p_ϕ are the coordinates conjugate to (r, θ, φ), respectively. There are no factors $p_r^2 \sin(p_\theta)$ in

the phase space integral. For some purposes, it might be more convenient to work in a system in which the Jacobian $|J|$ is not unity, in which case the phase space integral becomes

$$Q = \int dq_1 \, dq_2 \cdots dq_N \, |J|^{-1} \exp(-\beta E)$$

and the generalized equipartition theorems become

$$\left\langle q_A \frac{\partial E}{\partial q_A} \right\rangle = k_B T \left\{ 1 - \left\langle q_A \frac{\partial \ln|J|}{\partial q_A} \right\rangle \right\} , \tag{9a}$$

$$\left\langle q_A q_B \frac{\partial E}{\partial q_A} \frac{\partial E}{\partial q_B} \right\rangle = (k_B T)^2 \left\{ 1 - 2 \left\langle q_A q_B \frac{\partial \ln|J|}{\partial q_A} \frac{\partial \ln|J|}{\partial q_B} \right\rangle \right.$$

$$+ \left\langle q_A q_B \frac{\partial^2 |J|}{\partial q_A \partial q_B} |J|^{-1} \right\rangle + \left\langle q_B \frac{\partial q_A}{\partial q_B} \frac{\partial \ln|J|}{\partial q_A} \right\rangle \right\}$$

$$+ k_B T \left\{ \left\langle q_A q_B \frac{\partial^2 E}{\partial q_A \partial q_B} \right\rangle + \left\langle q_B \frac{\partial q_A}{\partial q_B} \frac{\partial E}{\partial q_A} \right\rangle \right\}$$

$$- \left\langle q_A q_B \left(\frac{\partial E}{\partial q_A} \frac{\partial \ln|J|}{\partial q_B} + \frac{\partial E}{\partial q_B} \frac{\partial \ln|J|}{\partial q_A} \right) \right\rangle . \tag{9b}$$

For an atom of a three-dimensional monoatomic gas, $E = (p^2/2m)$. For spherical polar coordinates for p, $|J_p|^{-1} = p^2 \sin\theta_p$; the well known results $\langle E \rangle = \frac{3}{2} k_B T$ and $\langle E^2 \rangle = \frac{15}{4}(k_B T)^2$ follow.

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Two-component bimolecular systems cannot have limit cycles: A complete proof

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Hanusse[1] studied in 1972 the oscillatory behavior of two-component bimolecular reaction systems. He classified the stationary states that might occur in such systems and proved that among those, the nodes and foci must remain stable for any values of rate constants. Thus, in case of mono- and bimolecular reactions the phase plane cannot contain limit cycles surrounding unstable nodes and foci. In 1973, Tyson and Light[2] independently performed the classification of the stationary states. From the stability of nodes and foci they concluded that in the phase plane limit cycles cannot occur, except in "unusual cases." By analyzing the conservative oscillations left, they stated that in two-component bimolecular systems there is only one oscillator, the conservative Volterra–Lotka model.

These general statements are now rather widely known.[3–6] However, Tyson and Light have already indicated themselves that from a mathematical point of view their approach is a conjecture only, since in a strict way the stability of the nodes and foci does not imply the absence of limit cycles. For example, one may suppose that there are two limit cycles around a stable focus, one of them being stable the other unstable. Tyson and Light considered this an unlikely case, given the limitations of bimolecular mass-action kinetics in planar systems.

The aim of this short note is to present a strict proof of statements of Tyson and Light.[2]

By the aid of Dulac's criterion,[7(a)] this can be done in a surprisingly easy way. Henceforth, we shall apply the notation of Tyson and Light.[2] Let us consider a homogeneous isothermal system which includes mono-, and bimolecular reactions only. The system is open to matter transport, so we may hold the concentrations of components fixed—except for the two intermediates interesting us. According to the mass-action kinetics the concentrations of the two intermediates are described by the following equations[2]:

$$\dot{x} = k_0 \pm k_1 x + k_2 y - k_3 x^2 \pm k_4 x y + k_5 y^2 , \tag{1}$$

$$\dot{y} = c_0 \pm c_1 y + c_2 x - c_3 y^2 \pm c_4 x y + c_5 x^2 .$$

Dulac's criterion states the following[7(a)]: Let G be a simply connected domain in the domain of analytic system

$$\dot{x} = P(x, y), \quad \dot{y} = Q(x, y) . \tag{2}$$

If there exists a continuously differentiable function $B: G \to R$, such that expression

$$D = \frac{\partial}{\partial x}(BP) + \frac{\partial}{\partial y}(BQ) \tag{3}$$

has constant sign on G, then G does not contain simple closed curves consisting of trajectories of system (2). Assume that system (1) has a closed trajectory in the positive quadrant and that positive domain G contains this trajectory. Since the right-hand sides of Eqs. (1) are analytic, Dulac's criterion can be applied. The key step of the proof is to find an appropriate B function. Define B on domain G simply as $B(x, y) = (xy)^{-1}$ and compute value $D(x, y)$. After algebraic manipulations and differentiation we have