Elias P. Gyftopoulos

email: epgyft@aol.com
Massachusetts Institute of Technology
Room 24-111
77 Massachusetts Avenue
Cambridge, MA 02139

Michael R. von Spakovsky

email: vonspako@vt.edu
Virginia Polytechnic Institute and State
University
Energy Management Institute
Department of Mechanical Engineering
Blacksburg, VA 24061-0238

Quantum-theoretic Shapes of Constituents of Systems in Various States

In previous publications, it has been shown that entropy is a measure of the quantum-theoretic shape of the constituents of a system. In this paper, we present examples of quantum-theoretic shapes of some systems each consisting of one unit of a single constituent, in either a stable (thermodynamic) equilibrium state or in states that are not stable equilibrium. The systems that we consider are a structureless particle confined in either a linear box or a square box, and a harmonic oscillator. In general, we find that the shape of each constituent is "smooth"—without ripples—for each thermodynamic equilibrium state, and oscillatory or rippled for states that are either nonequilibrium or unstable equilibrium. [DOI: 10.1115/1.1525245]

1 Introduction

In the exposition of thermodynamics by Gyftopoulos and Beretta [1], entropy is shown to be a nonstatistical property—to have a value at an instant in time independent of statistical probabilities and other times—of the constituents of any system in any state in the same sense that inertial mass is a property of the constituents of any system in any state. Said differently, no statistical probabilities that reflect the inabilities of scientists and engineers to make complicated calculations at an instant in time are required and relevant to the understanding of thermodynamic phenomena.

In contrast to the plethora of entropy expressions appearing in various formulations of statistical mechanics, in the unified quantum theory of mechanics and thermodynamics by Hatsopoulos and Gyftopoulos [2], and in an article by Gyftopoulos and Cubukcu [3], the entropy of thermodynamics is shown to be represented by one and only one functional of a special quantum mechanical density operator ρ. A brief discussion of this operator is given in the Appendix, Part I.

In many textbooks, the probability density function associated with measurement results of the spatial coordinates of the constituents of a system is interpreted as the spatial shape of the constituents of the system (Leighton [4]; Brandt and Dahmen [5]), and the shape is used to calculate atomic, molecular, and ionic radii (Slater [6]) as well as explain the formation of various compounds. The probability density function of the spatial coordinates also enters into the evaluation of the entropy S. Therefore, we can think of entropy as a measure of the spatial shape of the constituents of a system and, thus, achieve a pictorial visualization of a concept that has been puzzling scientists and engineers for over more than a century.

In what follows, we present examples of quantum-theoretic shapes of some systems, each consisting of one unit of a single constituent in various states: nonequilibrium, equilibrium, and stable (thermodynamic) equilibrium. In general, we find that the shape of each constituent is oscillatory or rippled for states that are either nonequilibrium or unstable equilibrium, and smooth—without ripples—for each stable equilibrium state.

2 Particle in a Linear Box

2.1 Energy Eigenstates. We consider a structureless particle of mass M confined in a linear box—infinitely deep potential

well—extending from x=−d to x=d (Fig. 1). The Hamiltonian operator of such a particle is given by the relation

$$H = -\frac{\hbar^2}{2M}\frac{d^2}{dx^2} + V(x) \tag{1}$$

where $\hbar$ is Planck's constant divided by 2π, and $V(x)$ the potential energy such that

$$V(x) = \infty \quad \text{for} \quad |x| > d \tag{1a}$$

$$V(x) = 0 \quad \text{for} \quad |x| \le d \tag{1b}$$

The Hamiltonian operator defines the energy eigenvalue problem

$$H\varphi_n(x) = \varepsilon_n\varphi_n(x) \tag{2}$$

where ε_n and $\varphi_n(x)$ are the nth energy eigenvalue and energy eigenfunction, respectively. We can readily verify that the energy eigenvalues and normalized energy eignfunctions are given by the relations

$$\varepsilon_n = \frac{h^2 n^2}{8Md^2} \quad \text{for all integer values of n} \tag{3}$$

$$\varphi_n(x) = \left(\frac{2}{d}\right)^{0.5}\cos\left(\frac{n\pi x}{d}\right) \quad \text{for} \quad n=1,3,\ldots, \quad \text{and} \quad |x| \le d \tag{4}$$

$$\varphi_n(x) = \left(\frac{2}{d}\right)^{0.5}\sin\left(\frac{n\pi x}{d}\right) \quad \text{for} \quad n=2,4,\ldots, \quad \text{and} \quad |x| \le d \tag{5}$$

$$\varphi_n(x) = 0 \quad \text{for all} \quad \text{and} \quad |x| > d \tag{6}$$

and that each energy eigenfunction yields zero value of momentum, that is,

$$\langle p_n \rangle = \int_{-\infty}^{\infty}\varphi_n^*(x)\frac{\hbar}{i}\frac{d}{dx}\varphi_n(x)dx = 0 \tag{7}$$

where the * indicates the complex conjugate function.

We can use the energy eigenstates to express the probability density function of any state of the particle.

2.2 A Zero Entropy Nonequilibrium State. We consider a zero entropy nonequilibrium state. It is characterized by a value of momentum different than zero, a time dependent wave function—wave packet—

$$\psi(x,t) = \sum_{n=1}^{\infty} a_n\varphi_n(x)\exp(-i\varepsilon_n t/\hbar) \tag{8}$$

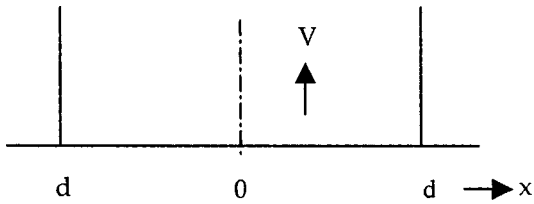and a shape—probability density function—

Fig. 1 Schematic of a linear box.

$$|\psi(x,t)|^2 = \psi^*(x,t)\,\psi(x,t) \tag{9}$$

It is noteworthy that the wave function can also be written as a density operator ρ. In matrix form and in the energy eigenfunction representation, the km-element of the matrix is given by the relation

$$\rho_{km} = a_k^* \exp(+i\varepsilon_k t/\hbar)a_m \exp(-i\varepsilon_m t/\hbar) \quad \text{for all k and m} \tag{10}$$

Moreover, in a representation that has as one of its orthogonal axes $\psi(x, t)$ itself, the density operator matrix of $\psi(x, t)$ is diagonal and has only one element along the diagonal equal to unity.

A graph of the evolution of the shape of the wave packet in time prescribed by the Schroedinger equation is shown in Fig. 2. At t=0, the wave packet is bell-shaped. Then, it moves toward one wall of the linear box, is reflected and eventually spreads so widely as to touch both walls simultaneously. Though the shape of the wave packet changes in time, we can easily prove that its entropy is time independent and equal to zero. In general, any shape determined by a wave function has entropy equal to zero (see Appendix).

Other nonequilibrium states correspond to density operators that cannot be represented by a wave function. The entropy of each such state is positive and in general increasing spontaneously in time.

2.3 A Nonequilibrium and an Equilibrium State of the Same Energy and Same Dimensionality. In many discussions, the terms equilibrium state and thermodynamic (stable) equilibrium state are used as synonyms. They are not. In general the former is unstable. To clarify the difference, we consider a nonequilibrium state that at an instant in time has a density operator matrix, which in the energy representation is diagonal with only three nonzero elements, that is

$$\rho_{22}=0.1 \quad \rho_{33}=0.2 \quad \rho_{88}=0.7 \tag{11}$$

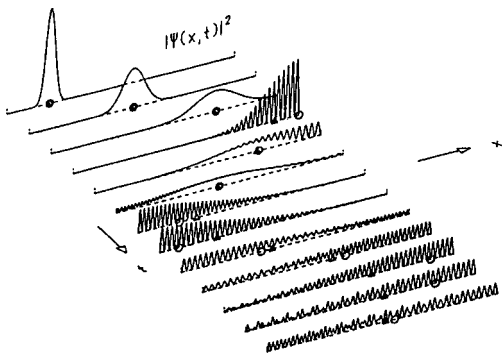The only three energy eigenvalues that are relevant to this state are

Fig. 2 Shape—probability density function versus position and time—of a particle in a linear box (infinitely deep potential well) in a zero entropy nonequilibrium state. Arbitrary dimensionless units (Brandt and Dahmen [7]).
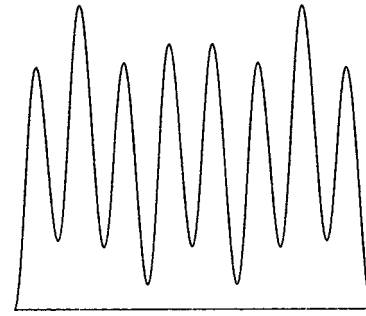

Fig. 3 Shape—probability density function versus position—of a particle in a linear box (infinitely deep potential well) in a nonequilibrium state of energy _E_ (Eq. 13). Arbitrary dimensionless units of the spatial coordinate and the probability density function.

$$\varepsilon_n = h^2 n^2/8M d^2 \quad \text{for} \quad n=2,3,8 \tag{12}$$

and the energy E, shape—probability density function p(x)—and entropy are given by the relations

$$E=(h^2/8M d^2)[0.1(4)+0.2(9)+0.7(64)]=47 h^2/8M d^2 \tag{13}$$

$$p(x)/(2/d)=0.1\sin^2(2\pi x/d)+0.2\cos^2(3\pi x/d)$$
$$+0.7\sin^2(8\pi x/d) \tag{14}$$

$$S=-k[0.1\ln(0.1)+0.2\ln(0.2)+0.7\ln(0.7)]=0.802k \tag{15}$$

A graph of the shape—probability density function versus position—is shown in Fig. 3. The shape is wavy and, according to the equation of motion of quantum thermodynamics (Beretta et al. [8]) evolves in time—is nonequilibrium.

As a result of the evolution just cited, the system reaches an equilibrium state that is not stable. Its density operator matrix is diagonal in the energy representation, and has again only three nonzero eigenvalues given by the relations (Beretta et al. [8])

$$\rho'_{22}=\frac{\exp(-4\alpha')}{Q'}; \quad \rho'_{33}=\frac{\exp(-9\alpha')}{Q'}; \quad \rho'_{88}=\frac{\exp(-64\alpha')}{Q'} \tag{16}$$

where $Q'=\exp(-4\alpha')+\exp(-9\alpha')+\exp(-64\alpha')$ and the value of α' is such that

$$E=\frac{47 h^2}{8M d^2}=\frac{4h^2}{8M d^2}\rho'_{22}+\frac{9h^2}{8M d^2}\rho'_{33}+\frac{64h^2}{8M d^2}\rho'_{88} \tag{17a}$$

or, equivalently,

$$4\rho'_{22}+9\rho'_{33}+64\rho'_{88}=47 \tag{17b}$$

Upon solving Eq. 17b numerically, we find

$$\alpha'=-0.02712; \quad \rho'_{22}=0.13822; \quad \rho'_{33}=0.15829;$$
$$\rho'_{88}=0.70349 \tag{18}$$

$$p(x)/(2/d)=0.13822\sin^2(2\pi x/d)+0.15829\cos^2(3\pi x/d)$$
$$+0.70349\sin^2(8\pi x/d) \tag{19}$$

$$S=-k[0.13822\ln(0.13822)+0.15829\ln(0.15829)$$
$$+0.70349\ln(0.70349)]=0.813k \tag{20}$$

It is noteworthy that the solution of Eq. 17 yields a negative value of α'. A brief discussion of this interesting and important result is given in the Appendix, Part II.

A graph of the shape—probability density function versus position (Eq. 19)—is shown in Fig 4. The shape is wavy, and associated with an unstable equilibrium state. The instability can be
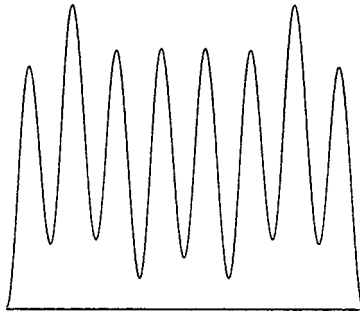
Fig. 4 Shape—probability density function versus position—of a particle in a linear box (infinitely deep potential well) in an unstable equilibrium state of energy E (Eq. 13). Arbitrary dimensionless units of the spatial coordinates and the probability density function.

verified by the introduction of a minute perturbation that increases the dimensionality of the density operator matrix, and precipitates a spontaneous tendency for the peaks and valleys to proceed to an evening-out evolution and an increase in entropy. The concept of dimensionality of a density operator is discussed in the Appendix, Part III.

The following example illustrates the ultimate result of the evening-out evolution just cited. We consider the stable equilibrium state that corresponds to the same energy E (Eq. 13) as that for the unstable equilibrium state associated with Fig 4. For such a state, the probability density function is given by the relation

$$p(x)/(2Q/d) = \sum_{n=odd} \cos^2(n\pi x/d)\exp(-\alpha n^2)$$
$$+ \sum_{n=even} \sin^2(n\pi x/d)\exp(-\alpha n^2) \qquad (21)$$

where the partition function $Q = \sum_{n=1}^{\infty} \exp(-\alpha n^2)$, $\alpha = h^2/8M d^2 kT$, and T is the temperature of the stable equilibrium state.

In thermodynamics, the temperature of a stable equilibrium state is determined solely by its energy. Moreover, for a particle confined in a linear box, an excellent approximation for the temperature is $kT/2 = E$ (Hatsopoulos and Gyftopoulos [9]). Therefore, we have the relations

$$E = 47h^2/8M d^2 = kT/2 \qquad (22)$$

$$\alpha = h^2/8M d^2 kT = 1/94 \qquad (23)$$

where use has been made of Eq. 13.

The graph of the shape—probability density function versus position—of the particle in a linear box in the stable equilibrium state that corresponds to energy E (Eq. 13) is shown in Fig. 5. For this calculation, we use $\alpha = 1/94$, and only 30 terms on the right
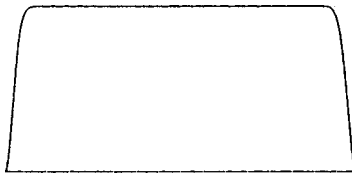

Fig. 5 Shape—probability density function versus position—of a particle in a linear box (infinitely deep potential well) in a stable equilibrium state having the same energy E (Eq. 13) as the unstable equilibrium state in Fig. 4, and evaluated for 30 terms on the right hand side of Eq. 21. Arbitrary dimensionless units of the spatial coordinate and the probability density function.
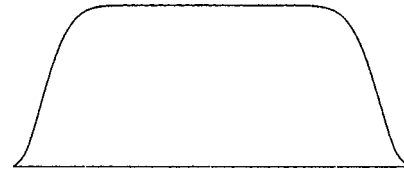

Fig. 6 Shape—probability density function versus position—of a particle in a linear box (infinitely deep potential well) in a stable equilibrium state that corresponds to $\alpha = 0.1$. The shape is evaluated for 30 terms on the right hand side of Eq. 21. Arbitrary dimensionless units of the spatial coordinate and the probability density function.

hand side of Eq. 21 because the contribution of terms for $n > 30$ turns out to be negligible. In contrast to the equilibrium state with the same energy (Fig. 4), we see that the shape of the stable equilibrium state is uniform almost throughout the entire range of position except near the walls of the linear box where the probability density function must reduce to zero.

Upon approximating the partition function Q by an integral (Hatsopoulos and Gyftopoulos [9]), we find that

$$Q = (2\pi mkT d^2/h^2)^{1/2} = 8.6 \qquad (24)$$

$$S = k \ln Q + E/T = 2.65k \qquad (25)$$

We see that, for the given energy, the entropy of the stable equilibrium state is more than 3.30 times larger than the entropy of the nonequilibrium state, and 3.26 times larger than the entropy of the unstable equilibrium state.

2.4 Other Stable Equilibrium States. For further confirmation of the idea that stable equilibrium states correspond to smooth probability density functions, we consider a stable equilibrium state that corresponds to different values of M, d, and E or T, and compute the shape—probability density function versus position (Eq. 21)—for $\alpha = 0.1$. A graph of this shape with 30 terms on the right hand side of Eq. 21 is shown in Fig. 6. Again, we observe that the shape is uniform throughout almost the entire range of values of position except near the walls of the box where the probability density function must reduce to zero.

It is noteworthy that the one-particle results for stable equilibrium states are the basis for the calculation of properties of systems that behave as ideal gases because under such behavior the interactions—internal forces—between the particles are negligible.

3 Particle in a Square Box

3.1 Energy Eigenstates. Next, we consider a structureless particle of mass M confined in a square box—two-dimensional, infinitely deep potential well—extending from $x = -d$ to $x = d$, and from $y = -d$ to $y = d$. The Hamiltonian operator of such a particle is given by the relation

$$H = -\frac{\hbar^2}{2M}\frac{d^2}{dx^2} - \frac{\hbar^2}{2M}\frac{d^2}{dy^2} + V(x,y) \qquad (26)$$

where

$$V(x,y) = \infty \quad \text{for } |x| > d \text{ and } |y| > d \qquad (26a)$$

and

$$V(x,y) = 0 \quad \text{for } |x| \leq d \text{ and } |y| \leq d \qquad (26b)$$

The two degrees of freedom x and y are separable, and the quantum probabilities associated with x are not correlated with those associated with y. Therefore, the energy eigenvalues, the normalized energy eigenfunctions, and the probability density function f(x, y) are given by the relations
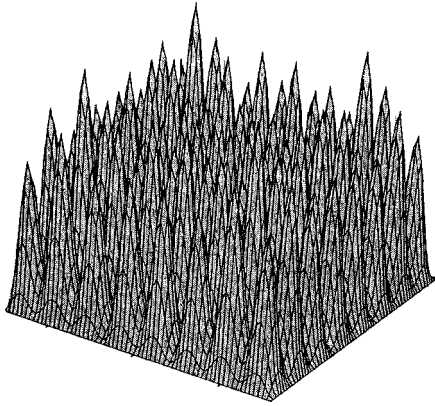
Fig. 7 Shape—probability density function versus positions—of a particle in a square box (infinitely deep potential well) in a nonequilibrium state of energy $E = 94h^2/8Md^2$. Arbitrary dimensionless units of the two spatial coordinates and the probability density function.

$$\varepsilon_{n_x n_y} = h^2(n_x^2 + n_y^2)/8Md^2 \tag{27}$$

$$\varphi_{n_x n_y}(x,y) = \varphi_{n_x}(x)\varphi_{n_y}(y) \tag{28}$$

$$f(x,y) = p(x)p(y) \tag{29}$$

where $\varphi_{n_x}(x)$ and $\varphi_{n_y}(y)$ are given by Eqs. 4 and 5 for both x and y and for all positive integer values of n_x and n_y, and p(x) and p(y) by Eq. 21 for x and y, respectively. Said differently, each degree of freedom defines a subsystem.

3.2 Nonequilibrium and Stable Equilibrium States. We consider a nonequilibrium state such that the energy of each of the two subsystems is given by Eq. 13, the probability density function for the x subsystem by Eq. 14, and the probability density function for the y subsystem by Eq. 14 with x replaced by y.

A graph of the shape—probability density function versus positions—of the particle in a square box in the nonequilibrium state just described is shown in Fig. 7. The shape is wavy and, according to the Beretta equation (Beretta et al. [8]), evolves to an unstable equilibrium state. Minute perturbations that increase the dimensionality of the density operator matrix precipitate the spontaneous tendency for the peaks and valleys to even out. The next example illustrates the ultimate result of this evening-out evolution.

Next, we consider a stable equilibrium state that corresponds to the same energy as that of the nonequilibrium state just discussed. In other words, we have that
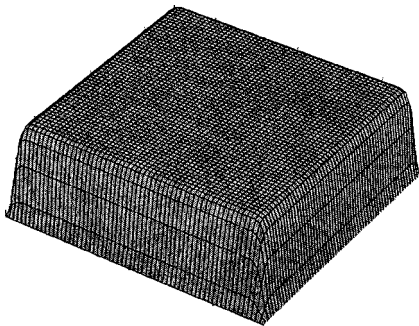

Fig. 8 Shape—probability density function versus positions—of a particle in a square box (infinitely deep potential well) in a stable equilibrium state of the same energy E as the nonequilibrium state in Fig. 7. Arbitrary dimensionless units of the two spatial coordinates and the probability density function.

$$E = \frac{2(47)h^2}{8Md^2} = \frac{94h^2}{8Md^2} = 2(kT/2) \tag{30}$$

$$\alpha = h^2/8Md^2kT = 1/94 \tag{31}$$

A graph of the shape—probability density function versus positions—of the particle in a square box in a stable equilibrium state for $\alpha = 1/94$ is shown in Fig. 8. In this calculation, we use only 30 terms on the right hand side of Eq. 21 for each degree of freedom. In contrast to the nonequilibrium state, the shape of the particle in the stable equilibrium state with the same energy as that of the nonequilibrium state is uniform throughout the square box except near the walls where, as was pointed out earlier, the probability density function must reduce to zero.

4 Harmonic Oscillator

4.1 Energy Eigenstates. We consider a structureless particle of mass M that experiences a continuously acting force $F(x)$ which can be thought of as the force of a spring, and which follows Hooke's law

$$F(x) = -kx \tag{32}$$

where the proportionality constant k is the stiffness of the spring. Such a force is called *harmonic*, and the particle a *harmonic oscillator*.

In classical mechanics, the potential energy stored in the spring is given by the relation

$$V(x) = kx^2/2 \tag{33}$$

and, therefore, in quantum mechanics the Hamiltonian operator of the oscillator is

$$H = -\frac{\hbar^2}{2M}\frac{d^2}{dx^2} + \frac{k}{2}x^2 \tag{34}$$

The Hamiltonian operator defines the energy eigenvalue problem

$$H\varphi_n(x) = \varepsilon_n \varphi_n(x) \tag{35}$$

where ε_n and $\varphi_n(x)$ are the nth energy eigenvalue and energy eigenfunction, respectively. Upon introducing the *harmonic oscillation angular frequency*

$$\omega = (k/M)^{1/2} \tag{36}$$

and the dimensionless variable

$$\xi = x/\sigma_0 \quad \text{where} \quad \sigma_0 = (\hbar/M\omega)^{1/2} \tag{37}$$

we can readily verify that the energy eigenstates are such that

$$\varepsilon_n = (n+1/2)\hbar\omega \tag{38}$$

$$\phi_n(\xi) = (\sqrt{\pi}2^n n!)^{-1/2} H_n(\xi)\exp(-\xi^2/2) \tag{39}$$

for $n = 0,1,2,\ldots$, where $\phi_n(\xi)$ is normalized in ξ, and $H_n(\xi)$ is the nth Hermite polynomial. The eigenfunction $\varphi_n(x)$, normalized in x, is

$$\varphi_n(x) = (\sigma_0\sqrt{\pi}2^n n!)^{-1/2} H_n(x/\sigma_0)\exp(-x^2/2\sigma_0^2) \tag{40}$$

4.2 Stable Equilibrium State. We consider a stable equilibrium state. The shape of the oscillator—probability density function $p(\xi)$ versus the dimensionless position ξ—is given by the relation

$$p(\xi)\left[\sqrt{\pi}\sum_{n=0}^{\infty}\exp(-\alpha n)\right] = \exp(-\xi^2)\sum_{n=0}^{N}H_n^2(\xi)\exp(-\alpha n)/2^n n! \tag{41}$$

where $N = \infty$, and $\alpha = \hbar\omega/kT$.

Graphs of the shapes for $\alpha = 0.1$, and $N = 5$, 30, and 108 instead of ∞ are shown in Figs. 9–11, respectively. We see that the ripples in Fig. 9 are smoothed out as the number of energy eigenstates included in the evaluation of the shape is increased above 5.
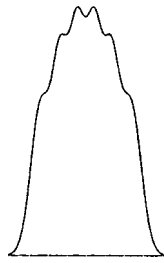
Fig. 9 Shape—probability density function p(ξ) versus the dimensionless position ξ—of a harmonic oscillator in a stable equilibrium state evaluated for $\alpha=0.1$ and N=5 (see text). Arbitrary dimensionless units.
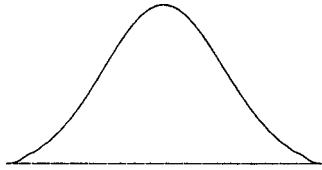

Fig. 10 Shape—probability density function versus the dimensionless position ξ—of a harmonic oscillator in a stable equilibrium state evaluated for $\alpha=0.1$ and N=30 (see text). Arbitrary dimensionless units.

Fig. 11 Shape—probability density function p(ξ) versus the dimensionless position ξ—of a harmonic oscillator in a stable equilibrium state evaluated for $\alpha=0.1$ and N=108 (see text). Arbitrary dimensionless units.

Fig. 12 Shape—probability density function p(ξ) versus the dimensionless position ξ—of a harmonic oscillator in a stable equilibrium state, evaluated for $\alpha=1$ and N=148 (see text). Arbitrary dimensionless units.

Fig. 13 Shape—probability density function p(ξ) versus the dimensionless position ξ—of a harmonic oscillator in a stable equilibrium state evaluated for $\alpha=10$ and N=148 (see text). Arbitrary dimensionless units.
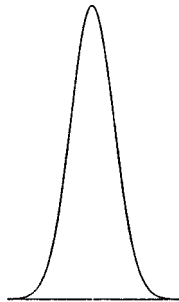

Fig. 14 Shape—probability density function p(ξ) versus the dimensionless position ξ—of a harmonic oscillator in a stable equilibrium state evaluated for $\alpha=100$ and N=148 (see text). Arbitrary dimensionless units.
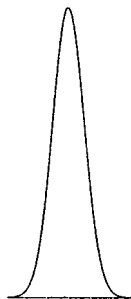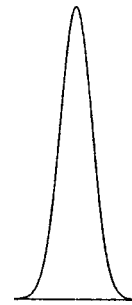
Graphs of the shapes for $\alpha=1$, 10, and 100, and N=148 are shown in Figs. 12–14, respectively. We see that they are all smooth (without ripples), and conclude that for each of the three cases N=148 is an excellent approximation of the shape of the stable equilibrium state of the harmonic oscillator.

5 Concluding Remarks

The results and conclusions presented in this paper are based on a unified quantum theory of mechanics and thermodynamics. To illustrate certain fundamental aspects of this theory, we provide graphical illustrations of quantum mechanical shapes—probability density functions with respect to spatial coordinates—of various systems in various states. Admittedly, we have selected very simple examples—one structureless particle confined either in a linear box or in a square box, and a one-dimensional harmonic oscillator—in order to achieve analytically explicit and transparent quantum-theoretic results, and to facilitate the computations. In each case, we find that the shape of either a nonequilibrium or an unstable equilibrium state is rippled (not smooth), whereas for each stable equilibrium state the shape has no ripples (is smooth).

In addition, we find that the thermodynamic entropy—a measure of the shape of the state of a system and a fundamental property of matter—increases if the system proceeds spontaneously from a state that is not stable equilibrium to the stable equilibrium state dictated by the second law of thermodynamics. Our examples, thus, provide graphical illustrations of both entropy—a concept, which has puzzled scientists and engineers for over a century—and the cause of irreversibility.

Nomenclature

d	=	distance
E	=	energy
F	=	force
$\hbar$	=	Planck's constant divided by 2π
h	=	Planck's constant
H_n	=	nth Hermite polynomial
H	=	Hamiltonian operator
k	=	spring stiffness constant
k	=	Boltzmann's constant
l	=	angular momentum quantum number
m	=	z-component of the angular momentum quantum number
M	=	mass
n	=	energy quantum number

p = momentum

p(x) = probability density function in x

Q = partition function

Q' = given in the paragraph immediately following Eq. 16

S = thermodynamic entropy

T = thermodynamic temperature

t = time

V = potential energy

x = spatial dimension

y = spatial dimension

Greek Letters

α = given in the paragraph immediately following Eq. 21

α' = constant defined by Eqs. 16 and 17a

α_i = ith statistical (informational) probability

ε_n = nth energy eigenvalue

ξ = dimensionless variable

ρ = density operator

σ_0 = given by Eq. 31

φ_n = nth energy eigenfunction

ϕ_n = nth energy eigenfunction normalized with respect to ξ or x

ψ = wave function

ω = harmonic oscillation angular frequency

Appendix

1 The Density Operator of the Unified Quantum Theory of Mechanics and Thermodynamics. In many textbooks on quantum mechanics, probabilities associated with measurement results are derived from a normalized wave function $\psi(x)$ or equivalently from either a Dirac ket $|\psi\rangle$ or a projector $|\psi\rangle\langle\psi|$, where x are the spatial coordinates of the constituents of a system, and $\langle\psi|$ is the bra of ket $|\psi\rangle$ (Shankar [10]). For example, for a system with one degree of spatial freedom x, the probability density function of measurement results of x is given by $|\psi(x)|^2 = \langle\psi|x\rangle\langle x|\psi\rangle = |\langle x|\psi\rangle|^2$.

In statistical quantum mechanics, probabilities associated with measurement results are derived from a density operator $\rho = \Sigma_i \alpha_i \rho_i$ which represents a mixture of quantal probabilities derived from projectors $p_i = |\psi_i\rangle\langle\psi_i|$ for i=1,2,..., and statistical (informational) probabilities α_i which reflect the lack of information about some or all aspects of the state of a system.

In general, the foundations and theorems of the unified quantum theory of mechanics and thermodynamics differ from those of the ordinary expositions of quantum mechanics and statistical quantum mechanics. Among the many novel concepts and results, two deserve special emphasis for the purposes of this paper. The first is that in contrast to statistical quantum mechanics, a novel concept of the unified quantum theory is that its postulates—quantum-theoretic and thermodynamic—do not apply to density operators that represent mixtures of quantal probabilities derived from projectors $\rho_i = |\psi_i\rangle\langle\psi_i|$, and statistical (informational) probabilities α_i that reflect the lack of information about some or all aspects of the quantal probabilities associated with the state of a system. Instead, the unified theory avers that the laws of physics apply only to density operators each of which is construed as the seat of exclusively quantal probabilities, that is, only to operators ρ that can be represented by a homogeneous ensemble of identical systems, identically prepared. A homogeneous ensemble is an ensemble in which the probabilities of results of measurements on any member are represented by the same density operator p as those on any other member. Accordingly, experimentally (in contrast to algebraically) the ensemble cannot be decomposed into statistical mixtures of projectors or other non-projector density operators. The concept of a homogeneous ensemble was introduced by von Newmann [11], but he assumed that it applies only to projectors ($\rho_i = \rho_i^2$), whereas here the concept is extended to all
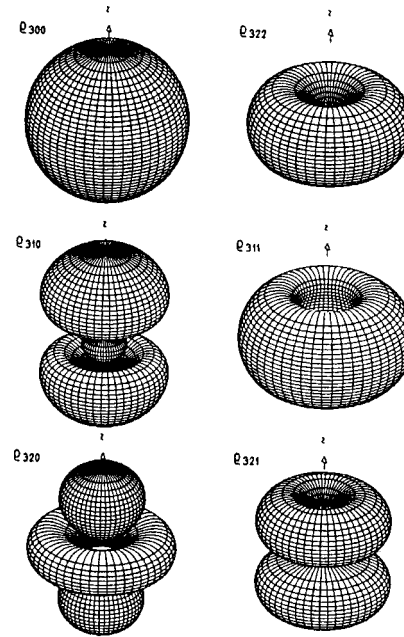

Fig. 15 Subensemble surfaces—shapes—of the constant probability density function $\rho_{3\ell m} = 0.0002$ in full x, y, z-space of the heterogeneous ensemble of the electron in a hydrogen atom in a stable equilibrium state (Brandt and Dahmen [12]). The shapes for m=−1 and −2 are identical to the ones shown for m=1 and 2, respectively.

self-adjoint, nonnegative definite, linear, unit trace density operators. Each such operator satisfies the relation $\rho \geq \rho^2$.

The second concept which deserves special emphasis here is that, in contrast to the plethora of expressions for entropy that have been proposed in the scientific literature over the past 140 years, it has been shown that only one conforms with the criteria that must be satisfied by the entropy of thermodynamics, and this expression is (Gyftopoulos and Cubukcu [3])

$$S = -k \ \mathrm{Tr}[\rho \ln \rho] \qquad (A1)$$

where k is Bolzmann's constant, Tr stands for the trace of the operator that follows, and ρ is a density operator which can be represented solely by a homogeneous ensemble. It is noteworthy that, if ρ cannot be represented by a homogeneous ensemble, then $-k \mathrm{Tr}[\rho \ln \rho]$ does not represent the entropy of thermodynamics.

For given values of energy, volume, and amounts of constituents, if ρ is a projector (wave function), then $S=0$; if ρ is not a projector but corresponds to a state which is not stable equilibrium (not thermodynamic equilibrium), then S has a positive value smaller than the largest possible for the given specifications; and if p corresponds to the unique stable equilibrium state, then S has the largest value of all the entropies of the system which share the given values of energy, volume, and amounts of constituents.

To illustrate the fundamental difference between an ensemble that is heterogeneous and one that is homogeneous, we consider the density operator ρ^0 of the electron of a hydrogen atom in a stable equilibrium state. The heterogeneous ensemble would be a combination of sub-ensembles, each of which is specified by one set of values of three quantum numbers: the energy quantum number n, the angular momentum quantum number $0 \leq \ell \leq n-1$, and the z-component of the angular momentum quantum number $-\ell \leq m \leq \ell$. So for n=3, there would be nine sub-ensembles because the energy eigenstate is n^2-fold degenerate. For each of these subensembles, the electron has the shape shown in Fig. 15. In contrast, the density operator ρ^0 of the homogeneous ensemble cannot be in any conceivable way subdivided into subensembles. Each member of the ensemble is described by the same ρ^0 and has a spherical shape as shown in Fig. 16
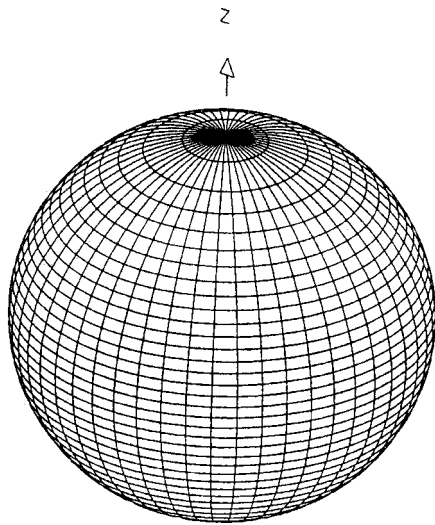
Fig. 16 Surface—shape—of the constant probability density function in full x,y,z-space of the homogeneous ensemble of the electron in a hydrogen atom in a stable equilibrium state (arbitrary units).

2 Negative Temperatures. It is noteworthy that the value of α' (Eq. 18) is negative. The reason is that the calculation of the density operator ρ' of the unstable equilibrium state is identical with the one that would have been made for a pseudo stable equilibrium state of a system, which has only three energy eigenvalues and eigenfunctions and, therefore, an upper bound ε_8 on energy. We call the state pseudo stable equilibrium because it satisfies the condition of largest entropy for a given value of the energy, but it corresponds to a density operator consisting of energy eigenvalues and eigenfunctions that are arbitrarily chosen from a complete set that has no upper bound on energy. The system with only three energy eigenvalues admits both positive and negative temperatures. Specifically, the inverse temperature $1/T$ ranges from minus infinity at the expectation value of the energy E equal to the highest eigenvalue, here ε_8, to plus infinity at the expectation value of E equal to the smallest eigenvalue, here ε_2. The value of α' in our example is negative because the expectation value of the energy of the unstable equilibrium state we selected falls in the range of negative temperatures of the system with the upper bound on energy.

Finally, the preceding discussion also illustrates the thermodynamic fact that temperature is not energy, and energy is not temperature for at least three reasons: (i) the dimension of tempera-ture is not expressible in terms of the dimensions of energy; (ii) positive energy may correspond to a negative temperature; and (iii) upon changing the arbitrary reference state of energy, we can have a spectrum of energy values that correspond to the same (positive or negative) temperature.

3 The Dimensionality of a Density Operator. In classical mechanics, the dimensionality of phase space is determined by the number of the spatial degrees of freedom of the system. For example, if the number of spatial degrees of freedom is three, the dimensionality of phase space is six. Moreover, unless the number of spatial degrees of freedom is changed by a change of the number of particles, the dimensionality of phase space cannot and is not altered by Newton's equation of motion.

In quantum theory, the dimensionality of a density operator ρ equals the number of nonzero eigenvalues of the density operator ρ. For example, a normalized projector $\rho_1 = |\psi_1\rangle\langle\psi_1|$ (wave function $\psi_1(\mathrm{x}) = \langle\mathrm{x}|\psi_1\rangle$) has one eigenvalue equal to unity, and its dimensionality equals one. Again, if $|\psi_1\rangle\langle\psi_1|$ and $|\psi_2\rangle\langle\psi_2|$ are orthonormal, that is, $\langle\psi_i|\psi_i\rangle = 1$ for i=1, 2, and $\langle\psi_j|\psi_i\rangle = 0$ for i =1, 2, j=1, 2, and i$\neq$j, the density operator $\rho = \rho_{11}|\psi_1\rangle\langle\psi_1| + \rho_{22}|\psi_2\rangle\langle\psi_2|$ has two positive eigenvalues ρ_{11} and ρ_{22}, and its dimensionality is two, where $\rho_{11} + \rho_{22} = 1$. The dimensionality of a density operator can be changed only through an increase of the number of eigenvalues of ρ by means of suitable perturbations, and cannot and is not altered by the quantum theoretic equation of motion (Beretta et al. [8]), or by any other equation of motion.

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Dr. von Spakovsky has over 13 yrs of teaching and research experience in academia and over 17 yrs of industry experience in mechanical engineering, power utility systems, aerospace engineering and software engineering. He was at NASA from 1970-74, in the power utility industry from 1974-89, and at the Swiss Federal Institute of Technology from 1989-96. He is currently Professor of Mechanical Engineering, and Director of the Energy Management Institute at Virginia Tech where he teaches courses in thermodynamics, industrial energy systems, fuel cell systems, and energy system design. His research interests and activities include computational methods for modeling and optimizing complex energy systems, methodological approaches for the integrated synthesis, design, operation and diagnosis of such systems (stationary power as well as high performance aircraft systems), theoretical non-equilibrium and equilibrium thermodynamics as well as the unified quantum theory of mechanics and thermodynamics, and fuel cell applications for both transportation and distributed power generation. He has published widely in scholarly journals, conference proceedings, etc. (over 100 publications) and has given talks, seminars and short courses worldwide. Included among his various professional activities and awards is membership to the AIAA, ASME Fellow, ASME representative to the U.S. CADDET National Team, elected member of Sigma Xi and Tau Beta Pi, and current Editor-in-Chief of the International Journal of Applied Thermodynamics.

Prof. Gyftopoulos has been a member of the engineering faculty at the Massachusetts Institute of Technology (MIT) since 1958 and was the Ford Professor of Mechanical Engineering and Nuclear Engineering from 1970 to 1996. He has published 4 books and over 140 journal articles and, since becoming Professor Emeritus in 1996, has continued to be very active in his scholarly endeavors. In addition to his academic work, Prof. Gyftopoulos has served or is serving as a member of the Board of Directors of the American Nuclear Society, the International Institute of Energy Conservation, and six U.S. private corporations. He is also currently a member of the Governing Board of the Constantine G. Karamanlis Institute of Democracy, and is a member of the Scientific Committee of the Foundation of the Hellenic World. Prof. Gyftopoulos has also served as a trustee for a number of institutions of higher learning including Anatolia College, the American Farm School, and Hellenic College, and is currently vice chairman of the Board of Trustees for Anatolia College. He is a fellow of the American Academy of Arts and Sciences, the American Nuclear Society, and the American Society of Mechanical Engineers (ASME), and is a member of the National Academy of Engineering, and a corresponding member of the Academy of Athens. He has received a number of honorary doctorates as well as the prestigious ASME James Harry Potter Gold Medal Award, the ASME Robert H. Thurston Award and the ASME Edward F. Obert Award, and has been appointed Commander of the Order of Merit by the President of the Republic of Greece.