Int. J. Therm. Sci. (1999) 38, 845–853

A scale-invariant model of statistical mechanics and modified forms of the first and the second laws of thermodynamics

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(Received 25 February 1999, accepted 22 April 1999)

Abstract — A scale-invariant statistical theory of fields is presented that leads to invariant definition of density, velocity, temperature, and pressure. The definition of Boltzmann constant is introduced as $k_{\mathrm{k}} = k = m_{\mathrm{k}}\,\nu_{\mathrm{k}}\; c = 1.381{\cdot}10^{-23}$ J·K^{-1}, suggesting that the Kelvin absolute temperature scale is equivalent to a length scale. Two new state variables called the reversible heat $Q_{\mathrm{rev}} = TS$ and the reversible work $W_{\mathrm{rev}} = PV$ are introduced. The modified forms of the first and second law of thermodynamics are presented. The microscopic definition of heat (work) is presented as the kinetic energy due to the random (peculiar) translational, rotational, and pulsational motions. The Gibbs free energy of an element at scale β is identified as the total system energy at scale $(\beta - 1)$, thus leading to an invariant form of the first law of thermodynamics $U_\beta = Q_\beta - W_\beta + N_{\mathrm{e}\beta}\, U_{\beta-1}$.

fundamental thermodynamics / first and second laws / invariant form / statistical thermodynamics / thermophysical characteristics

Nomenclature

c	light velocity	m·s^{-1}
$\overline{E}$	average energy	J
G	Gibbs free energy	J
h	Planck constant	J·s
H	enthalpy	J
I	moment of inertia	kg·m^2
k	Boltzmann constant	J·K
m	mass of element	kg
N	number of molecule	
N°	Avogadro number	
P	pressure	Pa
p	momentum	kg·m·s^{-1}
Q	thermal energy, heat	J
R	universal gas constant	J·K^{-1}
r	distance: molecule/axis of rotation	m
R_β	constant of element	J·kg^{-1}·K^{-1}
S	entropy	J·K^{-1}
T	temperature	K
U	internal energy	J
u, v, w	velocity of element atom, system...	m·s^{-1}
V	volume	m^3
W	mechanical energy, work	J
x	coordinate	m
Z	partition function	

Greek symbols

λ	wave length	m
ρ	density	kg·m^{-3}
ν	frequency	s^{-1}
ε	internal energy of one element	J
μ_i	chemical potentiel	J
ω	angular velocity	s^{-1}

Subscripts

β	scale of cluster
act	actuel or real
ext	external
f	distribution fonction
int	internal
P	isobare
rev	reversible

S	isentropic
T	isothermic
V	isochoric

Superscripts

i	internal
k	kinetic
p	potential
r	rotational
t	translational
v	pulsational kinetic

1. INTRODUCTION

Turbulent phenomena are common features in diverse and seemingly unrelated branches of physical sciences. This is in part evidenced by the similarities between the stochastic quantum fields [1–16] on the one hand, and classical hydrodynamic fields [17–26], on the other one. Thus, the problem of turbulence involves stochastic motion of a cluster of galaxies [23, 27], turbulent eddies [17–26], and photons [28] at cosmological, hydrodynamic, and chromodynamic scales. In recent investigations [29–30], a scale-invariant model of statistical mechanics was shown to result in a modified theory of Brownian motions and the hypothesis of the existence of an equilibrium statistical field called *cluster-dynamics*. In the present study, the application of the scale-invariant model of statistical mechanics to the field of statistical thermodynamics is described.

2. A SCALE-INVARIANT MODEL OF STATISTICAL MECHANICS AND INVARIANT DEFINITION OF DENSITY, VELOCITY, TEMPERATURE AND PRESSURE

The scale-invariant model of statistical mechanics for equilibrium galacto-, planetary-, hydro-system, fluid-element-, eddy-, cluster-, molecular-, atomic-, subatomic-, kromo-, and tachyon-dynamics corresponding to the scale $\beta = g, p, h, \mathrm{f}, e, c, m, a, s, k$, and t are shown in *figure 1* [29]. Also shown are the corresponding *non-equilibrium*, laminar flow fields. Each statistical field, described by a distribution function $\mathrm{f}_\beta(\mathbf{u}_\beta) = \mathrm{f}_\beta(\mathbf{r}_\beta, \mathbf{u}_\beta, \mathrm{t}_\beta)\,\mathrm{d}\mathbf{r}_\beta\,\mathrm{d}\mathbf{u}_\beta$, defines a "system" that is composed of an ensemble of "elements", each element is composed of an ensemble of small particles viewed as *point-mass* "atoms". The element (system) of the smaller scale (j) becomes the atom (element) of the larger scale ($j+1$).

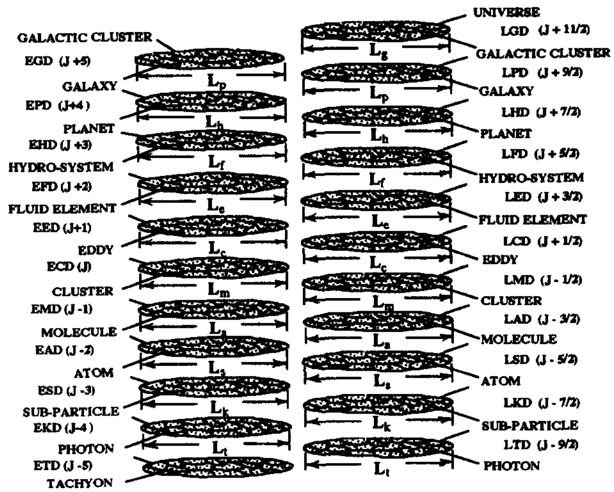

Figure 1. A scale-invariant view of statistical mechanics from cosmic to tachyonic scales. Equilibrium galacto-dynamics (EGD), planetary-dynamics (EPD), hydro-system-dynamics (EHD), fluid-element-dynamics (EFD), eddy-dynamics (EED), cluster-dynamics (ECD), molecular-dynamics (EMD), atomic-dynamics (EAD), subatomic-dynamics (ESD), kromo-dynamics (EKD), tachyon-dynamics (ETD).

Following the classical methods [31–35], the invariant definitions of the density ρ_β, and the velocity of *element* $\mathbf{v}_\beta$, *atom* $\mathbf{u}_\beta$, and *system* $\mathbf{w}_\beta$ at the scale β are [29]:

$$\rho_\beta = n_\beta\, m_\beta = m_\beta \int \mathrm{f}_\beta\, \mathrm{d}\mathbf{u}_\beta, \quad \mathbf{v}_\beta = \rho_\beta^{-1}\, m_\beta \int \mathbf{u}_\beta\, \mathrm{f}_\beta\, \mathrm{d}\mathbf{u}_\beta \tag{2.1}$$

$$\mathbf{u}_\beta = \mathbf{v}_{\beta-1}, \qquad \mathbf{w}_\beta = \mathbf{v}_{\beta+1} \tag{2.2}$$

The *invariant equilibrium and non-equilibrium translational temperature and pressure* are:

$3\,\mathrm{k}\,T_\beta = m_\beta < u_\beta^2 >, P_\beta = \rho_\beta < u_\beta^2 > /3, 3\,\mathrm{k}\,\mathbb{T}_\beta = m_\beta < {V'}_\beta^2 >$,

and $\mathbb{P}_\beta = n_\beta m_\beta < {V'}_\beta^2 > /3$, leading to the corresponding *invariant ideal "gas" laws* [29]:

$$P_\beta V = N_\beta\, \mathrm{k}\, T_\beta \qquad \text{and} \qquad \mathbb{P}_\beta V = N_\beta\, \mathrm{k}\, \mathbb{T}_\beta \tag{2.3}$$

At the scale of EKD, one obtains the temperature and pressure of *photon gas*:

$$\begin{aligned} \mathrm{k}\, T_\mathrm{k} &= m_\mathrm{k} < u_\mathrm{k}^2 > /3 = m_\mathrm{k} < u_\mathrm{kx}^2 + u_\mathrm{ky}^2 + u_\mathrm{kz}^2 > /3 \\ &= m_\mathrm{k}\,(3c^2)/3 = m_\mathrm{k}\, c^2 \end{aligned} \tag{2.4}$$

$$\begin{aligned} P_\mathrm{k} &= \rho_\mathrm{k} < u_\mathrm{k}^2 > /3 = \rho_\mathrm{k}\, c^2 = n_\mathrm{k}\, m_\mathrm{k}\, c\, \lambda_\mathrm{k}\, \nu_\mathrm{k} = n_\mathrm{k}\, h_\mathrm{k}\, \nu_\mathrm{k} \\ &= n_\mathrm{k}\, E_\mathrm{k} = \overline{E}_\mathrm{k} \end{aligned} \tag{2.5}$$

where $h_\mathrm{k} = m_\mathrm{k}\, \lambda_\mathrm{k}\, c = h = 6.626 \cdot 10^{-34}$ J·s is the Planck constant. Following this definition of h by Planck [36, 37] involving the wavelength λ_k (*space*), we introduce the definition of the Boltzmann constant as:

$$k_\mathrm{k} = k = m_\mathrm{k}\, \nu_\mathrm{k}\, c = 1.381 \cdot 10^{-23}\ \mathrm{J \cdot K^{-1}} \tag{2.6}$$

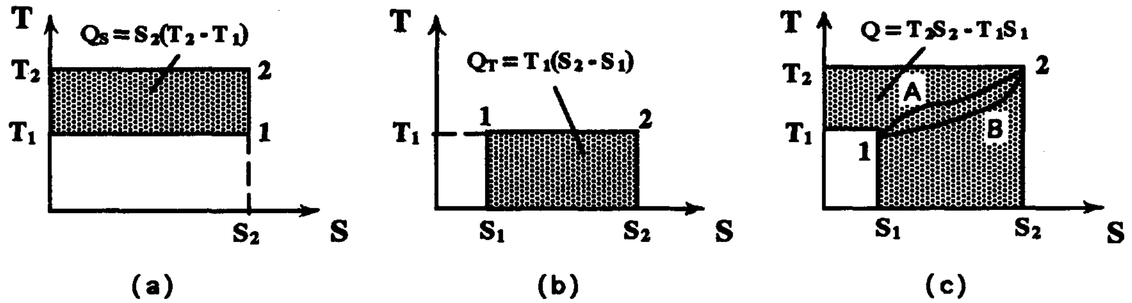

Figure 2. Schematic diagram of reversible heats: **(a)** reversible isentropic heat Q_S, **(b)** reversible isothermal heat Q_T, **(c)** total reversible heat $Q_{rev} = Q_S + Q_T$.

involving frequency ν_k (*time*). Hence, the *Kelvin absolute temperature scale* is identified as a *length scale*, $n\,k\,T_k = n\,k\,\lambda_k = P_k = \overline{E}_k$. Also, following *de Broglie* hypothesis for the wavelength of matter waves [2]:

$$\lambda_\beta = h/p_\beta \tag{2.7}$$

where $p_\beta = m_\beta v_\beta$ is the momentum, we introduce the relation

$$\nu_\beta = k/p_\beta \tag{2.8}$$

for the frequency of matter waves. Therefore, the mass of photon is predicted as

$$m_k = (h\,k/c^3)^{1/2} = 1.84278 \cdot 10^{-41}\ \mathrm{g} \tag{2.9}$$

that is much larger than the reported value of $4 \cdot 10^{-51}$ kg [38]. This leads to the mean- free-path and the frequency of photons in equilibrium kromodynamic field EKD (*figure 1*)

$$\lambda_k = 0.119935\ \mathrm{m}, \quad \nu_k = 2.49969 \cdot 10^9\ \mathrm{Hz} \tag{2.10}$$

the Avogadro number $N^\circ = 1/(m_k c^2) = 6.0376 \cdot 10^{23}$, the universal gas constant $R = N^\circ k = 1/\lambda_k = 8.3379\ \mathrm{m}^{-1}$, and the photon molecular weight $W_k = N^\circ m_k = 1.1126 \cdot 10^{-17}\ \mathrm{kg \cdot mol^{-1}}$. In view of definition of N° given above, equation (2.4) leads to the ideal gas law for photons in equilibrium *vacuum* state, EKD field at $T_k = \lambda_k = 0.119935$ m, as

$$N^\circ\,k\,T_k = 1 \tag{2.11}$$

3. DEFINITION OF REVERSIBLE HEAT AND WORK

3.1. Definition of reversible heat

A new thermodynamic state-variable called *reversible heat* is introduced as

$$dQ_{rev} = d(TS) = T\,dS + S\,dT = dQ_T + dQ_S \tag{3.1}$$

The *isothermal reversible heat* dQ_T and the *isentropic reversible heat* dQ_S are respectively the area under the $(T-S)$ and $(S-T)$ curves, schematically shown in *figures 2a* and *2b*. Therefore, the total reversible heat between the initial and the final states becomes independent of the actual path taken as shown in *figure 2c*.

3.2. Definition of reversible work

Another new thermodynamic state-variable called the *reversible work* is introduced as

$$dW_{rev} = d(PV) = PdV + VdP = dW_P + dW_V \tag{3.2}$$

The *reversible isobaric (dilatational) work* dW_P and the *reversible isochoric (stress) work* dW_V represent the areas under the $(V-P)$ and $(P-V)$ curves, as shown in *figures 3a* and *3b*, respectively. Therefore, the total reversible work $W_{rev} = P_2 V_2 - P_1 V_1$ is path-independent, as shown in *figure 3c*. The isochoric work $W_V = V(P_2 - P_1)$, that is like the shaft work [39], maybe also considered in one-dimension in terms of an elongation of an *elastic medium* according to the *generalized definition of work*

$$dW_{rev} = d(\boldsymbol{F} \cdot \mathbf{x}) = \boldsymbol{F} \cdot d\mathbf{x} + \mathbf{x} \cdot d\boldsymbol{F} \tag{3.3}$$

that is composed of the *reversible displacement work* $dW_D = \boldsymbol{F} \cdot d\mathbf{x}$ and the *reversible stress work* $dW_S = \mathbf{x} \cdot d\boldsymbol{F}$.

An example of stress work is the *iso-kinetic* type of work that is done by a person holding a weight at the end of a horizontally-stretched and motionless arm, in the presence of a *gravitational field.* In this case, the larger the weight being held by the person, the larger will be the volume of the active body muscles under unbalanced stress, and the larger will be the magnitude of such muscular stress gradients in order to keep the larger weight stationary. Similarly, when a person pushes against a stationary and rigid wall, thus creating higher stresses on the contact surfaces, this person is doing work even though there is no visible displacement.

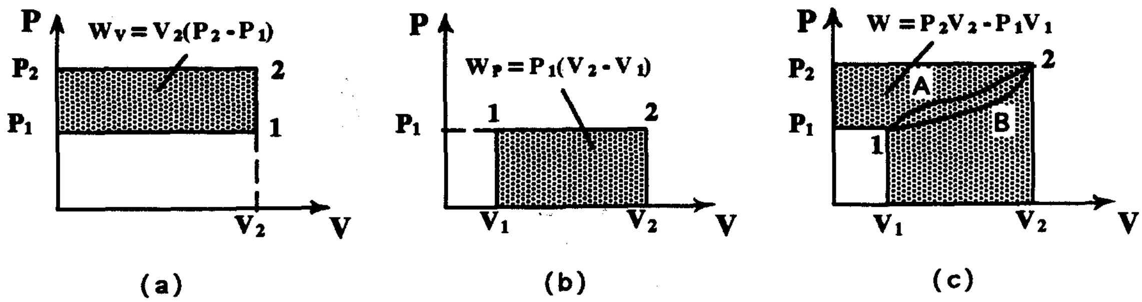

Figure 3. Schematic diagram of reversible work: **(a)** reversible isochoric work W_V, **(b)** reversible isobaric work W_P, **(c)** total reversible work $W_{rev} = W_V + W_P$.

4. MODIFIED FORMS OF THE FIRST LAW AND THE SECOND LAW OF THERMODYNAMICS

4.1 Modified form of the first law of thermodynamics

In view of equations (3.1) and (3.2), *the modified form of the first law of thermodynamics* is introduced as:

$$d(T\,S) = dU + d(P\,V) - d(\Sigma\,\mu_i\,N_i) \tag{4.1}$$

or

$$dQ_{rev} = dU + dW_{rev} - \Sigma\,d(\mu_i\,N_i) \tag{4.2}$$

that leads directly to the Euler equation for a simple fluid:

$$U = T\,S - P\,V + \mu\,N \tag{4.3}$$

For non-reactive systems, equation (4.1) reduces to:

$$dG = d(H - T\,S) = 0 \tag{4.4}$$

when $H = U + PV$ is the enthalpy. The modified form of the first law in equation (4.1) may be obtained directly by addition of the *Gibbs equation*:

$$dU = T\,dS - P\,dV + \Sigma\,\mu_i\,dN_i \tag{4.5}$$

and the *Gibbs-Duhem equation*

$$S\,dT - V\,dP + \Sigma\,N_i\,d\mu_i = 0 \tag{4.6}$$

4.2. Modified form of the second law of thermodynamics

Following the classical statement of the second law of thermodynamics by Clausius $\delta Q_{act} \leqslant T\,dS$, the *modified form of the second law of thermodynamics* is introduced as:

$$\delta\,Q_{act} \leqslant dQ_{rev} = d(T\,S) \tag{4.7}$$

The above inequality states that during any real, non-quasistatic process, the actual thermal energy δQ_{act} that is added to the system will be always less than what is calculated on the basis of the change of state variables from the beginning to the end of the process $dQ_{rev} = d(TS)$. This is because, during all real processes some energy will always be dissipated into heat,

$$\delta Q_{act} + \delta Q_{dis} = dQ_{rev} = d(T\,S) \tag{4.8}$$

and since dissipation is always positive $\delta Q_{dis} \geqslant 0$, one arrives at the inequality

$$Q_{act} \leqslant Q_{rev} = T_2\,S_2 - T_1\,S_1 \tag{4.9}$$

According to the classical theory of Clausius, the reversible heat

$$\delta\,Q_{rev} = T\,dS \tag{4.10}$$

is not an exact differential because in general the temperature T varies along different paths. However, according to the modified theory being presented herein, the *reversible heat* $dQ_{rev} = d(T\,S)$ is in fact a *state property*. The definition of entropy will be based on the *reversible-isothermal heat* $Q_T = T\,(S_2 - S_1)$ schematically shown in *figure 2a*. Examination of *figure 2* shows that, with the modified definition of reversible heat in (3.1), one can construct a Carnot cycle composed entirely of heat transfer processes.

5. MACROSCOPIC DEFINITION OF HEAT, WORK, AND INTERNAL ENERGY

Following the classical procedures [40–42], the energy of each element, say molecule in the quantum state i, is decomposed into the *external kinetic energy*, the *external potential energy*, and the *internal energy* as:

$$(\varepsilon_i)_{tot} = (\varepsilon_i)^k_{ext} + (\varepsilon_i)^p_{ext} + (\varepsilon_i)^i_{int} = \varepsilon^k_i + \varepsilon^p_i + \varepsilon^i_i \quad (5.1)$$

Using the definition in equation (5.1), the total energy of the system becomes

$$U = \Sigma N_i(\varepsilon_i)_{tot} = \Sigma N_i (\varepsilon^k_i + \varepsilon^p_i + \varepsilon^i_i) \quad (5.2)$$

such that

$$dU = \{\Sigma \varepsilon^k_i \, dN_i + \Sigma N_i \, d\varepsilon^k_i\} + \{\Sigma \varepsilon^p_i \, dN_i + \Sigma N_i \, d\varepsilon^p_i\} + \{\Sigma \varepsilon^i_i \, dN_i + \Sigma N_i \, d\varepsilon^i_i\} \quad (5.3)$$

By comparisons between the above expression and equation (4.1), one arrives at the definitions:

$$Q = T\,S = \Sigma U^k_{i\,ext} = \Sigma \varepsilon^k_i N_i \quad \text{[thermal kinetic energy]} \quad (5.4)$$

$$W = P\,V = -\Sigma U^p_{i\,ext} = -\Sigma \varepsilon^p_i N_i \quad \text{[mechanical potential energy]} \quad (5.5)$$

$$G = \mu\,N = \Sigma U^i_{int} = \Sigma \varepsilon^i_i N_i \quad \text{[internal energy]} \quad (5.6)$$

6. MICROSCOPIC DEFINITION OF HEAT, WORK, AND INTERNAL ENERGY

6.1. Thermal kinetic energy

The classical expression for the internal energy associated with the random translational motions of monatomic ideal gas is

$$U = (3/2) N\,k\,T = (3/2)\,N\,m < u^2_x >$$

It is now argued that the classical reason for the occurrence of the numerical factor 3 in this expression, namely to account for *three-translational degrees of freedom*, is not correct. The principle of equipartition of energy requires that the three translational degrees of freedom be statistically equivalent *because of the isotropy of space*. However, this does not mean that at any instant of time, each molecule should be considered to move in all three directions *simultaneously*; that is physically impossible.

According to the modified theory being presented herein, the factor 3 in $U = (3/2)N\,k\,T$ is because there are *three distinguishable types of thermal kinetic energy* of molecules respectively called the *translational*, the *rotational*, and the *vibrational* thermal kinetic energy. The *isotropy of space* requires that the energy associated with the motions along the two directions of linear translation (x^+, x^-), angular rotation (θ^+, θ^-), and radial pulsation (r^+, r^-) must be identical (*figures 4a–4c*). Therefore, the elements are assumed to perform *forward-versus-backward harmonic translation, clockwise versus counter-clockwise harmonic rotation,* and *radially-outward (explosive) versus radially-inward (implosive) harmonic pulsations* as shown in *figure 4*.

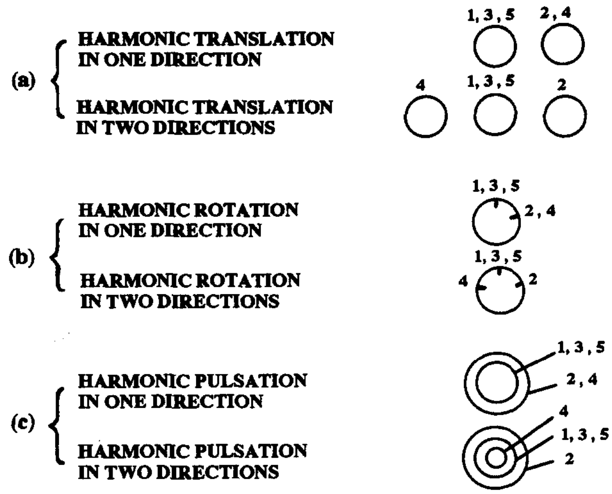

Figure 4. Schematic drawing of **(a)** translational, **(b)** rotational, and **(c)** pulsational harmonic motions in one and two directions. The five time steps t_1–t_5 show successive: **(a)** position of translating particle, **(b)** position of the marker on a rotating particle, **(c)** position of outer radius of a pulsating particle during each period.

6.1.1. Harmonic translator

The principle of equipartition of energy requires that for any arbitrary coordinate x, the energy of motions along each of the two arbitrary directions (x^+, x^-) should be identical $< u^2_{x+} > = < u^2_x >$ (*figure 4a*) such that the translational kinetic energy becomes:

$$TKE = \varepsilon^t_i = m_i < u^2_{ix+} > /2 + m_i < u^2_{ix-} > /2 = m_i < u^2_{ix+} > \quad (6.1)$$

This leads to the modified definition of temperature:

$$(1/2)\,k\,T = m_i < u^2_{ix+} > /2 \quad (6.2)$$

From the summation over all the molecules within a cluster one obtains:

$$U^t_i = \varepsilon^t_c = N_i\,k\,T \quad (6.3)$$

Next, another summation over all the clusters within the system gives:

$$U^t = \Sigma N_i\,k\,T = N\,k\,T \quad (6.4)$$

6.1.2. Harmonic rotator

Following classical methods [40], under *rigid-body rotation* of the cluster about an arbitrary axis (x^+) at angular velocity $\boldsymbol{\omega} = \boldsymbol{\omega}_{ix+}$, each molecule within the cluster has the orbital velocity $v_i = r_i \times \boldsymbol{\omega}_{ix+}$ when r_i is the minimum distance from the molecule i to the axis of rotation (x^+). Hence, the rotational kinetic energy is:

$$VKE = (1/2)\, m_i\, r_i^2\, \omega_i^2 = (1/2)\, I_i\, \omega_i^2\,. \tag{6.5}$$

where $I_i = m_i\, r_i^2$ is the moment of inertia. For rotation occurs in two-directions (θ^+, θ^-) as shown in *figure 4c*, the rotational kinetic energy per molecule becomes:

$$\varepsilon_i^r = I_i < \omega_{ix+}^2 > /2 + I_i < \omega_{ix-}^2 > /2 = I_i < \omega_{ix+}^2 > = k\,T \tag{6.6}$$

By summation over all the molecules that form the rotating cluster c, one obtains:

$$U_i^r = \varepsilon_c^r = \Sigma \varepsilon_i^r = \Sigma I_i < \omega_{ix+}^2 > = I_c < \omega_{ix+}^2 > = N_i\, k\,T \tag{6.7}$$

Next, from summation over all the clusters within each eddy one obtains:

$$U^r = \varepsilon_e^r = \Sigma \varepsilon_c^r = \Sigma U_i^r = \Sigma N_i\, I_i < \omega_{ix+}^2 > = N\,k\,T \tag{6.8}$$

6.1.3. Harmonic pulsator

The clusters are modeled as spherical balloons that undergo harmonic spherically-symmetric pulsations (*figure 4c*). Following the classical methods [40], the dynamic force on such a molecule is given by the Newton law of motion as $m_i\,(\mathrm{d}^2 r_i/\mathrm{d}t^2) = m_i\,(\mathrm{d}w_i/\mathrm{d}t)$, where the radial velocity is $w_i = \mathrm{d}r_i/\mathrm{d}t$. The vibrational kinetic energy is:

$$VKE = \int_{r_0}^{r_i} m_i\, \frac{\mathrm{d}w_j}{\mathrm{d}t}\, \mathrm{d}r_i = \int_{r_0}^{r_i} m_i\, \mathrm{d}w_i\, \frac{\mathrm{d}r_i}{\mathrm{d}t} = \int_0^{w_i} m_i\, w_i\, \mathrm{d}w_i = \frac{1}{2}\, m_i\, w_i^2 \tag{6.9}$$

If one now includes pulsation in two directions (r^+, r^-) as shown in *figure 4c*, one obtains the pulsational kinetic energy per molecule:

$$\varepsilon_i^v = m_i < w_{ir+}^2 > = 2\,(k\,T/2) = k\,T \tag{6.10}$$

The summation over all molecules within the pulsating cluster c results in

$$U_i^v = \varepsilon_c^v = \Sigma \varepsilon_i^v = \Sigma m_i < w_{ir+}^2 > = N_i\, k\,T \tag{6.11}$$

Finally, another summation over all clusters in an eddy gives

$$U^v = \varepsilon_e^v = \Sigma \varepsilon_c^v = N\,k\,T \tag{6.12}$$

In summary, because of the equipartition principle, the *total thermal kinetic energy per molecule, cluster, and eddy* become:

$$\varepsilon_i^k = \varepsilon_i^t + \varepsilon_i^r + \varepsilon_i^v = 3\,k\,T \tag{6.13}$$

$$U_i^k = \varepsilon_c^k = U_i^t + U_i^r + U_i^v = 3\,N_i\,k\,T \tag{6.14}$$

$$U^k = \varepsilon_e^k = U^t + U^r + U^v = 3\,N\,k\,T \tag{6.15}$$

Also, in view of equation (5.4), one obtains from (6.14) and (6.15)

$$T\,S_i = \varepsilon_i^k N_i = U_i^k = 3\,N_i\,k\,T \tag{6.16}$$

$$T\,S = \Sigma U_i^k = U^k = U = 3\,N\,k\,T \tag{6.17}$$

6.2. Mechanical potential energy

The mechanical potential energy of the system will be identified as the kinetic energy associated with the *non-equilibrium* translational, rotational, and pulsational motions of the molecules defined as:

$$\varepsilon_i^{pt} = 3\,k\,\mathbb{T}_i = m_i < (V_i')^2 > /2 = 3\,m_i < (V_{ix}')^2 > \tag{6.19}$$

$$\varepsilon_i^{pr} = 3\,k\,\mathbb{T} = m_i < (\Omega_i')^2 > /2 = 3\,m_i < (\Omega_{i\theta+}')^2 > \tag{6.20}$$

$$\varepsilon_i^{pv} = 3\,k\,\mathbb{T} = m_i < (W_i')^2 > /2 = 3\,m_i < (W_{ir+}')^2 > \tag{6.21}$$

where $\mathbf{V}_i' = \mathbf{u}_i - \mathbf{v}_i$, $\Omega_{ix+}' = \boldsymbol{\omega}_{ix+} - \boldsymbol{\omega}_{cx+}$, and $\mathbf{W}_i' = \mathbf{w}_i - \mathbf{w}_c$ are the *peculiar* translational, rotational, and pulsational velocity of the molecule. Collecting the separate contributions, the *total potential energy per molecule, cluster, and eddy* become:

$$\varepsilon_i^p = \varepsilon_i^{pt} + \varepsilon_i^{pr} + \varepsilon_i^{pv} = 3\,k\,\mathbb{T} \tag{6.22}$$

$$U_i^p = \Sigma \varepsilon_i^p = \varepsilon_i^p\, N_i = U_i^{pt} + U_i^{pr} + U_i^{pv} = 3\,N_i\,k\,\mathbb{T} \tag{6.23}$$

$$U^p = \Sigma U_i^p = U^{pt} + U^{pr} + U^{pv} = 3\,N\,k\,\mathbb{T} \tag{6.24}$$

6.3. Internal energy

Finally, the internal energy U^i of the system is identified by Eq. (5.6) that for a simple fluid gives the *Gibbs free energy*

$$G = \Sigma \mu_i\, N_i = U^i = \mu\, N \tag{6.25}$$

Therefore, the Gibbs free energy per molecule g_i (chemical potential μ_i) is expressed as the product of the internal molecular pressure $P_{mi} = P$ and volume

$$\mu_i = g_i = \varepsilon_i^i = P_{mi}\, V_{mi} = 3\,k\,T \tag{6.26}$$

where V_{mi} is the volume of the molecule. The summation of the preceding equation over all molecules in a cluster gives the *total internal energy per cluster*,

$$G_i = U_i^i = \mu_i N_i = P V_c = 3 N_i k T \tag{6.27}$$

where $V_c = \Sigma V_{mi} = N_i V_{mi}$ is the volume of the cluster. Similarly, the summation of equation (6.27) over all clusters in an eddy gives the *total internal energy of the system*

$$G = U^i = P V = 3 N k T \tag{6.28}$$

where $V_e = V = \Sigma V_c$ is the system or the eddy volume.

When the results of sections 6.1–6.3 are collected, the modified form of the first law of thermodynamics becomes

$$dU = d(T S) - d(\mathbb{P} V) + d(\mu N) \tag{6.29}$$

leading to the modified Euler equation

$$U = T S - \mathbb{P} V + \mu N \tag{6.30}$$

Because $G_{i\beta} = U_{i\beta}^i$ by (6.27), and according to *figure 1*, the internal energy of an *element* at scale β is the total energy of the *system* at the lower scale $(\beta - 1)$, $U_{i\beta}^i = U_{\beta-1}$, one arrives at the invariant form of the modified form of the first law of thermodynamics:

$$U_\beta = Q_\beta - W_\beta + G_\beta = Q_\beta - W_\beta + N_{e\beta} (G_i)_{\beta-1} = Q_\beta - W_\beta + N_{e\beta} U_{\beta-1} = \ldots \tag{6.31}$$

when $N_{e\beta}$ is the number of elements (energy levels) in the system at scale β.

7. DEFINITION OF ENTROPY AND ITS RELATION TO THE THERMAL KINETIC ENERGY

Under isothermal conditions, equation (5.4) reduces to

$$T\, dS = \Sigma \varepsilon_i^k\, dN_i \tag{7.1}$$

that may be expressed as

$$T\, d\Sigma S_i = \Sigma \varepsilon_i^k\, dN_i \tag{7.2}$$

and, through the removal of the summation, as

$$T\, dS_i = \varepsilon_i^k\, dN_i \tag{7.3}$$

Integration of the above equation, with zero integration constant due to Nernst–Planck statement of the third law of thermodynamics, gives

$$T S_i = \varepsilon_i^k N_i = U_i^k = 3 N_i k T \tag{7.4}$$

such that

$$S_i = 3 N_i k \tag{7.5}$$

Summation over all clusters within the system results in

$$S = 3 N k \tag{7.6}$$

and hence

$$T S = 3 N k T \tag{7.7}$$

in accordance with equation (6.17).

For an *adiabatic* system, when the potential energy is constant and reactions are absent, equation (5.3) reduces to:

$$dU = d\Sigma U_i^k = d(\Sigma \varepsilon_i^j N_i^j) = \Sigma \varepsilon_i^j\, dN_i^j + \Sigma N_i^j\, d\varepsilon_i^j = 0 \tag{7.8}$$

that leads to

$$\varepsilon_i^j\, dN_i^j = -N_i^j\, d\varepsilon_i^j \qquad j = t, r, v \tag{7.9}$$

Parallel to the classical methods [40, 41], when $d\varepsilon_i^j/(kT)$ is a constant, the above expression gives the classical relation for equilibrium distribution of particles N_i among various quantum states:

$$dN_i^j / N_i^j = -d\varepsilon_i^j / kT \qquad j = t, r, v \tag{7.10}$$

or

$$d \ln N_i^j = -d\varepsilon_i^j / kT \tag{7.11}$$

From the integration of the above equation one obtains the *modified Boltzmann distribution functions*:

$$N_i^j = e^{-\alpha} e^{-(\varepsilon_i^j / kT)} = e^{-(\varepsilon_i^j / kT) + 1} \qquad j = t, r, v \tag{7.12}$$

The choice $\alpha = -1$ in equation (7.12) insures that when the energy ε_i^j becomes equal to that of a single molecule kT, one obtains $N_i = 1$ as is to be expected.

The summation of equation (7.12) over all translational, rotational, or vibrational quantum states results in:

$$\sum_i N_i^j = N_i = \sum_i e^{-(\varepsilon_i^j / kT) + 1} = e \sum_i e^{-(\varepsilon_i^j / kT)} = e\, Z^j \qquad j = t, r, v \tag{7.13}$$

when the *translational*, the *rotational*, the *vibrational partition function* Z^j are defined as

$$Z^j = \sum_i e^{-(\varepsilon_i^j / kT)} \qquad j = t, r, v \tag{7.14}$$

Also, the product of equation (7.13) with $j = t, r$, and v, results in:

$$N_i = N_i^t N_i^r N_i^v = e^{-3\alpha} e^{-(\varepsilon_i^k / kT)} = e^{-(\varepsilon_i^k / kT) + 3} \tag{7.15}$$

The summation of equation (7.15) over all quantum states of the system gives

$$\Sigma N_{\mathrm{i}} = N = e^{3}\, Z^{\mathrm{t}} Z^{\mathrm{r}} Z^{\mathrm{v}} = e^{3}\, Z \tag{7.16}$$

when the *total partition function* Z is defined as

$$Z = \sum_{\mathrm{i}} e^{-(\varepsilon_{\mathrm{i}}^{\mathrm{k}}/kT)} \tag{7.17}$$

or $Z = Z^{\mathrm{t}}\, Z^{\mathrm{r}}\, Z^{\mathrm{v}}$, in accordance with the classical results [40–42].

For an ideal gas with only translational degree of freedom, one obtains the classical results [40–41]:

$$\frac{Z^{\mathrm{t}}}{N} = e^{\alpha} \tag{7.18}$$

$$G^{\mathrm{t}} = -\alpha\, N\, k\, T \tag{7.19}$$

$$\ln W^{\mathrm{t}} = N \ln \frac{Z^{\mathrm{t}}}{N} + \frac{U^{\mathrm{t}}}{k\,T} + N \tag{7.20}$$

When $\alpha = -1$, in accordance with the modified Boltzmann distribution function in equation (7.12), the results in (7.18)–(7.20) reduce to $G^{\mathrm{t}} = N\, k\, T$, and $T\, S^{\mathrm{t}} = T\, k\, \ln W^{\mathrm{t}} = N\, k\, T$. Therefore, including all three degrees of freedom and applying the equipartition principle leads to:

$$G = G^{\mathrm{t}} + G^{\mathrm{r}} + G^{\mathrm{v}} = 3\, N\, k\, T \tag{7.21}$$

$$T\, S = T\, (S^{\mathrm{t}} + S^{\mathrm{r}} + S^{\mathrm{v}}) = 3\, N\, k\, T \tag{7.22}$$

that are in accordance with equations (6.28) and (6.17).

8. CONCLUDING REMARKS

A new state function called the reversible heat was introduced that is composed of isothermal and isentropic heat. Also, another new state function called the reversible work was introduced that is composed of isobaric and isochoric work. The concepts of reversible heat and work resulted in the introduction of the modified forms of the first and the second law of thermodynamics. Both macroscopic as well as microscopic definitions of heat, work, and internal energy were presented and the relation between entropy and thermal kinetic energy was examined. The definition of the Boltzmann constant was introduced as $k = m_{\mathrm{k}}\, \nu_{\mathrm{k}}\, c = 1.381 \cdot 10^{-23}$ J·K^{-1}, suggesting an equivalence between the Kelvin absolute temperature scale and length scale. The new physical concepts are harmonious with the classical results, and appear to provide higher degrees of symmetry in the mathematical expressions of the laws of thermodynamics. The results will be useful for the future development of the grand unified statistical theory of fields.

Acknowledgements

This research is supported by NASA grant No. NAG3–1863 and in part by NSF grant No. 8820077.

REFERENCES

[1] Broglie L. de, C. R. Acad. Sci. Paris 183 (1926) 447; 184 (1927) 273; 185 (1927) 380.

[2] Broglie L. de, Non-Linear Wave Mechanics, A Causal Interpretation, Elsevier, New York, 1960

[3] Broglie L. de, Found. Phys. 1 (1970) 5.

[4] Madelung E., Z. Physik. 40 (1926) 332

[5] Schrödinger E., Berliner Sitzungsberichte (1931) 144.

[6] Fürth R., Phys. 81 (1933) 143.

[7] Bohm D., Phys. Rev. 85 (1952) 166.

[8] Takabayasi T., Prog. Theor. Phys. 70 (1952) 1.

[9] Bohm D., Vigier J.-P., Phys. Rev. 96 (1954) 208.

[10] Nelson E,. Phys. Rev. 150 (1966) 1079.

[11] Nelson E., Quantum Fluctuations, Princeton University Press, Princeton, New Jersey, 1985.

[12] de la Peña L., J. Math. Phys. 10 (1969) 1620.

[13] de la Peña L., Cetto A.M., Found. Phys. 12 (1982) 1017.

[14] Barut A.O., Ann. Physik. 7 (1988) 31.

[15] Barut A.O., Bracken A.J., Phys. Rev. D 23 (1981) 2454.

[16] Vigier J.-P., Lett. Nuvo Cim. 29 (1980) 467; Gueret P., Vigier J.-P., Found. Phys. 12 (1982) 1057; Cufaro Petroni C., Vigier J.-P., Found. Phys. 13 (1983) 253; Vigier J.-P., Found. Phys. 25 (1995) 1461.

[17] Reynolds O., Phil. Trans. Roy. Soc. A 186 (1895) 123.

[18] Taylor G.I., Proc. Roy. Soc. A 151 (1935) 421.

[19] Kármán T. von, Howarth L. Proc. Roy. Soc. A 164 (1938) 192.

[20] Robertson H.P., Proc. Camb. Phil. Soc. 36, 209 (1940).

[21] Kolmogoroff A.N., C. R. Acad. Sci. USSR 30 (1941) 301; 32 (1942) 16.

[22] Chandrasekhar S., Rev. Mod. Phys. 15 (1943) 1.

[23] Chandrasekhar S., Stochastic, Statistical, and Hydrodynamic Problems in Physics and Astronomy, Selected Papers, vol. 3, University of Chicago Press, Chicago, 1989.

[24] Batchelor G.K., The Theory of Homogeneous Turbulence, Cambridge University, Cambridge, 1953.

[25] Landau L.D., Lifshitz E.M., Fluid Dynamics, Pergamon Press, New York, 1959.

[26] Tennekes H., Lumley J.L., A First Course In Turbulence, MIT Press, 1972.

[27] Zeldovich Y.B., Annual Review of Fluid Mechanics 9 (1977) 215.

[28] Arecchi F.T., Harrison R.G., Instabilities and Chaos in Quantum Optics, Springer Verlag, Berlin, 1987.

[29] Sohrab S.H., Transport phenomena and conservation equations for multicomponent chemically-reactive

ideal gas mixtures, in: Proceeding of the 31st ASME National Heat Transfer Conference, HTD-Vol. 328, 1996, pp. 37–60.

[30] Sohrab S.H., Bull. Am. Phys. Soc. 40 (1) (1995) 646.

[31] de Groot R.S., Mazur P., Nonequilibrium Thermodynamics, North-Holland, 1962.

[32] Williams F.A., Combustion Theory, Benjamin Cummings, New York, 1985.

[33] Morse P., Thermal Physics, Benjamin Cummings, New York, 1969.

[34] Chapman S., Cowling T.G., The Mathematical Theory of Non-uniform Gases, Cambridge University Press, Cambridge, 1953.

[35] Hirschfelder J.O., Curtiss C.F., Bird R.B., Molecular Theory of Gases and Liquids, Wiley, New York, 1954.

[36] Planck M., The Theory of Heat Radiation, Dover, New York, 1991.

[37] Planck M., Ann. Physik. 4 (1901) 553.

[38] Jackson J.D., Classical Electrodynamics, Wiley, New York, 1975.

[39] Van Wylen G.J., Sonntag R.E., Borgnakke C., Fundamentals of Classical Thermodynamics, Wiley, New York, 1994.

[40] Sonntag R.E., van Wylen G.J., Fundamentals of Statistical Thermodynamics, Wiley, New York, 1966.

[41] Giet H.W., Thermophysics, Van Nostrand, New York, 1971.

[42] Zemansky M.W., Heat and Thermodynamics, McGraw-Hill, New York, 1957.