In conclusion it should be pointed out that the use of the classical-path approximation down to $\hbar$ is rather extreme and quantum effects are possibly significant in this region. Nevertheless the present treatment of strong collisions should be an improvement over previous treatments.

ACKNOWLEDGMENTS

The author would like to express his appreciation to Dr. W. G. Braun and Dr. J. W. Birkeland for the opportunity of working in the Plasma Physics Research Laboratory at the Aerospace Research Laboratories. Thanks are also due to Dr. J. Cooper for his interest and encouragement during the course of this work, to Captain R. Franklin for his help with various programming problems that the author had, and to J. Raymond of the Systems Engineering Group ASD (SEQ) at Wright Field who developed the program for determining the radial integrals involved in the present calculations.

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[1]M. E. Bacon, K. Y. Shen, and J. Cooper, Phys. Rev. 188, 50 (1969).

[2]M. E. Bacon, Aerospace Research Laboratories Report No. 70-0276, 1970 (unpublished).

[3]H. R. Griem, Plasma Spectroscopy (McGraw-Hill, New York, 1964).

[4]C. F. Hooper, Jr., Phys. Rev. 149, 77 (1966); 165, 215 (1968); 169, 193 (1968).

[5]H. R. Griem, A. C. Kolb, and K. Y. Shen, Phys.

Rev. 116, 4 (1959).

[6]M. E. Bacon and D. F. Edwards, Phys. Rev. 170, 125 (1968); Aerospace Research Laboratories Report No. 69-0109, 1969 (unpublished).

[7]K. Y. Shen and J. Cooper, Astrophys. J. 165, 37 (1969). The application of the formalism developed in this paper was extended to the two-state case for the calculations characterized as SC in this report (see Ref. 2).

[8]P. Kepple and H. R. Griem, Phys. Rev. 173, 317 (1968); P. Kepple, University of Maryland Technical Report No. 831, 1968 (unpublished).

Entropy, the Wigner Distribution Function, and the Approach to Equilibrium of a System of Coupled Harmonic Oscillators*

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(Received 28 August 1970)

The entropy is determined of a quantum-mechanical system whose statistical state is characterized by a Wigner distribution function that is Gaussian in form. It is found to depend only on the variance of the distribution function. This enables us to study quantum mechanically the approach to equilibrium of coupled harmonic-oscillator chains, a system for which a classical treatment has been given recently by Robertson and Huerta.

In this paper we calculate the entropy of a quantum-mechanical system that is in a state characterized by a Wigner distribution function[1,2] which is Gaussian in form. We then study the approach to equilibrium of a system of an infinite harmonically bound weakly coupled *quantum-mechanical* harmonic-oscillator chain. The approach to equilibrium of this system, when each harmonic oscillator is replaced by a classical harmonic oscillator, has been recently studied in great detail by Robertson and Huerta.[3,4] We find that the reduced N-particle Wigner distribution function is the same as the classical one that was calculated by Robertson and Huerta [Ref. 3(a), Eq. (9)]. We also find that in the limit as $t \to \infty$ the entropy is the same as the equilibrium entropy for a system of N-independent quantum oscillators.

Let the quantum-mechanical system be in a state characterized by a Wigner distribution function of the form

$$f^{(W)}(q,p) = [(2\pi)^2(\alpha\beta - \gamma^2)]^{-1/2}$$

$$\times \exp\left(-\frac{1}{2}\frac{\alpha q^2 + \beta p^2 - 2\gamma qp}{\alpha\beta - \gamma^2}\right). \qquad (1)$$

The parameters α, β, and γ may be shown to be related to the average values of the operators $\hat{q}^2$, $\hat{p}^2$, and $\hat{q}\hat{p}$ by the following relations:

$$\alpha = \langle\hat{p}^2\rangle, \quad \beta = \langle\hat{q}^2\rangle, \quad \gamma = \tfrac{1}{2}\langle\hat{q}\hat{p} + \hat{p}\hat{q}\rangle . \qquad (2)$$

We shall show that such a Wigner distribution function occurs in the problem mentioned above. It also occurs in other problems such as parametric amplification[5(a)] and Browian motion.[5(b)]

The entropy of a quantum-mechanical system in a state characterized by the density operator $\hat{\rho}$ is given by

$$S = - k_B \, \text{Tr}(\hat{\rho} \ln \hat{\rho}) \equiv - k_B \langle \ln \hat{\rho} \rangle \; , \tag{3}$$

where k_B is the Boltzmann constant. The entropy S can thus be calculated if $\ln \hat{\rho}$ is known. We will first calculate $\hat{\rho}$ corresponding to the Wigner distribution function (1). It is well known that there is one, and only one, density operator corresponding to a given Wigner distribution function and this is obtained by

$$\hat{\rho} = \Omega^{(W)}[2\pi f^{(W)}(q,p)] \; , \tag{4}$$

where $\Omega^{(W)}$ is the mapping operator for the Weyl rule of association.[6] The relation (4) can be rewritten

$$\hat{\rho} = \Omega^{(S)}[2\pi f^{(S)}(q,p)] \; , \tag{5}$$

where $\Omega^{(S)}$ is the mapping operator for the standard rule of association and $f^{(S)}(q,p)$ is the phase-space distribution function which is obtained from $\hat{\rho}$ by the standard rule of mapping.[6] It is easily shown that $f^{(S)}(q,p)$ is related to $f^{(W)}(q,p)$ by the following formula:

$$f^{(S)}(q,p) = (2\pi)^{-2} \int\int dx \, dy \, \exp(\tfrac{1}{2}ixy - ixq - iyp)$$

$$\times \int\int dq_0 \, dp_0 \, f^{(W)}(q_0, p_0) \exp(ixq_0 + iyp_0) \; .$$

On substituting (1) into (6), we find that $f^{(S)}(q,p)$ is given by

$$f^{(S)}(q,p) = [(2\pi)^2(\alpha\beta - \gamma'^2)]^{-1/2} \tag{6}$$

$$\times \exp\left(-\frac{1}{2} \frac{\alpha q^2 + \beta p^2 - 2\gamma' qp}{\alpha\beta - \gamma'^2}\right) , \tag{7}$$

where

$$\gamma' = \gamma - \tfrac{1}{2}i \; . \tag{8}$$

The density operator $\hat{\rho}$ is then obtained by expressing $(2\pi f^{(S)})$ in standard form, i.e., by putting all the q operators to the left of all the p operators. Now $\hat{\rho}$ may be expressed in the form $\exp(\hat{G})$, where $\hat{G}$ is an operator that may be determined with the help of the identity[7]

$$\exp(a\hat{p}^2 + b\hat{q}^2 + c\hat{q}\hat{p} - g) = \Omega^{(S)}[\exp(Ap^2 + Bq^2 + Gqp)] \; , \tag{9}$$

where

$$a = H^{-1}A, \quad b = H^{-1}B, \quad c = \tfrac{1}{2}iH^{-1}(4AB - G^2 - 2iG) \; ,$$

$$g = \tfrac{1}{2} \ln(1 - iG) + \tfrac{1}{2}ic, \quad J = (1 - iG)^{-1} \; , \tag{10}$$

$$H^{-1} = \frac{2J^2 \cosh^{-1}\{(2J)^{-1}[J^2(1 + 4AB) + 1]\}}{[J^4(1 + 4AB)^2 + 1 - 2J^2 + 8ABJ^2]} \; .$$

A straightforward, but lengthy, calculation gives then the following expression for $\hat{\rho}$:

$$\hat{\rho} = [\tfrac{1}{4}(e^{2\varphi} - 1)]^{-1/2} \exp\{- e^{-\varphi} \cosh^{-1}(\coth\varphi)$$

$$\times [\alpha\hat{q}^2 + \beta\hat{p}^2 - \gamma(\hat{q}\hat{p} + \hat{p}\hat{q})]\} \; , \tag{11}$$

where

$$\varphi = \tfrac{1}{2} \ln[4(\alpha\beta - \gamma^2)] \; . \tag{12}$$

Hence $\ln \hat{\rho}$ is given by

$$\ln\hat{\rho} = - \tfrac{1}{2} \ln[\tfrac{1}{4}(e^{2\varphi} - 1)] - e^{-\varphi} \cosh^{-1}(\coth\varphi)$$

$$\times [\alpha\hat{q}^2 + \beta\hat{p}^2 - \gamma(\hat{q}\hat{p} + \hat{p}\hat{q})] \; . \tag{13}$$

The expression for the entropy is then obtained by substituting from (13) into (3) and by making use of (2). One then finds that

$$S = \tfrac{1}{2}k_B \ln(\tfrac{1}{2}e^{\varphi} \sinh\varphi) + \tfrac{1}{2}k_B e^{\varphi} \cosh^{-1}(\coth\varphi) \; . \tag{14}$$

This expression for entropy can be rewritten as follows:

$$S = k_B[(\sigma + 1) \ln(\sigma + 1) - \sigma \ln\sigma] \; , \tag{15}$$

where

$$\sigma = [(\alpha\beta - \gamma^2)^{1/2} - \tfrac{1}{2}] \; . \tag{16}$$

Expression (15) represents the entropy of a quantum-mechanical system in a statistical state characterized by the Wigner distribution function that has the Gaussian form [Eq. (1)]. It is worth noting that the entropy depends only upon the variance of the Wigner distribution function. It should also be noted that the expression (15) has the same form as the entropy of a system of harmonic oscillators in thermal equilibrium. In the latter case, σ represents, of course, the average of the number operator $(\hat{a}^\dagger \hat{a})$.

We now study the approach to equilibrium of an infinite harmonically bound weakly coupled harmonic-oscillator chain. The classical treatment of this problem is given by Robertson and Huerta.[3,4] Our treatment is completely *quantal*. The Hamiltonian for such a system is given by

$$\hat{H} = \sum_{n = -\infty}^{+\infty} [\hat{p}_n^2/2m + \tfrac{1}{2}k(\hat{q}_{n+1} - \hat{q}_n)^2 + \tfrac{1}{2}Kq_n^2] \; . \tag{17}$$

The Heisenberg equations of motion are easily solved and it is then found that

$$\hat{q}_n(t) = \sum_{r = -\infty}^{+\infty} [\hat{q}_{n+r}(0)f_r(t) + \hat{p}_{n+r}(0)g_r(t)/m\Omega] \; , \tag{18a}$$

$$\hat{p}_n(t) = m \frac{d\hat{q}_n}{dt} \; , \tag{18b}$$

where, in the weak-coupling limit $(k \ll K)$ one has

$$f_r(t) = J_r(\gamma \Omega t) \cos(\Omega t - \tfrac{1}{2}r\pi) \; , \tag{19a}$$

$$g_r(t) = J_r(\gamma \Omega t) \sin(\Omega t - \tfrac{1}{2}r\pi) \; . \tag{19b}$$

Here we have

$$\Omega^2 = (K + 2k)/m, \quad \omega^2 = k/m, \quad \gamma = (\omega/\Omega)^2 \; , \tag{20}$$

and J_r is the Bessel function of first kind and order r.

The Wigner distribution function is given by

$$f^{(W)}[\{q_n\}, \{p_n\}; t] = \int \dots \int d\{x_r/2\pi\} \, d\{p_r/2\pi\} \exp[-i\textstyle\sum_r(q_r x_r + p_r k_r)] \, \text{Tr}\{\rho(t) \exp[i\textstyle\sum_r (\hat{q}_r x_r + \hat{p}_r k_r)]\}$$

$$= \int \dots \int d\{x_r/2\pi\} \, d\{p_r/2\pi\} \exp[-i\textstyle\sum_r (q_r x_r + p_r k_r)] \, \text{Tr}\{\rho(0) \exp[i\textstyle\sum_r (\hat{q}_r(t) x_r + \hat{p}_r(t) k_r)]\} \quad .$$
$$\tag{21}$$

The reduced N-particle Wigner distribution is obtained as usual by integrating over coordinates of the remaining particles. We assume that the initial Wigner distribution function be given by [cf. Ref. 3(a), Eq. (8)]

$$f^{(W)}[\{q_n\}, \{p_n\}; 0] = \prod_{n=1}^{N} [(2\pi)(\alpha_0\delta_0)]^{-1} \exp\left(-\frac{1}{2\alpha_0^2} (q_n - u_n)^2 - \frac{1}{2\delta_0^2} (p_n - v_n)^2\right)$$

$$\times \prod{'} (2\pi\zeta\epsilon)^{-1} \exp\left(-\frac{1}{2\epsilon^2} q_n^2 - \frac{1}{2\zeta^2} p_n^2\right) ,$$
$$\tag{22}$$

where $\prod{'}$ denotes the product over the rest of the members in the chain. The N-particle distribution function is then obtained by using (22), (21), and (18). The mathematical steps involved in this calculation are the same as given in Ref. 4, and hence we merely quote the result:

$$f^{(W)}[\{q_n\}, \{p_n\}; t] = (2\pi)^{-N}(\det W)^{-1/2} \exp\left(-\tfrac{1}{2}\tilde{X} W^{-1} X\right) ,$$
$$\tag{23}$$

where $\tilde{X}$ is the row vector,

$$\tilde{X} = (q_1 - \langle\hat{q}_1(t)\rangle, \dots, q_n - \langle\hat{q}_n(t)\rangle, p_1 - \langle\hat{p}_1(t)\rangle, \dots, p_n - \langle\hat{p}_n(t)\rangle) ,$$

and

$$W = \begin{pmatrix} M & H \\ \tilde{H} & Q \end{pmatrix} , \quad M_{ij} = [\langle\hat{q}_i(t)\hat{q}_j(t)\rangle - \langle\hat{q}_i(t)\rangle\langle\hat{q}_j(t)\rangle] ,$$

$$Q_{ij} = [\langle\hat{p}_i(t)\hat{p}_j(t)\rangle - \langle\hat{p}_i(t)\rangle\langle\hat{p}_j(t)\rangle] , \quad H_{ij} = \tfrac{1}{2} [\langle\hat{q}_i(t)\hat{p}_j(t) + \hat{p}_j(t)\hat{q}_i(t)\rangle - 2\langle\hat{q}_i(t)\rangle\langle\hat{p}_j(t)\rangle] .$$
$$\tag{24}$$

We thus find that the N-particle Wigner distribution function is multidimensional Gaussian in form. The average values are given by

$$\langle\hat{p}_r^2/2m\rangle = \int \dots \int d\{p_n\} d\{q_n\} (p_r^2/2m) f^{(W)}[\{q_n\}, \{p_n\}; t]$$

$$= \tfrac{1}{4}m\,\Omega^2\epsilon^2 [1 - J_0(2\gamma\,\Omega t)\cos(2\Omega t)] + (\zeta^2/4m)[1 + J_0(2\gamma\,\Omega t)\cos(2\Omega t)]$$

$$\longrightarrow \Big|\, \tfrac{1}{2}(\zeta^2/2m + \tfrac{1}{2}m\Omega^2\epsilon^2), \quad \text{as } t \to \infty$$
$$\tag{25a}$$

and

$$\tfrac{1}{2}m\Omega^2\langle\hat{q}_r^2\rangle = \int \dots \int d\{p_n\} \, d\{q_n\}\tfrac{1}{2}m\Omega^2 q_r^2 f^{(W)}[\{q_n\}, \{p_n\}; t]$$

$$= \tfrac{1}{4}m\Omega^2\epsilon^2 [1 + J_0(2\gamma\,\Omega t)\cos(2\Omega t)] + (\zeta^2/4m)[1 - J_0(2\gamma\,\Omega t)\cos(2\Omega t)] \longrightarrow \tfrac{1}{2}(\zeta^2/2m + \tfrac{1}{2}m\Omega^2\epsilon^2), \quad \text{as } t \to \infty. \tag{25b}$$

Equations (25a) and (25b) imply the equipartition of energy for $t \to \infty$. We introduce a *temperature* T defined by the formula

$$(1/\Omega)\,(p^2/2m + \tfrac{1}{2}m\Omega^2\epsilon^2) - \tfrac{1}{2} = [\exp(\Omega/k_BT) - 1]^{-1} \equiv \bar{n}(\text{say}) . \tag{26}$$

It is also found that as $t \to \infty$, we have

$$f^{(W)}[\{q\}, \{p\}; t] \longrightarrow \prod_{n=1}^{N} [2\pi(\bar{n} + \tfrac{1}{2})]^{-1} \exp[-(\bar{n} + \tfrac{1}{2})^{-1}(\tfrac{1}{2}m\Omega q_n^2 + p_n^2/2m\Omega)], \quad \text{as } t \to \infty. \tag{27}$$

The entropy is then obtained by comparing (27) with (1) and by using (15). It is found that

$$S = Nk_B[(\bar{n} + 1)\ln(\bar{n} + 1) - \bar{n}\ln\bar{n}] . \tag{28}$$

It is obvious that (28) is equal to the entropy of a system of N-independent quantum harmonic oscillators interacting with a heat bath at temperature T, given by (26). We therefore find that as $t \to \infty$ this quantal system approaches equilibrium as it should.

[1]E. Wigner, Phys. Rev. **40**, 749 (1932).

[2]J. E. Moyal, Proc. Cambridge Phil. Soc. **45**, 99 (1949).

[3](a) H. S. Robertson and M. A. Huerta, Phys. Rev.

Letters 23, 825 (1969); (b) Am. J. Phys. 38, 619 (1970).

[4]M. A. Huerta and H. S. Robertson, J. Stat. Phys. 1, 393 (1969).

[5](a) B. R. Mollow and R. J. Glauber, Phys. Rev. 160, 1076 (1967); (b) G. S. Agarwal (unpublished).

[6]G. S. Agarwal and E. Wolf, Phys. Rev. Letters 21,

180 (1968); Phys. Rev. D 2, 2161 (1970); 2, 2187 (1970); 2, 2206 (1970).

[7]This identity may be obtained by the inversion of the identity (10.27) of R. M. Wilcox [J. Math. Phys. 8, 962 (1967)] and by appropriate change of variables.

Nonresonant Vibrational Excitation of CO_2 by Electron Collision

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(Received 31 August 1970)

Experimental cross sections for the electron-impact vibrational excitation of CO_2 are compared with the theoretical calculation in the Born approximation. It is found that the optically forbidden mode (100) can be excited through the polarization interaction, whereas the dipole interaction is responsible for the excitation of both the infrared-active modes (010) and (001).

In a recent paper, Stamatovic and Schulz[1] summarized the experimental results of the nonresonant vibrational excitation of CO_2 by electron impact, which had been obtained by several investigators. Comparing with the Born calculation, they concluded that the experimental ratio of the cross sections for the (010) and (001) vibrational levels of CO_2 can be satisfactorily explained by the theory of dipole excitations. However, such a theory cannot be applicable to the excitation of the infrared-inactive level (100). In the present note, it is examined whether the (100) mode can be excited through the polarization interaction between the incident electron and CO_2. Also, more elaborate comparisons will be made between the theoretical and experimental cross sections for the dipole excitation of the (010) and (001) levels.

In the first Born approximation, the cross section for the vibrational transition $v \rightarrow v'$ through the polarization interaction is obtained in the form[2] (in atomic units)

$$\sigma(v \rightarrow v') = |\langle v' | \alpha | v \rangle|^2 \frac{k'}{k} \int d\hat{k}' N^2 K^2,$$

$$N = \frac{1}{K^2} \int_0^\infty dr \frac{1}{r^3} \sin(Kr) C(r),$$

(1)

where $\vec{k}, \vec{k}'$ are, respectively, the initial and final wave vectors of the scattered electron ($\hat{k}'$ being the unit vector along $\vec{k}'$), $\vec{K} = \vec{k} - \vec{k}'$, $\langle v' | \alpha | v \rangle$ is the matrix element of the (spherical) polarizability of CO_2 between the initial and final vibrational states, and $C(r)$ is the cutoff function which enters to remove the singularity of the potential at the origin. The form

$$C(r) = 1 - e^{-(r/r_c)^6}$$

(2)

is adopted here,[2] where r_c is the so-called cutoff

distance. The value of the matrix element of α between the ground and the (100) vibrational levels can be estimated from the Raman intensity measurement[3] to be

$$|\langle 100 | \alpha | 000 \rangle | = 0.52 \text{ a.u.}$$

The contribution from the nonspherical part of the polarizability is of minor importance, as has been shown in the case of N_2 and H_2.[2]

Now we compare the theoretical result in the Born approximation with the experimental values. Table I shows the ratio of the vibrational cross sections for the (010) and (100) levels normalized to that for the (001) level. For comparison with the experimental data, the differential cross sections have been calculated. For the polarization excitation, the formula (1) before integrating over $d\hat{k}'$ gives the differential cross section. For the dipole excitation, the Born formula[4]

$$\sigma(v \rightarrow v'; \theta) = \frac{4}{3} \frac{k'}{k} |\langle v' | D | v \rangle|^2 \frac{1}{k^2 + k'^2 - 2kk' \cos\theta}$$

(3)

TABLE I. Comparison between the experimental and theoretical ratios of cross sections for excitation of the fundamental vibrational modes in CO_2.

Energy (eV)	Scattering angle		Modes (100)	(010)	(001)
1.9[a]	3.5°	Expt	0.03	1.0	1.0
		Theory	0.01	0.64	1.0
	15°	Expt	0.08	0.4	1.0
		Theory	0.06	0.28	1.0
35[b]	2°	Expt	0.06	0.38	1.0
		Theory	0.02	0.26	1.0

[a]Experiment by Andrick *et al.* (Ref. 6).
[b]Experiment by Skerbele *et al.* (Ref. 7).