

Some Implications of the Modified Forms of the First and the Second Laws of Thermodynamics and the Variational Principles in Chemically Reactive Systems

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Abstract: - The application of a scale-invariant statistical theory of fields to statistical thermodynamics is discussed. Defining the *Boltzmann* constant as $k_k = k = m_k < v_k > c = 1.381 \times 10^{-23}$ J/K, *Kelvin* absolute temperature scale becomes a length scale. The thermal equilibrium between matter and radiation fields is described. The modified definition of temperature results in the speed of sound in atmosphere 358 m/s and a modified mechanical equivalent of heat equal to the universal gas constant $J = R^0$. The physical foundation of the first and the second laws of thermodynamics are described in terms of two new state variables defining the reversible heat $Q_{rev} = TS$ and the reversible work $W_{rev} = \mathbf{P}V$. The variational principles in reactive systems are described in terms of an invariant *Lagrangian* defined as $L_\beta = U_\beta = Q_\beta - W_\beta + G_\beta = K_\beta - \Pi_\beta + L_{\beta-1}$.

Key-Words: - First and second laws of thermodynamics. Variational principles in reactive systems.

1 Introduction

The similarities between the stochastic quantum fields [1-16] and the classical hydrodynamic fields [17-26] resulted in the introduction of a scale-invariant model of statistical mechanics [27, 28], leading to a modified theory of Brownian motions, and the hypothesis of the existence of an equilibrium statistical field called *cluster-dynamics*. The application of the scale-invariant model of statistical mechanics to the field of statistical thermodynamics was recently described [29]. In the present study, further implications of the modified definition of temperature, reversible heat and work and their impact on the physical foundation of the modified forms of the first and the second law of thermodynamics will be described.

2 A Scale-Invariant Model of Statistical Mechanics

The scale-invariant model of statistical mechanics (shown in Fig.1) for equilibrium galacto-, planetary-, hydro-system-, fluid-element-, eddy-, cluster-, molecular-, atomic-, subatomic-, kromo-, and tachyon-dynamics corresponding to the scale $\beta = g, p, h, f, e, c, m, a, s, k,$ and t has been introduced [28]. Each statistical field is identified as the "system" and is composed of an ensemble of "elements" described by a distribution function $f_\beta(\mathbf{u}_\beta) = f_\beta(\mathbf{r}_\beta, \mathbf{u}_\beta, t_\beta)$

$d\mathbf{r}_\beta d\mathbf{u}_\beta$. Each element is composed of an ensemble of small particles called the "atoms" of the field and are viewed as *point-mass*. The element (system) of the smaller scale (j) becomes the atom (element) of the larger scale ($j+1$). Because of the finite extension of the elements of the statistical fields, they possess harmonic translational, rotational, and vibrational motion described earlier [28].

Following the classical methods [30-34] the invariant definition of density ρ_β , and velocity of *element* \mathbf{v}_β , *atom* \mathbf{u}_β , and *system* \mathbf{w}_β at the scale β are [28]

$$\rho_\beta = n_\beta m_\beta = m_\beta \int f_\beta d\mathbf{u}_\beta \quad , \quad \mathbf{u}_\beta = \mathbf{v}_{\beta-1} \quad (1)$$

$$\mathbf{v}_\beta = \rho_\beta^{-1} m_\beta \int \mathbf{u}_\beta f_\beta d\mathbf{u}_\beta \quad , \quad \mathbf{w}_\beta = \mathbf{v}_{\beta+1} \quad (2)$$

Similarly, the invariant definition of the peculiar and diffusion velocities are introduced as

$$\mathbf{V}'_\beta = \mathbf{u}_\beta - \mathbf{v}_\beta \quad , \quad \mathbf{V}_\beta = \mathbf{v}_\beta - \mathbf{w}_\beta \quad (3)$$

such that

$$\mathbf{V}_\beta = \mathbf{V}'_{\beta+1} \quad (4)$$

The invariant equilibrium and non-equilibrium translational temperature and pressure are $3kT_\beta = m_\beta < \mathbf{u}_\beta^2 >$, $P_\beta = \rho_\beta < \mathbf{u}_\beta^2 > / 3$,

$3kT_\beta = m_\beta \langle \mathbf{V}_\beta'^2 \rangle / 3$, and $\mathbf{P}_\beta = \rho_\beta \langle \mathbf{V}_\beta'^2 \rangle / 3$, leading to the corresponding *invariant ideal "gas" laws* [28]

$$P_\beta V = N_\beta kT_\beta, \quad \mathbf{P}_\beta V = N_\beta k\mathbf{T}_\beta \quad (5)$$

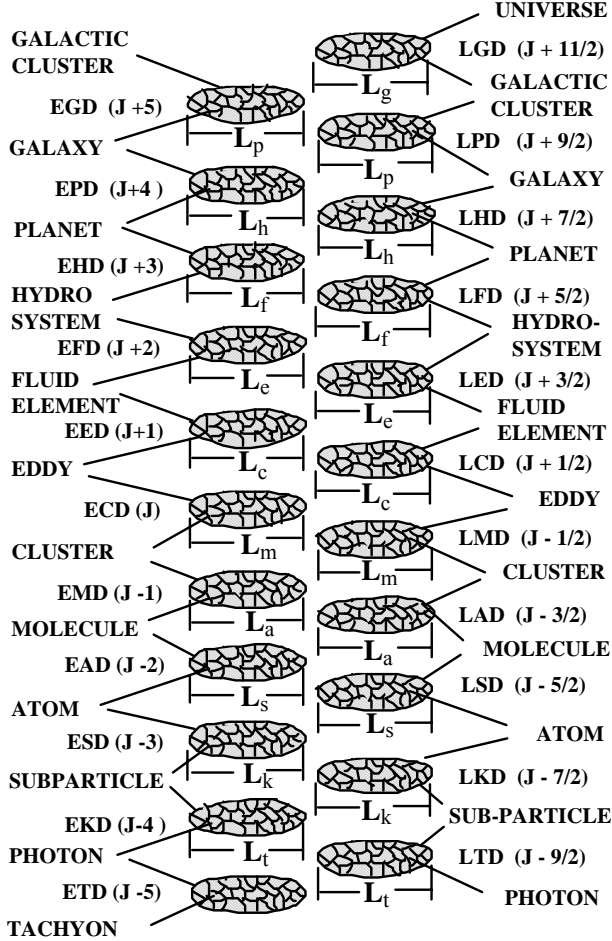


Fig.1. A scale-invariant view of statistical mechanics from cosmic to tachyonic scales.

3 Definition of Boltzmann Constant and Identification of the Absolute Temperature Scale as a Length Scale

Because at the state of thermodynamic equilibrium the mean velocity of each particles (virtual oscillators) vanishes $\langle u_\beta \rangle = 0$, the energy of the particle could be expressed as [29]

$$\begin{aligned} \varepsilon_\beta &= m_\beta \langle u_\beta^2 \rangle = m_\beta \langle \lambda_\beta v_\beta \lambda_\beta v_\beta \rangle = \\ &= m_\beta \langle (\lambda_\beta v_\beta)^2 \rangle^{1/2} \langle (\lambda_\beta v_\beta)^2 \rangle^{1/2} \\ &= m_\beta \langle u_\beta^2 \rangle^{1/2} \langle \lambda_\beta^2 \rangle^{1/2} \langle v_\beta^2 \rangle^{1/2} = p_\beta \langle \lambda_\beta^2 \rangle^{1/2} \langle v_\beta^2 \rangle^{1/2} \end{aligned} \quad (6)$$

where $p_\beta = m_\beta \langle u_\beta^2 \rangle^{1/2}$ is the root-mean-square momentum of particle. The above result could be expressed either in terms of mean frequency or mean wavelength as

$$\varepsilon_\beta = m_\beta \langle u_\beta^2 \rangle = \langle p_\beta \rangle \langle \lambda_\beta^2 \rangle^{1/2} \langle v_\beta^2 \rangle^{1/2} = h_\beta \langle v_\beta^2 \rangle^{1/2} = h_\beta \langle v_\beta \rangle \quad (7)$$

$$\varepsilon_\beta = m_\beta \langle u_\beta^2 \rangle = \langle p_\beta \rangle \langle v_\beta^2 \rangle^{1/2} \langle \lambda_\beta^2 \rangle^{1/2} = k_\beta \langle \lambda_\beta^2 \rangle^{1/2} = k_\beta \langle \lambda_\beta \rangle \quad (8)$$

when the definition of stochastic *Planck* and *Boltzmann* factors are introduced as [29]

$$h_\beta = \langle p_\beta \rangle \langle \lambda_\beta^2 \rangle^{1/2} \quad (9)$$

$$k_\beta = \langle p_\beta \rangle \langle v_\beta^2 \rangle^{1/2} \quad (10)$$

At the important scale of $\beta = k$ associated with *vacuum*, equilibrium chromodynamic field EKD (Fig.1), the results (9) and (10) are identified as the *Planck* [35, 36] and the *Boltzmann* constants [29]

$$h_k = h = \langle p_k \rangle \langle \lambda_k^2 \rangle^{1/2} = 6.626 \times 10^{-34} \text{ J.s} \quad (11)$$

$$k_k = k = \langle p_k \rangle \langle v_k^2 \rangle^{1/2} = 1.381 \times 10^{-23} \text{ J/K} \quad (12)$$

Hence, *Planck* and *Boltzmann* constants respectively relate to the *spatial* and *temporal* aspects of vacuum fluctuations.

Following *de Broglie* hypothesis for the wavelength of matter waves [2]

$$\lambda_\beta = h / p_\beta \quad (13)$$

the frequency of matter waves was introduced as [28]

$$v_\beta = k / p_\beta \quad (14)$$

leading to the gravitational mass of photon [28]

$$m_k = (hk / c^3)^{1/2} = 1.84278 \times 10^{-41} \text{ kg} \quad (15)$$

that is much larger than the reported value of $4 \times 10^{-51} \text{ kg}$ [37]. Therefore, light particles are predicted to have a small *gravitational mass* and hence a finite spatial extent, in accordance with the perceptions of *Newton* [38].

According to the present field theory [29], photons are considered to be composed of a cluster of much smaller particles called *tachyons* [39]. Since the velocity of light is the mean thermal speed of tachyons, $u_k = c = \langle u_t^2 \rangle^{1/2} = 2.998 \times 10^8 \text{ m/s}$, some of the tachyons must be *superluminal* $u_t > c$. Therefore, the *physical space*, i.e. *vacuum*, is

identified as a *tachyonic fluid* that is *Dirac* stochastic ether [40] or *de Broglie* [3] hidden thermostat. The mean-free-path and the mean-free-frequency of photons in *vacuum* are given as [29]

$$\langle \lambda_k^2 \rangle^{1/2} = 1/R^\circ = 0.119935 \text{ m}$$

$$\langle v_k^2 \rangle^{1/2} = 2.49969 \times 10^9 \text{ Hz} \quad (16)$$

The tachyonic fluid that constitutes the physical space is considered to be *compressible*, in accordance with *Planck's compressible ether* [41]. Compressibility of space is evidenced by the fact that the velocity of light is finite $c < \infty$, while velocity of signals in an absolutely incompressible medium would be infinite. Parallel to atmospheric air that becomes compressible when *Mach* number $Ma = v/a$ approaches unity, the tachyonic fluid that constitutes the physical space becomes compressible when *Michelson* number $Mi = v/c$ approaches unity. Here, a (c) is the speed of sound (light) in atmosphere (vacuum). Thus, $Ma > 1$ ($Mi > 1$) corresponds to supersonic (superchromatic) flow of air (tachyonic fluid) leading to the formation of *Mach (Poincaré-Minkowski)* cone that separates the zone of sound (light) from the zone of silence (darkness). The compressibility of physical space was suggested to account for the *Lorentz-Fitzgerald* contraction [29], thus providing a *causal* [42] explanation of the relativistic effects [43] in harmony with the perceptions of *Poincaré* and *Lorentz* [44-46].

The atomic mass unit is identified to be exactly the total energy of the photon

$$\text{amu} = m_k c^2 = 1.656 \times 10^{-23} \quad (17)$$

such that the *Avogadro-Loschmidt* number is predicted as [28]

$$N^\circ = 1/(m_k c^2) = 6.0376 \times 10^{23} \quad (18)$$

that leads to the universal gas constant $R^\circ = N^\circ k = 8.3379 \text{ m}^{-1}$.

Since all known forms of matter are made of atoms, the relation (17) reveals the central importance of photons in the constitution of matter. The metamorphosis of matter and radiation was first recognized by *Newton* [38]

" Qu. 30. Are not gross bodies and light convertible into one another, and may not bodies receive much of their activity from the particles of light which enter their composition? ". " The changing of bodies into light, and light into bodies, is very comfortable to the course of Nature, which seems delighted with transmutations, ". " And among such various and strange transmutations, why may not Nature change bodies into light and light into bodies? "

Indeed, conversion of gravitational mass into light is as simple as striking a match, when minute amounts of gravitational mass associated with the bound energy between atoms is converted to photons as a result of chemical reactions at molecular-dynamic scales [28].

Because of the definition of *Boltzmann* constant in (12), *Kelvin absolute temperature scale* is identified as a *length scale*

$$nkT_k = nk \langle \lambda_k \rangle = P_k = \bar{E}_k \quad (19)$$

Thus, the important limit of $T \rightarrow 0$ corresponds to the approach to zero wavelength $\lambda \rightarrow 0$ of oscillations, requiring zero physical extension that would constitute a singularity of the field. At the scale of equilibrium atomic-dynamics EAD, the elements of the field are molecules with the energy

$$\epsilon_m = kT_m = k \langle \lambda_m \rangle \quad (20)$$

Similarly, at the scale of equilibrium cluster dynamics ECD, the kinetic energy of each cluster is the summation of the kinetic energy of all the molecules within it. This procedure can be extended to higher and lower scales such that one obtains

$$\begin{aligned} \epsilon_{\beta+1} &= \sum kT_\beta = \sum k \langle \lambda_\beta \rangle = N_\beta k \langle \lambda_\beta \rangle \\ &= k \langle \lambda_{\beta+1} \rangle = kT_{\beta+1} \end{aligned} \quad (21)$$

One defines the rest energy of an element at the scale $\beta+1$ as the sum of the total, dynamic plus rest energies $\epsilon_\beta = m_\beta c^2 = m_{o\beta} c^2 + m_{o\beta} \langle u_\beta^2 \rangle$ of the atoms composing it (Fig.1), for harmonic oscillations in two directions $\langle u_{\beta x+}^2 \rangle = \langle u_{\beta x-}^2 \rangle$ [29]. Therefore, following *Lorentz* [44], one can define the relativistic mass as

$$m_{\beta} = m_{o\beta} + m_{o\beta} \langle u_\beta^2 \rangle / c^2 = m_{o\beta} + m_{d\beta} \quad (22)$$

to be composed of the rest mass $m_{o\beta}$ and the dynamic mass $m_{d\beta}$. that can be viewed as *dark matter*. Also, the relation between the gravitational mass and energy was introduced as [29]

$$\begin{aligned} \epsilon_{oc} &= \sum \epsilon_m = N_m \epsilon_m = N_m \sum \epsilon_a = N_m N_a \epsilon_a = \dots \\ &= N_m N_a N_s N_k \epsilon_k = N_m N_a N_s N_k m_k c^2 = m_{oc} c^2 \end{aligned} \quad (23a)$$

Hence, the rest energy of a molecular cluster with the gravitational mass $m_{oc} = Nm_k$ is the same as the energy of $N = N_m N_a N_s N_k$ photons with the gravitational mass m_k moving at the speed of light [29]. The kinetic energy of a cluster under harmonic translation involves inertial mass and is expressed as

$$\begin{aligned} \epsilon_c &= m_{ic} \langle u_c^2 \rangle = N_m m_{im} \langle u_c^2 \rangle = N_m N_a m_{im} \langle u_c^2 \rangle \\ &= \dots = N_m N_a N_s N_k m_k \langle u_c^2 \rangle = m_{oc} \langle u_c^2 \rangle \end{aligned} \quad (23b)$$

that by (23a) leads to the *equivalence principle* or the equality of gravitational and inertial mass

$$m_{ic} = m_{oc} \quad (23c)$$

The finite gravitational mass of photon given by (15) is also in accordance with the perceptions of *Poincaré* [47, 48] who first introduced

$$E = mc^2 \quad (24)$$

However, one notes that the expression introduced five years later by *Einstein* [49, 50]

$$E_o = mc^2 \quad (25)$$

was conceived for massless photons. Since photons are considered to be composed of a large number of tachyons [29], (17), (22), and (23) suggest that all matter could be defined as *dark matter*. That is, without any motions all matter in the universe, as we know it will also cease to exist. According to (23), mass is simply associated with numbers in harmony with the perceptions of *Sommerfeld* [51]

"Our spectral series, dominated as they are by integral quantum numbers, correspond, in a sense, to the ancient triad of the lyre, from which the Pythagoreans 2500 years ago inferred the harmony of the natural phenomena; and our quanta remind us of the role which the Pythagorean doctrine seems to have ascribed to the integers, not merely as attributes, but as the real essence of physical phenomena."

as well as *Weyl* [52].

The model thus suggests that particles are wave-packets, such that one encounters eddy-waves in each fluid element, cluster-waves in each eddy, molecular-waves in each cluster, and so on until one reaches tachyon waves in each photon as schematically shown in Fig.2.

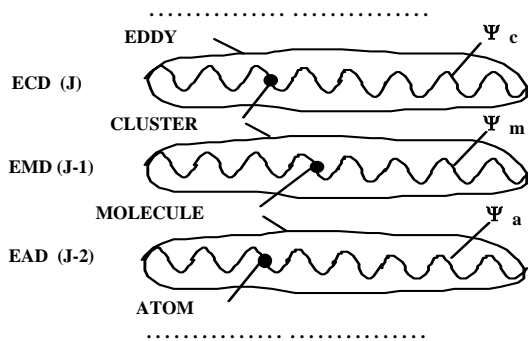


Fig.2 Cascade of wave packets, wave functions Ψ_β , and particles for equilibrium cluster-dynamic (ECD), molecular-dynamic (EMD), and atomic-dynamic (EAD) scales.

The representation of particles as wave packets is consistent with the quantum mechanics [2, 53-55].

4 Thermal Equilibrium Between Matter Particles and Physical Space

Let us consider molecules of type A and B as particles of gas that is in thermal equilibrium. One notes that the molecules A and B are not only in thermal equilibrium with each other, but also with the radiation field, the physical space, within which they reside. Thus, one considers that matter and photons, i.e. space, form a multi-component mixture under steady-state condition. The equality of the energy of individual particles under the condition of thermal equilibrium between the matter and the radiation fields by (7) leads to

$$\begin{aligned} \varepsilon_A = h_A \langle v_A \rangle &= \varepsilon_B = h_B \langle v_B \rangle = \\ &= \varepsilon_k = h_k \langle v_k \rangle = hv \end{aligned} \quad (26)$$

According to the *de Broglie* relation (13), the *Planck* factors $h_\beta = m_\beta v_\beta \lambda_\beta$ (9) of all particles are equal to the important universal constant that is the *Planck* constant

$$h_A = h_B = \dots = h_\beta = h_k = h \quad (27)$$

Therefore, the criteria of thermal equilibrium (26) and (27) require that the mean frequency of all oscillators be identical to that of the photons in equilibrium with them such that

$$\langle v_A \rangle = \langle v_B \rangle = \dots = \langle v_k \rangle = \langle v \rangle \quad (28)$$

If rather than the frequency, the energy of the particles (virtual oscillators) are expressed in terms of the wavelengths (8), under thermal equilibrium one requires

$$\varepsilon_A = k_A \langle \lambda_A \rangle = \varepsilon_B = k_B \langle \lambda_B \rangle = k_k \langle \lambda_k \rangle = kT \quad (29)$$

Now, parallel to (26), the definition of the frequency of matter waves (14) requires that the *Boltzmann* factors $k_\beta = m_\beta v_\beta \lambda_\beta$ (10) of all oscillators be equal to an important universal constant that is the *Boltzmann* constant first calculated by *Planck* [29]

$$k_A = k_B = \dots = k_\beta = k_k = k \quad (30)$$

Since according to the classical thermodynamics, thermal equilibrium requires the equality of temperatures of all particles

$$T_A = T_B = \dots = T_\beta = T_k = T \quad (31)$$

and (29)-(30) relate the temperature T to the mean wavelength of the oscillators.

In the description of the radiation energy spectrum, at any given temperature a photon of total

energy $\varepsilon = m_k c^2 = h\nu = k\lambda$ can manifest itself at any point within the spectrum from radio waves to gamma rays. As the frequency ν (wavelength λ) changes from gamma to radio (radio to gamma) rays, the energy of the photon $h\nu$ ($k\lambda$) will be the same and the equality $\varepsilon = h\nu = k\lambda$ holds since $h/k = \lambda/\nu$ and $\lambda\nu = c = \text{constant}$. In the long-wavelength cosmic *gravitational waves*, the spatial energy density will be very low since the energy ε is distributed over an extremely long (*cosmic strings*) spatial extension at cosmic scales. On the other hand, in the high frequency gamma rays, all the photon energy will be concentrated in a very short wavelength wave-packet under extremely rapid temporal agitations.

According to the classical results [56-58], the relation between pressure and energy of radiation field $P_k V = (1/3)U$ is different from that for an ideal monatomic gas $P_g V = (2/3)U$. However, according to the present theory, the factor of (2) in the latter expression is removed since molecules of ideal gas are considered to possess harmonic translational motions in two directions (x^+ , x^-) as discussed earlier [28]. Furthermore, since one assumes that the finite size particles possess translational, rotational, and vibrational energy, the factor of (1/3) in the expressions also cancel. That is, the total pressure (energy) becomes the sum of translational, rotational, and vibrational $P = P_t + P_r + P_v = 3P_t$ ($U = U_t + U_r + U_v = 3U_t$) contributions. The equality of the three components is required by the equipartition principle. At the scale of EKD, vacuum, one obtains the temperature and pressure of *photon gas*

$$kT_k = m_k \langle u_k^2 \rangle / 3 = m_k \langle u_{kx}^2 + u_{ky}^2 + u_{kz}^2 \rangle / 3 \\ = m_k (3c^2) / 3 = m_k c^2 \quad (32)$$

$$P_k = \rho_k \langle u_k^2 \rangle / 3 = \rho_k c^2 = n_k m_k c \langle \lambda_k \rangle \langle \nu_k \rangle \\ = n_k h\nu_k = n_k E_k = \bar{E}_k \quad (33)$$

Therefore, the present theory leads to symmetric treatment of matter and radiation fields $PV = U$.

5 The Spatial Versus the Temporal Uncertainty Principles

In view of the above considerations, the two fundamental universal constants of physics, (h , k) help to define the state of equilibrium between the radiation field, the physical space, and the matter-fields within it. If one now considers that the temperature of matter be always larger than that of

the radiation field within which it resides, and expresses this in terms of the *Planck* constant by application of (7)

$$\Delta\varepsilon_\beta = \Delta v_\beta \Delta p_\beta = \Delta v_\beta \Delta \lambda_\beta \Delta p_\beta \geq \Delta\varepsilon_k = h\Delta v_\beta \quad (34)$$

one obtains the *Heisenberg* uncertainty principle [53]

$$\Delta\lambda_\beta \Delta p_\beta \geq h \quad (35)$$

which could be called *Heisenberg spatial uncertainty principle* since it involves $\Delta\lambda$. In a parallel fashion, if one expresses the criteria of matter being hotter than space $T_\beta > T_k$ in terms of the *Boltzmann* constant by applying (8)

$$\Delta\varepsilon_\beta = \Delta v_\beta \Delta p_\beta = \Delta v_\beta \Delta \lambda_\beta \Delta p_\beta \geq \Delta\varepsilon_k = k\Delta\lambda \quad (36)$$

then one arrives at what may be called the *temporal uncertainty principle* [29]

$$\Delta v_\beta \Delta p_\beta \geq k \quad (37)$$

since it involves Δv . Also, because $T_\beta > T_k$, one arrives at the counter-intuitive fact, supported by the observed refraction of light, that the density of vacuum exceeds that of matter $\rho_k > \rho_\beta$ in accordance with the perceptions of *Newton* [38]. The connection between the scale-invariant statistical fields being described herein and the invariant *Schrödinger* equation has been addressed [59].

6 The Modified Definitions of the Thermodynamic Temperature and the Mechanical Equivalent of Heat

The modified definition of thermodynamic temperature was introduced as [60]

$$(1/2)kT_m = m_m \langle u_{mx+}^2 \rangle / 2 \quad (38)$$

and is based on the energy per degree of freedom according to the classical results [56-58]. Because each molecule is considered to undergo harmonic translational oscillations in two directions (x^+ , x^-) [28], the total translational energy per molecule becomes

$$kT'_m = m_m \langle u_{mx+}^2 \rangle / 2 + m_m \langle u_{mx-}^2 \rangle / 2 = m_m \langle u_{mx}^2 \rangle \quad (39)$$

The inclusion of two translational degrees of freedom in the definition of temperature in (39) resolves the classical problem associated with the relationship between the velocity of propagation of sound in atmosphere and the mean thermal speed of molecules in air, a problem that was examined by

both *Newton* and *Laplace*. The classical definition of temperature T' in (39) and the modified definition in (38) are related as

$$kT'_m = m_m \langle u_{mx}^2 \rangle = 2m_m \langle u_{mx+}^2 \rangle = 2kT \quad (40)$$

With $T' = 298$ K, $m_m = 28.8 \times 1.67 \times 10^{-27}$ kg, one obtains from the preceding equation the mean translational velocity of molecules in air as [60]

$$\langle u_{mx+}^2 \rangle^{1/2} \approx 358 \text{ m/s} \quad (41)$$

in close agreement with the observed velocity of sound in standard atmosphere. Similar calculations lead to rms molecular speeds (1346, 336, 360, 300, 952, 287) m/s to be compared with the observed velocity of sound (1286, 332, 337, 308, 972, 268) m/s for gases (H_2 , O_2 , N_2 , Ar, He, CO_2) at standard conditions [60]. By comparison, one finds that the mean cluster velocity under equilibrium $T_c = T_m$ condition in air is about 11.3 cm/s for a molecular-cluster that contains 10^6 molecules. The above analysis does not require the classical assumption that propagation of sound be an *adiabatic* and *reversible*, i.e. isentropic, hence non-dissipative process. Indeed, it is known that sound propagation is a dissipative phenomenon and the acoustic energy dissipates into thermal energy.

Because of the factor of two between the classical and the modified definitions of temperature in (40), the mechanical equivalent of heat becomes modified. The factor of two appears in the thermal energy expressed as

$$Q = CdT' = 2CdT = 2CdT \quad (42)$$

where C is the specific heat. Because of the factor of two in (42), the unit of mechanical work (Joules) and heat (calorie) will be related by the modified value of the mechanical equivalent of heat [60]

$$J = 2J_c = 2 \times 4.18 = 8.36 \text{ J/Cal} \quad (43)$$

where $J_c \approx 4.18$ J/cal is the classical empirically determined mechanical equivalent of heat.

The modified definition of reversible work and heat were given as $W_{rev} = PV$ and $Q_{rev} = TS$ [60]. One can express thermal energy as $Q_{rev} = TS = NkT = \bar{N}R^\circ T$, where $\bar{N} = N/N^\circ$ and $R^\circ = N^\circ k$. Therefore, for one mole of an ideal gas the mechanical work and heat may be related by

$$W_{rev} = PV \propto Q_{rev} = R^\circ T \quad (44)$$

In view of (43)-(44), it is suggested that the mechanical equivalent of heat be identified as the universal gas constant R° [60]

$$J^\circ = R^\circ = N^\circ k = 8.3379 \text{ J/cal} \quad (45)$$

7 Physical Foundation and Derivation of the First Law of Thermodynamics

The modified definition of heat and work were introduced as [60]

$$dQ_{rev} = d(TS) = TdS + SdT = dQ_T + dQ_S \quad (46)$$

and

$$W_{rev} = d(PV) = PdV + VdP = dW_P + dW_V \quad (47)$$

that consists of the *isothermal reversible heat* dQ_T , the *isentropic reversible heat* dQ_S , the *reversible isobaric (dilatational) work* dW_P and the *reversible isochoric (stress) work* dW_V . One notes that $Q_1/Q_2 = T_1/T_2$ for a reversible $S_1 = S_2$ process.

With the definitions (46)-(47), it is possible to *derive* the first law of thermodynamics from the definition of the peculiar velocity in (3). By squaring (3) and taking its average and multiplying the result by the particle mass m_β one obtains

$$m_\beta \langle u_{\beta x+}^2 \rangle = m_\beta \langle v_{\beta x+}^2 \rangle + m_\beta \langle V_{\beta x+}'^2 \rangle \quad (48a)$$

because $\langle 2v_{\beta x+} V_{\beta x+}' \rangle = 0$. The sum of (48a) over all particles gives the first law of thermodynamics

$$Q_\beta = U_\beta + W_\beta \quad (48b)$$

if one defines the quantities

$$U_\beta = \sum m_\beta \langle v_{\beta x+}^2 \rangle = \sum m_\beta \langle v_{\beta x}^2 \rangle / 2 = \sum \epsilon_\beta \quad (49a)$$

$$Q_\beta = \sum m_\beta \langle u_{\beta x+}^2 \rangle = N_\beta kT_\beta = P_\beta V \quad (49b)$$

$$W_\beta = \sum m_\beta \langle V_{\beta x+}'^2 \rangle = NkT_\beta = P_\beta V \quad (49c)$$

A generalized definition of work under one, two, or three dimensions that includes the variation of force as well as displacement could be written as the sum of the *reversible displacement work* and the *reversible stress work*

$$dW_{rev} = d(\tau x) = \tau dx + x d\tau \quad (50a)$$

$$dW_{rev} = d(\sigma A) = \sigma dA + A d\sigma \quad (50b)$$

$$dW_{rev} = d(PV) = PdV + VdP \quad (50c)$$

In the above expressions, one has two possible paradigms. First, one can follow the conventional point of view that considers the parameters (τ , σ , P) as three types of stress, namely [60]

$$\begin{aligned} \tau &= \{\text{Force at a point}\} \\ \tau x &= \tau L = E = \text{Line Energy} \end{aligned} \quad (51a)$$

$$\begin{aligned} \sigma &= \{\text{Force per unit length}\} \\ \sigma x^2 &= \sigma A = E = \text{Surface Energy} \end{aligned} \quad (51b)$$

$$\begin{aligned} P &= \{\text{Force per unit area}\} \\ Px^3 &= PV = E = \text{Volumetric Energy} \end{aligned} \quad (51c)$$

A second paradigm that is perhaps more appealing is to identify each one of the intensive properties (τ , σ , \mathbf{P}) as *potential energy density* [60]

$$\begin{aligned} \tau &= \{\text{Energy per unit length}\} \\ \tau x &= E = \text{Energy} \end{aligned} \quad (52a)$$

$$\begin{aligned} \sigma &= \{\text{Energy per unit area}\} \\ \sigma x^2 &= E = \text{Energy} \end{aligned} \quad (52b)$$

$$\begin{aligned} \mathbf{P} &= \{\text{Energy per unit volume}\} \\ \mathbf{P} x^3 &= E = \text{Energy} \end{aligned} \quad (52c)$$

The second paradigm is preferable because the tension τ as force at a mathematical point, a singularity of the field, is not well defined. But viewing τ as potential energy per unit length that is extended in space is well defined.

8 Modified Forms of the First and the Second Laws of Thermodynamics and the Variational Principles in Chemically Reactive Systems

The modified form of the first law of thermodynamics was introduced as [60]

$$d(TS) = dU + d(\mathbf{P}V) - \sum d(\mu_i N_i) \quad (53)$$

or

$$dQ = dU + dW - dG \quad (54)$$

where the *Gibbs* function is

$$G = \sum \mu_i N_i = \Sigma G_i \quad (55)$$

The result (53) leads directly to the *Euler* equation for a simple fluid

$$U = TS - \mathbf{P}V + \mu N = Q - W + G \quad (56)$$

that may also be written as

$$U = Q - W + G = U_k - U_p + U_i \quad (57)$$

According to (57), the *Gibbs* function G_β has been identified as the internal energy of the system at that particular scale $U_{i\beta}$ [28]. Next, one relates the internal energy of the system at scale β to the total energy of the system at the lower scale ($\beta-1$) [28]

$$G_\beta = U_{i\beta} = U_{\beta-1} \quad (58)$$

Substituting from (58) in (57) leads to the scale invariant form of the first law of thermodynamics [28]

$$U_\beta = Q_\beta - W_\beta + G_\beta = Q_\beta - W_\beta + U_{\beta-1} = \dots \quad (59)$$

For a system that is non-reactive one obtains

$$\begin{aligned} d(U_\beta + W_\beta - Q_\beta) &= d(U_\beta + \mathbf{P}_\beta V - T_\beta S_\beta) = \\ &= d(\mathbf{H}_\beta - T_\beta S_\beta) = dG_\beta = 0 \end{aligned} \quad (60)$$

as required, where $\mathbf{H}_\beta = U_\beta + \mathbf{P}_\beta V$ is the non-equilibrium enthalpy.

The problem of reducing chemical reactions in classical thermodynamics to that of dynamical systems by the application of variational principles investigated by *Helmholtz* [61, 62] and *Fényes* [63] has thus far been unsuccessful as discussed by *Yourgrau and Mandelstam* [64]

“In spite of all these superficial resemblances, any rigid attempt at reducing chemical reactions *in toto* to dynamical systems and thus to variational principles is doomed to failure”

It is interesting to examine if the modified form of the first law of thermodynamics described above could help in arriving at a variational principle for reactive systems. By definitions (49b), and (49c) heat and work may be identified as

$$Q_\beta = T_\beta S_\beta = K_\beta \quad \text{Kinetic energy} \quad (61)$$

$$W_\beta = \mathbf{P}_\beta V = \Pi_\beta \quad \text{Potential energy} \quad (62)$$

The above definitions apply to a system of particles with total kinetic energy $K_\beta(\dot{q}_\beta)$ that is only a function of particle velocities (\dot{q}_β) given by (49b)

$$K_\beta = \sum m_{i\beta} \langle \dot{q}_{i\beta x}^2 \rangle = \sum m_{i\beta} \langle u_{i\beta x}^2 \rangle / 2 \quad (63)$$

The potential energy $\Pi_\beta(q_\beta)$ is only a function of the coordinates (q_β) and is due to particle interactions, such as is associated with expansion or contraction of an elastic medium (52c).

Following the classical methods [64] and in view of (59), (61), and (62), one introduces the *Lagrangian* L_β for chemically reactive systems as

$$L_\beta = U_\beta = K_\beta - \Pi_\beta + G_\beta \quad (64)$$

In the absence of chemical reactions or at equilibrium condition $dG = 0$ hence $G = \text{constant}$, and because the potential energy $\Pi_\beta(q_\beta)$ is only defined to within and additive constant, (64) reduces to the classical *Lagrangian* for non-reactive systems that leads to the *Euler-Lagrange* equation of motion

$$\frac{d}{dt} \left(\frac{\partial L_\beta}{\partial \dot{q}_\beta} \right) = \frac{\partial L_\beta}{\partial q_\beta} \quad (65)$$

for the particles. Also, because the definition (58) identifies *Gibbs* function as the total energy of system at the lower scale $U_{\beta-1}$, (64) leads to the scale-invariant form of the *Lagrangian*

$$U_\beta = L_\beta = G_{\beta+1} = K_\beta - \Pi_\beta + G_\beta = K_\beta - \Pi_\beta + U_{\beta-1} = \\ = K_\beta - \Pi_\beta + L_{\beta-1} = \dots \quad (66)$$

The definition (66) is therefore in accordance with the definition given by *Yourgrau and Raw* [65] who assumed that the *Lagrangian* function may be identified as the *Gibbs* free energy G .

The modified forms of the second law of thermodynamics for heat and work were introduced as [60]

$$\delta Q_{\text{act}} \leq dQ_{\text{rev}} = d(TS) \quad (67)$$

$$\delta W_{\text{act}} \geq dW_{\text{rev}} = d(\mathbf{P}\mathbf{V}) \quad (68)$$

Also, for real (non-quasi-static) heat or work transfer processes one may write

$$\delta Q_{\text{act}} + \delta Q_{\text{dis}} = dQ_{\text{rev}} \quad (69)$$

$$\delta W_{\text{act}} = dW_{\text{rev}} + \delta W_{\text{loss}} \quad (70)$$

This is because during all real processes some energy of ordered motions δW_{loss} will be dissipated into energy of random motions δQ_{dis} . Since δW_{loss} is always finite for all real processes, (69)-(70) lead to the second law of thermodynamics for heat and work in (67) and (68). Also, the equality $|\delta W_{\text{loss}}| = -|\delta Q_{\text{dis}}|$ insures that the difference between the actual heat and the actual work from (69)-(70) becomes a state variable

$$\delta Q_{\text{act}} - \delta W_{\text{act}} = dQ_{\text{rev}} - dW_{\text{rev}} = dU \quad (71)$$

such that

$$\oint (\delta Q_{\text{act}} - \delta W_{\text{act}}) = 0 \quad (72)$$

in accordance with the classical results [56-58].

In view of the above discussions, for an isolated system, since dissipation is always present $\delta W_{\text{loss}} = \delta Q_{\text{dis}} \geq 0$, one obtains from (69)

$$dQ_{\text{rev}} = d(TS) \geq \delta Q_{\text{act}} \quad (73)$$

that is the modified form of the second law of thermodynamics (67) and can also be expressed as

$$TdS + SdT \geq \delta Q_{\text{act}} \quad (74)$$

Now, if one assumes that all heat transfer processes in the system are ideal and hence occur isothermally $dT = 0$, then (74) reduces to the classical *Clausius* statement of the second law of thermodynamics

$$TdS = (\delta Q_{\text{act}})_T = \delta Q_{\text{rev}} \quad (75)$$

Therefore, when left to itself an isolated system will tend to maximize its entropy i.e. the total number of

virtual oscillators N that participate in thermal motions [28].

9. Concluding Remarks

A scale-invariant model of statistical mechanics was applied to describe the physical foundation of the first and the second laws of thermodynamics. Defining the *Boltzmann* constant as $k_k = k = m_k < v_k > c = 1.381 \times 10^{-23}$ J/K, *Kelvin* absolute temperature scale was identified as a length scale. The condition of thermal equilibrium between matter and radiation field, the physical space, was formulated. Following *Heisenberg spatial uncertainty principle* $\Delta \lambda_\beta \Delta p_\beta \geq h$, the relation $\Delta v_\beta \Delta p_\beta \geq k$ was introduced as the *temporal uncertainty principle*. A modified definition of thermodynamic temperature was introduced and shown to result in the prediction of the velocity of sound in standard atmosphere as 358 m/s in close agreement with the observations, as well as the identification of the modified mechanical equivalent of heat as the universal gas constant $J^\circ = R^\circ = 8.334$ J/cal. Finally, the variational principles in chemically reactive systems were described in terms of an invariant *Lagrangian* $L_\beta = K_\beta - \Pi_\beta + L_{\beta-1}$.

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