



Thermodynamic disequilibrium of the atmosphere in the context of global warming

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1 **Thermodynamic Disequilibrium of the Atmosphere in the Context of global Warming**

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24 **Abstract**

25 The atmosphere is an example of a non-equilibrium system. This study explores the relationship
26 among temperature, energy and entropy of the atmosphere, introducing two variables that serve
27 to quantify the thermodynamic disequilibrium of the atmosphere. The maximum work, W_{max} ,
28 that the atmosphere can perform is defined as the work developed through a thermally reversible
29 and adiabatic approach to thermodynamic equilibrium with global entropy conserved. The
30 maximum entropy increase, $(\Delta S)_{max}$, is defined as the increase in global entropy achieved
31 through a thermally irreversible transition to thermodynamic equilibrium without performing
32 work. W_{max} is identified as an approximately linear function of $(\Delta S)_{max}$. Large values of W_{max}
33 or $(\Delta S)_{max}$ correspond to states of high thermodynamic disequilibrium. The seasonality and
34 long-term historical variation of W_{max} and $(\Delta S)_{max}$ are computed, indicating highest
35 disequilibrium in July, lowest disequilibrium in January with no statistically significant trend
36 over the past 32 years. The analysis provides a perspective on the interconnections of
37 temperature, energy and entropy for the atmosphere and allows for a quantitative investigation of
38 the deviation of the atmosphere from thermodynamic equilibrium.

39

40 **Keywords:** thermodynamic disequilibrium, energy, entropy, temperature, global warming

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47 **1. Introduction**

48 Most phenomena in the atmosphere are characterized by thermodynamic irreversibility and
49 evolve in time with increases in entropy. The circulation is maintained by the instability of the
50 atmospheric system, and this question has been studied from a variety of different perspectives.
51 Lorenz (1955) presented the Lorenz Energy Cycle (LEC) theory explaining the energetics of
52 atmosphere mainly from a mechanical perspective with kinetic energy produced at the expense
53 of available potential energy (*APE*), a measure of the instability of the atmosphere. A number of
54 other groups have sought to address the question from a thermodynamic perspective focusing on
55 the budget of atmospheric energy and entropy (e.g. Coleman and Greenberg 1967; Dutton 1973;
56 Paltridge 1975; Livezey and Dutton 1976; Peixoto et al. 1991; Goody 2000; Paltridge 2001;
57 Pauluis and Held 2002a, 200b; Ozawa 2003; Romps 2008; Lucarini et al. 2011; Bannon 2005;
58 Bannon 2012; Bannon 2013; Huang and McElroy 2014, 2015).

59 Lorenz (1955) defines *APE* as the difference in total static energy (internal plus potential)
60 between the current state of the dry air component of the atmosphere and that of an idealized
61 reference state, identified as the state that minimizes the static energy of the dry air component of
62 the atmosphere after a sequence of reversible isentropic and adiabatic transformations with air
63 parcels conserving their potential temperature, θ . The reference state is characterized by
64 horizontal stratification with absolute stability in pressure, potential temperature and height.

65 For an isentropic and adiabatic adjustment of the mass field, the surface of constant θ behaves as
66 a material surface. Thus, the average pressure over an isentropic surface, $\tilde{p}(\theta)$, can be quantified
67 based on the relation:

68
$$\tilde{p}(\theta) = \iint_{\sigma} p(x, y, \theta) \cdot dx dy / \iint_{\sigma} dx dy \quad (1)$$

69 where σ is the global area defined by a constant θ surface and $p(x, y, \theta)$ is the air pressure in an
70 (x, y, θ) coordinate system. When a constant θ surface intersects the earth's surface ($\theta \leq$
71 $\theta_{surface}$), $p(\theta)$ is set equal to $p_{surface}$. During an isentropic and adiabatic rearrangement of
72 mass, $\tilde{p}(\theta)$ is conserved, representing thus the pressure of the reference state. *APE* is defined as

$$73 \quad APE = \int (\Phi + I) \cdot dm - \int (\Phi_r + I_r) \cdot dm \quad (2)$$

74 where Φ and Φ_r represent the potential energy and the corresponding reference state of the
75 atmosphere respectively, and I and I_r denote the internal energy for the atmosphere and for the
76 corresponding reference state respectively (Peixoto and Oort, 1992).

77 Fig. 1 presents a schematic illustration of *APE*, computed based on assimilated meteorological
78 data from the Modern Era Retrospective-analysis for Research and Applications (MERRA). The
79 upper panels display the zonal-average potential temperature, θ , and the zonal-average
80 temperature, T , for year 2008. The lower panels present the zonal-average potential temperature,
81 θ , and the zonal-average temperature, T , for the associated reference state, computed based on
82 equation (1). According to the LEC theory, the maximum production of kinetic energy
83 corresponds to the expenditure of all of the *APE* when the structure of θ on the upper panel
84 collapses to the structure depicted on the lower panel. The structure of θ in the reference state
85 (lower panels in Fig. 1) defines the condition of absolute mechanical equilibrium, since the
86 horizontal pressure force has been eliminated and the vertical pressure force is balanced by
87 gravity.

88 A number of groups have investigated the *APE* of the atmosphere based on the LEC theory (Oort
89 1964; Oort and Yienger 1996; Li et al. 2007; Boer and Lambert 2008; Hernández-Deckers and
90 Storch 2010; Marques et al. 2009; Becker 2009; Marques et al. 2010; Marques et al. 2011; Kim

91 and Kim 2013). For example, using MERRA data, Kim and Kim (2013) estimated the global
 92 averaged APE as $4.34 MJ/m^2$ on an annual mean, $4.02 MJ/m^2$ for the June ~ August (JJA)
 93 mean and $4.75 MJ/m^2$ for the December ~ February (DJF) mean.

94 The reference state defined by Lorenz, although in mechanical equilibrium, is not in thermal
 95 equilibrium. The zonal-average temperature, T , for the associated reference state in Fig. 1
 96 indicates the existence of a vertical temperature gradient. The reference state has the potential to
 97 produce additional kinetic energy through a thermodynamically reversible process. According to
 98 the second law of thermodynamics, motions of the atmosphere should drive the system towards
 99 thermodynamic equilibrium. A thermodynamic equilibrium state requires both mechanical and
 100 thermal equilibrium. Fig. 2 presents a schematic illustration of an approach to thermodynamic
 101 equilibrium. The lower panels in Fig. 2 display the zonal-average potential temperature, θ , and
 102 zonal-average temperature, T , appropriate for a thermodynamic equilibrium state with the
 103 equilibrium temperature, T_{eq} , set equal to $249K$. When the atmosphere reaches thermodynamic
 104 equilibrium, it is completely divested of potential to produce kinetic energy.

105 With respect to entropy, the atmosphere is an open system exchanging energy and matter with its
 106 surroundings. According to Prigogine (1962) and De Groot and Mazur (2013), the total variation
 107 of the entropy of the atmosphere, dS^{atm}/dt , consists of two components: the transfer of entropy
 108 across the boundary, dS_e^{atm}/dt , and the entropy produced within the system, dS_i^{atm}/dt . The
 109 majority of the phenomena operational in the atmosphere, such as the frictional dissipation of
 110 kinetic energy, are thermodynamically irreversible. Thus dS_i^{atm}/dt is always greater than zero.
 111 dS^{atm}/dt can be expressed as:

$$112 \quad \frac{dS^{atm}}{dt} = \frac{dS_e^{atm}}{dt} + \frac{dS_i^{atm}}{dt} \quad (3)$$

113 Peixoto et al. (1991) provided a comprehensive analysis of the contributions to dS_i^{atm}/dt and
 114 dS_e^{atm}/dt . A relevant question is: if, since time t_0 the atmosphere had become an isolated
 115 system with zero exchange of energy and matter exchange with its environment ($dS^{atm} =$
 116 dS_i^{atm}), how much greater would be the eventual increase in entropy, $\int_{t_0}^{\infty} \frac{dS^{atm}}{dt} \cdot dt$, when the
 117 atmosphere had reached thermodynamic equilibrium. Similar to APE , $\int_{t_0}^{\infty} \frac{dS^{atm}}{dt} \cdot dt$ reflects the
 118 thermodynamic disequilibrium of the atmosphere.

119 The maximum entropy increase problem was studied by Coleman and Greenberg (1967)
 120 addressing a general fluid system other than specifically the atmosphere. Based on the work of
 121 Willard Gibbs (1873, 1875), they proposed a thermodynamic equilibrium state for any given
 122 fluid system together with the associated equilibrium entropy. They argued that the dynamical
 123 implication of the difference between the equilibrium state entropy and the entropy of the given
 124 system is “remarkable” because it provides a “stability criterion”. In the case of the atmosphere,
 125 this difference corresponds to $\int_{t_0}^{\infty} \frac{dS^{atm}}{dt} \cdot dt$ subject to the constraint $\frac{dS_e^{atm}}{dt} = 0$.

126 Dutton (1973) extended and applied Coleman and Greenberg's study to the atmosphere, and
 127 pointed out that every natural state of the atmosphere corresponds to a maximum entropy state, a
 128 motionless, hydrostatic state with the same mass and total energy. And this maximum entropy
 129 state is the equilibrium towards which an atmosphere in isolation will naturally tend. Bannon
 130 (2005, 2012, 2013) reexamined the question of the maximum entropy state and introduced the
 131 atmospheric available energy which is defined as a generalized Gibbs function between the
 132 atmosphere and an isothermal reference state. The reference atmosphere is in thermal and
 133 hydrostatic equilibrium and, thus, is dynamically and convectively "dead".

134 Landau and Lifshitz (1980) described an approach to study the thermodynamic disequilibrium
135 problem in an Entropy-Energy Diagram and to quantify the maximum work, W_{max} , and
136 maximum entropy increase, $(\Delta S)_{max}$, that a conceptual isolated system could perform or achieve.
137 Both variables represent the level of disequilibrium for a conceptual system. Their basic idea and
138 methodology is introduced in section 3 with a simple case for demonstration. In the case of the
139 atmosphere, the atmospheric available energy proposed by Bannon is equivalent to the maximum
140 work concept, though without consideration of the gravitational fractionation of the dry air
141 (Bannon 2013). In this study, we extend and apply Landau and Lifshitz's approach to the
142 atmosphere, investigating the level of thermodynamic disequilibrium for the atmosphere in the
143 context of global warming using assimilated meteorological data from MERRA. The analysis
144 provides a perspective on the relationship among temperature, energy and entropy and allows for
145 a quantitative investigation of the deviation of the atmosphere from thermodynamic equilibrium.

146 **2. Data**

147 The study is based on meteorological data from the MERRA compilation covering the period
148 January 1979 to December 2010 (Rienecker 2007). Air temperatures and geopotential heights
149 were obtained on the basis of retrospective analysis of global meteorological data using Version
150 5.2.0 of the GEOS-5 DAS. We use the standard 3-hourly output available for 42 pressure levels
151 with a horizontal resolution of 1.25° latitude \times 1.25° longitude. The highest pressure level at the
152 top of the atmosphere is 0.1 hPa. The global surface temperature anomalies employed in this
153 study are from the Goddard Institute for Space Studies (GISS) (Hansen et al. 2010).

154

155 **3. Maximum work and maximum entropy increase problem**

156 For a thermally isolated system consisting of several components out of thermal equilibrium,

157 while equilibrium is being established, the system can perform mechanical work. The transition
158 to equilibrium may follow a variety of possible paths. The final equilibrium states of the system
159 represented by its energy and entropy may differ as a consequence. The total work that can be
160 performed as well as the entropy increase that may occur from the evolution of a non-
161 equilibrium system will depend on the manner in which equilibrium is established. Here, we
162 explore two extreme paths to thermal equilibrium: one consistent with the performance of
163 maximum work, W_{max} ; the other corresponding to a maximum increase in entropy, $(\Delta S)_{max}$.

164 The system performs maximum work when the process of reaching thermal equilibrium is
165 reversible. Fig. 3 provides the simplest case with the thermally isolated system consisting of only
166 two components. When the hot component at temperature T_{hot} loses an amount of energy
167 $Q_h = -T_{hot}\delta S_{hot}$, where δS_h is the decrease in entropy for the hot component, the cold
168 component at temperature T_{cold} gains energy $Q_c = T_{cold}\delta S_c$, where δS_c is the entropy increase
169 for the cold component. If the process is reversible, then $\delta S_c + \delta S_h = 0$ and the work produced
170 in the process is equal to $Q_h - Q_c$. As the reversible process continues, T_{hot} and T_{cold} converge
171 to an equilibrium temperature T_{eq}^S , with the superscript " S " denoting zero entropy change, and
172 the thermally isolated system reaches thermal equilibrium with work output W_{max} . In this study,
173 the transition to thermal equilibrium with W_{max} is identified as Evolution 1.

174 The system achieves $(\Delta S)_{max}$ when the process of reaching thermal equilibrium is totally
175 irreversible and the internal energy remains constant. Fig. 4 provides the simplest case for this
176 with energy transfer, Q , occurring directly between the components without performing any
177 work. The process is thermally irreversible, and the entropy of the combination of the two
178 components increases by $Q(1/T_{cold} - 1/T_{hot})$. As the energy transfer continues, T_{hot} and T_{cold}

179 converge to another equilibrium temperature T_{eq}^W , with the superscript " W " representing the
180 condition where no work is performed and the subscript " eq " defining equilibrium. T_{eq}^W is
181 greater than T_{eq}^S , since zero work is performed on the external medium. Maximum increase in
182 entropy, $(\Delta S)_{max}$, for the entire system occurs in the end. In this study, the transition to thermal
183 equilibrium with $(\Delta S)_{max}$ is indicated as Evolution 2.

184 The maximum work and maximum entropy increase can be depicted in an Entropy-Energy
185 Diagram. If a system is in thermal equilibrium, its entropy, S_{eq} , and temperature, T_{eq} , are
186 functions of its total energy, E_{eq} : namely $S_{eq} = S_{eq}(E_{eq})$ and $T_{eq} = T_{eq}(E_{eq})$. In Fig. 5 the
187 continuous line defines the behavior of the function $S_{eq}(E_{eq})$ in an Entropy-Energy Diagram.
188 For a non-equilibrium system with thermal condition (E, S) corresponding to point b in Fig. 5,
189 the horizontal segment ΔE represents the work performed as the system approaches equilibrium
190 through Evolution 1 while the vertical segment ΔS illustrates the increase in entropy associated
191 with Evolution 2. Consequently $T_{eq}(E_{eq})$ at point a corresponds to T_{eq}^W , and $T_{eq}(E_{eq})$ at point b
192 corresponds to T_{eq}^S . The maximum work, W_{max} , and the maximum entropy increase, $(\Delta S)_{max}$,
193 reflect the magnitude of the thermodynamic disequilibrium of a non-equilibrium system: if the
194 isolated system is further removed from equilibrium, W_{max} and $(\Delta S)_{max}$ are increased; and vice-
195 versa.

196 **4. Ideal gas in a gravitational field**

197 In a uniform gravitational field with height represented by z , the potential energy, u , of a
198 molecule is given by $u = mgz$, where m is the mass of a molecule and g is the gravitational
199 acceleration. The distribution of density for a system consisting of an ideal gas at thermodynamic
200 equilibrium is given by the barometric formula:

201
$$\rho(\vec{r}) = \rho_0 e^{-mgz/(k_B T_{eq})} \quad (4)$$

202 where ρ_0 is the mass density at level $z = 0$, T_{eq} is the equilibrium temperature and k_B is the
 203 Boltzmann constant. The pressure in equilibrium, P_{eq} , at height z is given by:

204
$$P_{eq}(z) = \int_z^\infty \rho_0 e^{-mgh/(k_B T_{eq})} g \cdot dh \quad (5)$$

205 or

206
$$P_{eq}(z) = P_0 e^{-mgz/(k_B T_{eq})} \quad (6)$$

207 where P_0 is the pressure at level $z = 0$.

208 For a single mole of ideal gas, assuming temperature-independent specific heat, the associated
 209 entropy, S_m , is given by:

210
$$S_m = C_{p,m} \ln T - R \ln p + S_{m0} \quad (7)$$

211 where $C_{p,m}$ is the molar heat capacity at constant pressure, R is the gas constant, T is the
 212 temperature of the gas, p is the pressure and S_{m0} is a constant of integration. Thus, the total
 213 entropy of the system is defined by:

214
$$S = \int (C_{p,m} \ln T - R \ln p + S_{m0}) \cdot dn \quad (8)$$

215 and the total static energy (internal plus potential), E , is given by:

216
$$E = \int C_{v,m} T \cdot dn + \int \rho g z \cdot dv \quad (9)$$

217 where n is the number of moles, v is volume and $C_{v,m}$ is the molar heat capacity at constant
 218 volume.

219 If the initial density distribution of a system follows equation (4), the system consisting of the
 220 ideal gas is in thermodynamic equilibrium at T_{eq} . For a one-dimensional equilibrium system at
 221 two temperatures T_{eq}^1 and T_{eq}^2 , Dutton (1972) proved that the associated equilibrium energies, E_{eq}^1 ,

222 E_{eq}^2 and the equilibrium entropies S_{eq}^1, S_{eq}^2 are related by:

$$223 \quad S_{eq}^2 - S_{eq}^1 = C_{p,m} \cdot \ln(E_{eq}^2/E_{eq}^1) \cdot \int dn \quad (10)$$

224 Thus:

$$225 \quad S_{eq}(T_{eq} + \Delta T_{eq}) - S_{eq}(T_{eq}) = C_{p,m} \cdot \ln(E_{eq}(T_{eq} + \Delta T_{eq})/E_{eq}(T_{eq})) \cdot \int dn \quad (11)$$

226 For the case where $\Delta T_{eq} \rightarrow 0$ and $\ln(1+x) \sim x$ ($x \ll 1$),

$$227 \quad S_{eq}(T_{eq} + \Delta T_{eq}) - S_{eq}(T_{eq}) \approx C_{p,m} \cdot \frac{E_{eq}(T_{eq} + \Delta T_{eq}) - E_{eq}(T_{eq})}{E_{eq}(T_{eq})} \cdot \int dn \quad (12)$$

228 It follows that

$$229 \quad \frac{E_{eq}(T_{eq} + \Delta T_{eq}) - E_{eq}(T_{eq})}{S_{eq}(T_{eq} + \Delta T_{eq}) - S_{eq}(T_{eq})} \approx \frac{E_{eq}(T_{eq})}{C_{p,m} \int dn} \quad (13)$$

230 Under thermodynamic equilibrium conditions, $E_{eq}(T_{eq}) = C_{p,m} \int T_{eq} dn$ (Peixoto and Oort,

231 1992). Thus:

$$232 \quad \frac{\partial E_{eq}}{\partial S_{eq}} = T_{eq} \quad (14)$$

233 If the initial density distribution of a system departs from equation (4), the system consisting of

234 the ideal gas will not be in equilibrium. It can approach equilibrium through a number of paths

235 including evolution 1 depicted in Fig. 3 and evolution 2 depicted in Fig. 4. Consequently,

236 maximum work, W_{max} , is produced by the system if the transition to equilibrium at temperature

237 T_{eq}^S is reversible (evolution 1 in Fig. 3), namely $\Delta S = 0$. The maximum work, W_{max} , is equal to

238 ΔE , according to the first law of thermodynamics. W_{max} may be expressed as:

239
$$W_{max} = \int C_{v,m}(T - T_{eq}^S) \cdot dn + \int (\rho - \rho_{eq}^S)gz \cdot dv \quad (15)$$

240 where $\rho_{eq}^S(z) = \rho_0^S e^{-mgz/(k_B \cdot T_{eq}^S)}$. Reflecting the principle of mass conservation, $\int \rho_{eq}^S \cdot dv =$

241 $\int \rho \cdot dv$, or equivalently, $\rho_0^S = (\int \rho \cdot dv) / (\int e^{-mgz/(k_B \cdot T_{eq}^S)} \cdot dv)$.

242 Similarly, the system achieves maximum entropy increase if the transition to equilibrium at

243 temperature T_{eq}^W is thermally irreversible and produces no work (evolution 2 in Fig. 4), $\Delta E = 0$.

244 And the maximum entropy increase may be expressed as:

245
$$(\Delta S)_{max} = \int [C_{p,m}(\ln T_{eq}^W - \ln T) - R(\ln P_{eq}^W(z) - \ln p)] \cdot dn \quad (16)$$

246 where $P_{eq}^W(z) = P_0^W e^{-mgz/(k_B \cdot T_{eq}^W)}$. Because of the principle of mass conservation,

247 $\iint_{surface} P_{eq}^W(z) \cdot dxdy = \iint_{surface} P \cdot dxdy$. The equilibrium pressure P_{eq} at level $z = 0$,

248 namely P_0 , can be computed as:

249
$$P_0 = \iint_{surface} P \cdot dxdy / \iint_{surface} e^{-mgh/(k_B \cdot T_{eq})} \cdot dxdy \quad (17)$$

250 where h is the topographic height.

251 **5. A thermodynamic perspective on the atmosphere**

252 Oxygen (O₂) occupies 20.95% by volume of dry air in the atmosphere. Nitrogen (N₂) accounts

253 for 78.08%. The next two most abundant gases are argon (Ar) (0.93%) and carbon dioxide (CO₂)

254 (0.04%). To simplify the calculation in this study we assume that O₂ occupies 21% of dry air, N₂

255 78% and Ar 1% for well mixed dry air by volume and a constant gravity of 9.8 m/s². The molar

256 masses of O₂, N₂ and Ar equal 32 g/mol, 28 g/mol and 40 g/mol respectively.

257 For one mole of O₂, N₂ and Ar, the associated entropies $S_m^{O_2}$, $S_m^{N_2}$ and S_m^{Ar} are given by:

258
$$S_m^{O_2} = C_{p,m}^{O_2} \ln T - R \ln P^{O_2} + S_{m0}^{O_2} \quad (18)$$

259
$$S_m^{N_2} = C_{p,m}^{N_2} \ln T - R \ln P^{N_2} + S_{m0}^{N_2} \quad (19)$$

260
$$S_m^{Ar} = C_{p,m}^{Ar} \ln T - R \ln P^{Ar} + S_{m0}^{Ar} \quad (20)$$

261 where $C_{p,m}^{O_2}$, $C_{p,m}^{N_2}$ and $C_{p,m}^{Ar}$ represent the molar heat capacities at constant pressure for O₂, N₂ and
 262 Ar; P^{O_2} , P^{N_2} and P^{Ar} denote the partial pressures for O₂, N₂ and Ar; and $S_{m0}^{O_2}$, $S_{m0}^{N_2}$ and S_{m0}^{Ar} are
 263 the related constants of integration. Since O₂ and N₂ are diatomic gases, $C_{p,m}^{O_2}$ and $C_{p,m}^{N_2}$ are set
 264 equal to $\frac{7}{2}R$. Ar is monatomic gas, thus $C_{p,m}^{Ar}$ is equal to $\frac{5}{2}R$. And R is the ideal gas constant and
 265 equal to $8.3145 J/(mol \cdot K)$. Since in this study we are interested in changes in entropy,
 266 constants of integration are set to zero. The total entropy of dry air, S_{atm} , in the atmosphere may
 267 be expressed then as:

268
$$S_{atm} = S^{O_2} + S^{N_2} + S^{Ar} \quad (21)$$

269 where $S^{O_2} = \int (C_{p,m}^{O_2} \ln T - R \ln P^{O_2}) dn_{O_2}$, $S^{N_2} = \int (C_{p,m}^{N_2} \ln T - R \ln P^{N_2}) dn_{N_2}$ and $S^{Ar} =$
 270 $\int (C_{p,m}^{Ar} \ln T - R \ln P^{Ar}) dn_{Ar}$ respectively.

271 The total static energy of dry air, E_{atm} , is given by:

272
$$E_{atm} = E^{O_2} + E^{N_2} + E^{Ar} \quad (22)$$

273 where $E^{O_2} = \int C_{v,m}^{O_2} T \cdot dn_{O_2} + \int \rho^{O_2} g z \cdot dv$, $E^{N_2} = \int C_{v,m}^{N_2} T \cdot dn_{N_2} + \int \rho^{N_2} g z \cdot dv$ and $E^{Ar} =$
 274 $\int C_{v,m}^{Ar} T \cdot dn_{Ar} + \int \rho^{Ar} g z \cdot dv$ respectively.

275 For a specific equilibrium temperature, T_{eq} , the partial pressures, $P_{eq}^{O_2}$, $P_{eq}^{N_2}$ and P_{eq}^{Ar} , and the
 276 densities, $\rho_{eq}^{O_2}$, $\rho_{eq}^{N_2}$ and ρ_{eq}^{Ar} , for O₂, N₂ and Ar in equilibrium can be quantified according to the
 277 principle of mass conservation. For example, $\rho_{eq}^{O_2}$ can be computed based on $\int \rho_{eq}^{O_2} \cdot dv =$

278 $\int \rho^{O_2} \cdot dv$ and $\rho_{eq}^{O_2} = \rho_0^{O_2} \cdot e^{-m_{O_2}gh/(k_B \cdot T_{eq})}$. Subsequently, the entropy, S_{eq}^{atm} , and the static
 279 energy, E_{eq}^{atm} , of the atmosphere in equilibrium at T_{eq} can be computed based on equations (15)
 280 and (16).

281 The highest pressure level in the dataset is 0.1 hPa. S_{eq}^{atm} and E_{eq}^{atm} are quantified through
 282 integrations from the ocean or land surface to the 0.1 hPa level. Fig. 6 illustrates the behavior of
 283 the function $S_{eq}^{atm}(E_{eq}^{atm})$ with T_{eq} increasing from 100 K to 500 K. The behavior of $\partial E_{eq}^{atm}/$
 284 ∂S_{eq}^{atm} as a function of T_{eq} is shown in Fig.7. Reflecting the topographic height of the continents,
 285 $\partial E_{eq}^{atm}/\partial S_{eq}^{atm}$ is approximately equal, but not identical, to T_{eq} . When T_{eq} becomes warmer, the
 286 air molecules have higher kinetic energy and consequently have greater chances of moving to
 287 high altitudes and above the continents. Thus, the process of increasing T_{eq} involves a re-
 288 distribution of air between oceanic and continental regions.

289 In calculating (E^{atm}, S^{atm}) for a non-equilibrium real atmosphere, E^{atm} and S^{atm} are quantified
 290 through integrations from the topographic surface to 0.1 hPa level. The thermodynamic condition,
 291 (E^{atm}, S^{atm}) , of the atmosphere on May 30, 2002 is identified by point *b* in the Entropy-Energy
 292 Diagram in Fig. 8, below the line of $S_{eq}^{atm}(E_{eq}^{atm})$, confirming the fact that the atmosphere was
 293 out of thermodynamic equilibrium, with the associated $W_{max} = 29.2 MJ/m^2$ and $(\Delta S)_{max} =$
 294 $117 kJ/(m^2 \cdot K)$.

295 The seasonality of the thermodynamic condition, (E^{atm}, S^{atm}) , of the atmosphere in an Entropy-
 296 Energy Diagram is plotted in Fig. 9. The loop-shaped seasonality reflects the asymmetric
 297 distribution of land with respect to the equator in addition to the seasonally varying earth-sun
 298 distance. If the distributions of land in the Northern Hemisphere were the same as in the

299 Southern Hemisphere and the earth-sun distance was constant, the thermodynamic condition on
 300 June 22 (summer solstice) identified in an Entropy-Energy Diagram should be the same as for
 301 December 22 (winter solstice). Similarly, the thermodynamic condition on March 21 (vernal
 302 equinox) should overlap that for September 23 (autumnal equinox) (see Fig. 10). The seasonality
 303 in Fig. 9 would have been line-shaped with the conditions of June 22 and December 22 on one
 304 end, the conditions for March 21 and September 23 on the other.

305 A greater content of static energy in the atmosphere does not necessarily correspond to higher
 306 thermodynamic disequilibrium and vice versa. For example, the total static energy on May 1 is
 307 close to that on October 1. Since the associated total entropy on May 1 is greater than on October
 308 1, the atmosphere was thermodynamically more stable on May 1.

309 The seasonalities of W_{max} and $(\Delta S)_{max}$ are plotted in Fig. 11. The atmosphere reaches its state
 310 of highest thermodynamic disequilibrium in late July with $W_{max} = 31.4 \text{ MJ}/\text{m}^2$ and
 311 $(\Delta S)_{max} = 126 \text{ kJ}/(\text{m}^2 \cdot \text{K})$, its lowest state in mid January with $W_{max} = 27.7 \text{ MJ}/\text{m}^2$ and
 312 $(\Delta S)_{max} = 112 \text{ kJ}/(\text{m}^2 \cdot \text{K})$. W_{max} can be approximated as $W_{max} \approx 248\text{K} \cdot (\Delta S)_{max}$. Large
 313 values of W_{max} are associated with large values of $(\Delta S)_{max}$, corresponding to high states of
 314 thermodynamic disequilibrium. The thermodynamic condition (E^{atm}, S^{atm}) of the atmosphere is
 315 close to $S_{eq}^{atm}(E_{eq}^{atm})$ as depicted by Fig. 8. Thus, $W_{max}/(\Delta S)_{max}$ is approximately equal
 316 to $\partial E_{eq}^{atm}/\partial S_{eq}^{atm}$, and, consequently, to T_{eq} .

317 The long-term variation of W_{max} from January 1979 to December 2010 is illustrated in Fig. 12. The
 318 conspicuous intra-seasonal fluctuation depicted by the red line reflects the strong seasonal
 319 variation of the W_{max} . The blue line, computed using a 365-day running average, reflects the
 320 existence of an inter-annual variation. Linear regression of the annual mean average over this

321 period provides a regression slope of $2.4 J/(m^2 \cdot yr)$ with $R^2 = 0.004$, indicating that there is no
 322 statistically significant trend in thermodynamic disequilibrium. It is not yet clear what
 323 determines the inter-annual variability of W_{max} . The large scale atmosphere-ocean El Niño
 324 Southern Oscillation phenomenon could provide one possible explanation. We would note in this
 325 context that the highest peak in W_{max} is coincident with the major El Nino event of 1997-1998.

326 The seasonalities of the equilibrium temperatures, T_{eq}^S and T_{eq}^W , are displayed in Fig. 13. T_{eq}^W is
 327 greater than T_{eq}^S , reflecting the fact that no work is performed in evolution 2. Both T_{eq}^S and T_{eq}^W
 328 reach their peak values in late July, corresponding to the highest content of static energy. The 32-
 329 year averaged values for T_{eq}^S and T_{eq}^W are $248.9 K$ and $251.8 K$ respectively. The gap between
 330 T_{eq}^S and T_{eq}^W reflects the thermodynamic disequilibrium of the atmosphere.

331 In this study, the variation of T_{eq}^S is indicated by:

$$332 \quad \Delta T_{eq}^S = T_{eq}^S - 248.5K \quad (23)$$

333 and the variation of T_{eq}^W is defined by:

$$334 \quad \Delta T_{eq}^W = T_{eq}^W - 251.5K \quad (24)$$

335 The variation of T_{eq}^S and T_{eq}^W with the seasonal cycle removed is shown in Fig. 14. The increases
 336 of ΔT_{eq}^S and ΔT_{eq}^W generally follow the global surface temperature change, $\Delta T_{surface}$, with the
 337 correlation between ΔT_{eq}^S and $\Delta T_{surface}$ equal to 0.87 and correlation between ΔT_{eq}^W and
 338 $\Delta T_{surface}$ equal to 0.91. Thus, as the global surface temperature increased from January 1979 to
 339 December 2010, the thermodynamic conditions (E^{atm}, S^{atm}) of the atmosphere on an Energy-
 340 Entropy Diagram moved on a trajectory parallel to the line of $S_{eq}^{atm}(E_{eq}^{atm})$ in Fig. 8, resulting in
 341 increases in T_{eq}^S and T_{eq}^W , with W_{max} and $(\Delta S)_{max}$ remaining relatively constant.

342 6. Discussion and Summary

343 This study presented an approach for analysis of the interrelations of temperature, energy and
344 entropy of the atmosphere, and proposed two variables, W_{max} and $(\Delta S)_{max}$, as measures of the
345 thermodynamic disequilibrium of the atmosphere. W_{max} is approximately a linear function of
346 $(\Delta S)_{max}$: $W_{max} \approx 248K \cdot (\Delta S)_{max}$. The annual mean value of W_{max} was estimated at $29.6 MJ/m^2$
347 with $31.0 MJ/m^2$ for JJA and $28.0 MJ/m^2$ for DJF. The conservation of mass between the
348 atmospheric system and the isothermal reference is crucial for the quantification method
349 developed in this study.

350 Based on the same assimilated meteorological dataset as used in this study, Kim and Kim (2013)
351 estimated the global averaged APE at $4.34 MJ/m^2$ for the annual mean, $4.02 MJ/m^2$ for JJA
352 and $4.75 MJ/m^2$ for DJF. There are considerable differences in the absolute values for APE and
353 W_{max} . Fig. 15 provides a schematic illustration of the relationship between APE and W_{max} with
354 point b corresponding to the thermodynamic condition, (E^{atm}, S^{atm}) . APE is defined as the
355 difference in total static energy between the current state of the dry air component of the
356 atmosphere and that of an idealized reference state corresponding to the minimum content of
357 static energy present following a sequence of reversible isentropic transformations. When the
358 atmosphere fully releases its APE through a isentropic and adiabatic process to perform
359 mechanical work and reaches the associated reference state, the total value of S^{atm} should
360 remain constant. On the Entropy-Energy Diagram in Fig. 15, this process corresponds to a
361 thermodynamic transition from point b to point d with entropy conserved. However, the
362 reference state in mechanical equilibrium is not in thermal equilibrium, and the maximum work,
363 W_{max} , has not as yet been completely exerted. Thus, APE corresponding to the b -to- d
364 displacement in Fig. 15 should be smaller than W_{max} corresponding to the b -to- c displacement

365 in Fig. 15. It follows that APE may be considered as the mechanical component of W_{max} .

366 For an isothermal well-mixed atmosphere at 250 K, W_{max} is quantified to be $1.5 MJ/m^2$ using
367 the approach described in Section 4. This quantity, $1.5 MJ/m^2$, represents the contribution from
368 the gravitational separation of gases to W_{max} for a real atmosphere. Thus the part of W_{max}
369 attributed to the vertical temperature contrast can be estimated as $W_{max} - APE - 1.5 MJ/m^2 \approx$
370 $23.8 MJ/m^2$.

371 Fig. 16 presents a schematic illustration of the d -to- c displacement in Fig. 15. The upper panels
372 in Fig. 16 display the zonal-average potential temperature, θ , and the zonal-average temperature,
373 T , appropriate for the associated reference state proposed by Lorenz, with its thermodynamic
374 condition, (E^{atm}, S^{atm}) , corresponding to point d in Fig.15. The lower panels display zonal-
375 average potential temperatures, θ , and zonal-average temperatures, T , for the associated
376 thermodynamic equilibrium state with its thermodynamic condition, (E^{atm}, S^{atm}) ,
377 corresponding to point c in Fig.15. When the thermally non-equilibrium reference state proposed
378 by Lorenz approaches thermodynamic equilibrium through Evolution 1, the work performed is
379 equal to $(W_{max} - APE)$.

380 While Lorenz's concept of energetics is based on APE that can be extracted through a reversible
381 adiabatic transformation of dry air, his main concern was with the rate for its generation by
382 radiative heating and cooling, and the subsequent dissipation of this energy by mechanically
383 irreversible processes. The fundamental question he addressed was why and how the present
384 strength of the general circulation was determined. The main interest in this paper is to quantify
385 the thermodynamic disequilibrium of the present climate state, although the relationship between
386 W_{max} and APE is also investigated.

387 Considering the long-term variability of W_{max} , as the global surface temperature, $T_{surface}$,
388 increased from January 1979 to December 2010, the equilibrium temperatures, T_{eq}^S and T_{eq}^W ,
389 increased at about the same pace as $T_{surface}$. Consequently, there was no statistically significant
390 trend in W_{max} over this interval. It is important to understand how the atmosphere adjusted its
391 thermodynamic structure over this period, including its vertical temperature profile in order to
392 maintain a relatively constant W_{max} . A number of studies pointed out that the lower-tropospheric
393 temperatures have experienced slightly greater warming since 1958 than those at the surface.
394 Lower-stratospheric temperatures have exhibited cooling since 1979 while the tropopause height
395 has increased by 200m between 1979 and 2001 (Randel et al. 2000; Grody et al. 2004; Santer et
396 al. 2004; Simmons et al. 2004; Fu and Johanson 2005; Karl et al. 2006; Vinnikov et al. 2006). It
397 is important to explore the pertinent implications for W_{max} .

398 The global thermodynamic disequilibrium of the atmosphere was analyzed retrospectively in this
399 study based on the MERRA data. We also estimated the thermodynamic disequilibrium
400 corresponding to the one-dimensional international standard atmosphere (See Supplementary
401 Material). The value of W_{max} for the one-dimensional international standard atmosphere is
402 estimated at $16.8 MJ/m^2$. The previous study reported a value of $12.6 MJ/m^2$ for a 50 km
403 standard atmosphere (Bannon 2012). The one-dimensional international standard atmosphere
404 doesn't represent the thermodynamics of the time-resolved three-dimensional atmosphere. Thus,
405 there is a difference in the values of W_{max} between the one-dimensional model and the three
406 dimensional atmosphere. Nevertheless, a relevant question is whether the conclusions reached
407 here may be conditioned by the use of this specific data base. Other datasets including NCEP-1,
408 NCEP-2, ERA-40 and JRA-25 should be employed in future work to compare with the results
409 presented here.

410 This study focused on the dry air component of the atmosphere. In the real atmospheric system
411 consisting of dry air and water, its total entropy S^{total} and total static energy E^{total} , according to
412 thermodynamics, can be expressed as: $S^{total} = S^{atm} + S^{H_2O}$ and $E^{total} = E^{atm} + E^{H_2O}$, where
413 S^{H_2O} and E^{H_2O} represent the associated entropy and static energy of the water component.

414 The water component plays an important role in the thermodynamics of the atmosphere,
415 including maintenance of the general circulation (Lorenz 1978). When sunlight reaches the ocean
416 surface, much of the energy absorbed by the ocean is used to evaporate water. Water vapor in the
417 atmosphere acts as a reservoir for storage of heat to be released later. As the air ascends, it cools.
418 When it becomes saturated, water vapor condenses with consequent release of latent heat.
419 Heating is dominated in the tropical atmosphere by release of latent heat. Separate bands of
420 relatively deep heating are observed also at mid-latitudes where active weather systems result in
421 enhanced precipitation and release of latent heat. The condensation and evaporation of water
422 contribute to non-uniform diabatic heating and cooling of the dry air, and, consequently, to the
423 circulation of the atmosphere.

424 The water component is also an example of a thermodynamic non-equilibrium system. Under
425 thermodynamic equilibrium conditions, liquid and solid water would be totally absent above the
426 ground. The entire process of evaporation from the ocean, followed by condensation to form
427 clouds and precipitation is thermodynamically irreversible. The analytical approach developed
428 here could be used to investigate the thermodynamics of the water component by quantifying the
429 thermodynamic condition, (E^{H_2O}, S^{H_2O}) and the line of $S_{eq}^{H_2O}(E_{eq}^{H_2O})$ and by calculating W_{max}
430 and $(\Delta S)_{max}$ for the water component in an Entropy-Energy Diagram. The water component can
431 further increase the thermodynamic disequilibrium of the moist atmosphere.

432 **Acknowledgements**

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435 Environment. We acknowledge helpful and constructive comments from Michael J. Aziz and

436 Peter R. Bannon and from the reviewers.

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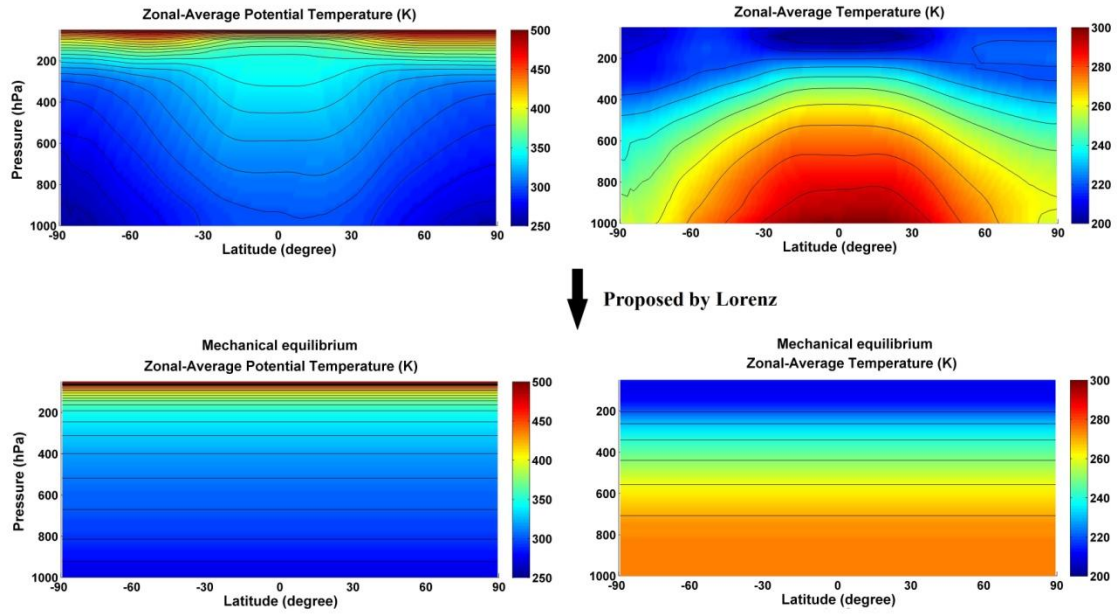
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553 **Figures:**



554

555 **Fig. 1** Schematic illustration of *APE*. The upper panels present zonal-average potential
556 temperatures, θ , and zonal-average temperatures, T , for year 2008. The lower panels indicate
557 zonal-average potential temperatures, θ , and zonal-average temperatures, T , for the associated
558 reference state proposed by Lorenz, again for year 2008.

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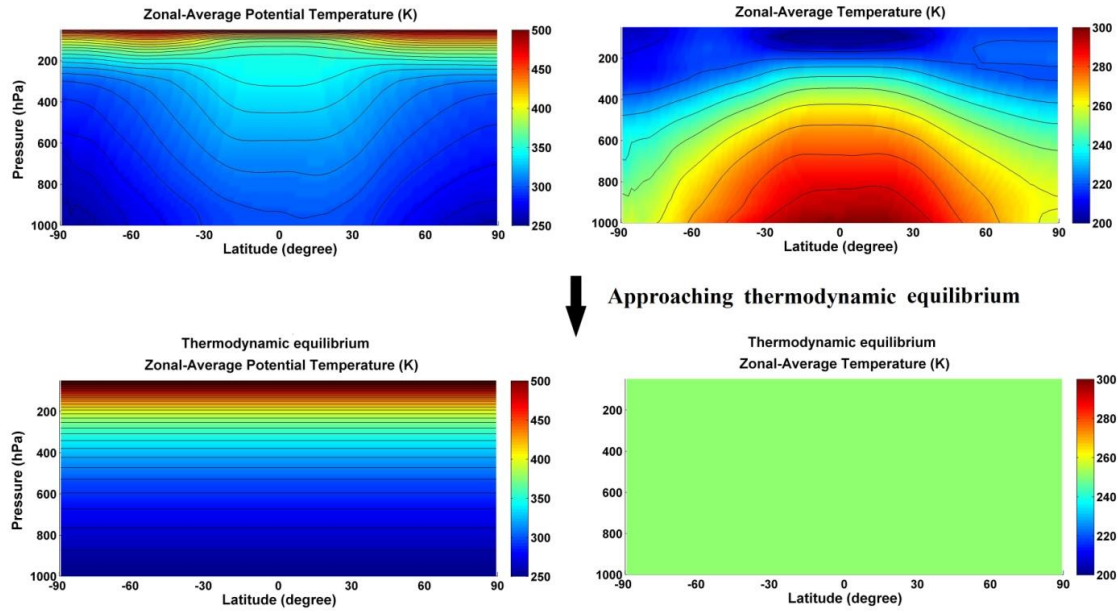
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569 **Fig. 2** Schematic illustration of the approach to thermodynamic equilibrium. The upper panels
 570 display zonal-average potential temperatures, θ , and zonal-average temperatures, T , for year
 571 2008. The lower panels indicate zonal-average potential temperatures, θ , and zonal-average
 572 temperatures, T , for the thermodynamic equilibrium state.

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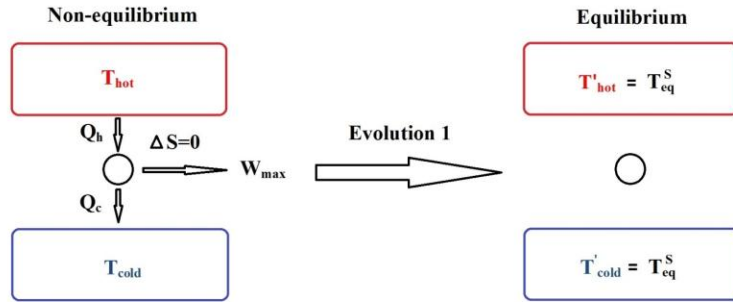
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584 **Fig. 3** Illustration of W_{max} produced from a non-equilibrium system. Initially, the thermally
 585 isolated system is out of equilibrium and can perform a maximum of mechanical work through
 586 reversible processes ($\Delta S = 0$). Finally, the system reaches equilibrium at T_{eq}^S in which the
 587 temperature contrast between its subcomponents has been eliminated.

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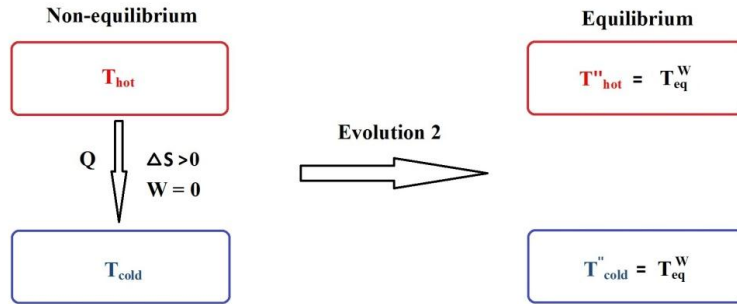
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599 **Fig. 4** Illustration of $(\Delta S)_{max}$ for the entire non-equilibrium system. Initially, the thermally
 600 isolated system is energetic and out of equilibrium. There is a flux of energy Q from the high
 601 temperature component at T_{hot} to the low temperature component at T_{cold} . As heat transfer
 602 continues, the system reaches thermal equilibrium at T_{eq}^W in which the temperature contrast
 603 between its subcomponents has been eliminated.

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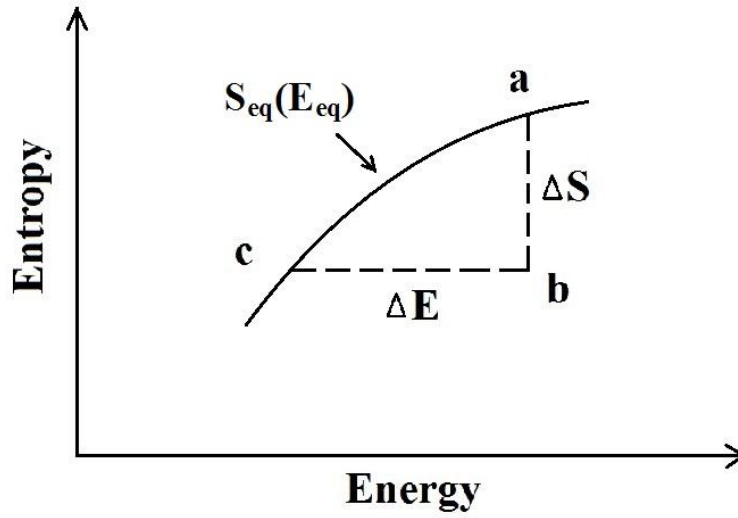
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615 **Fig. 5** Schematic illustration of the evolution of maximum work and maximum entropy increase
616 in an Entropy-Energy Diagram.

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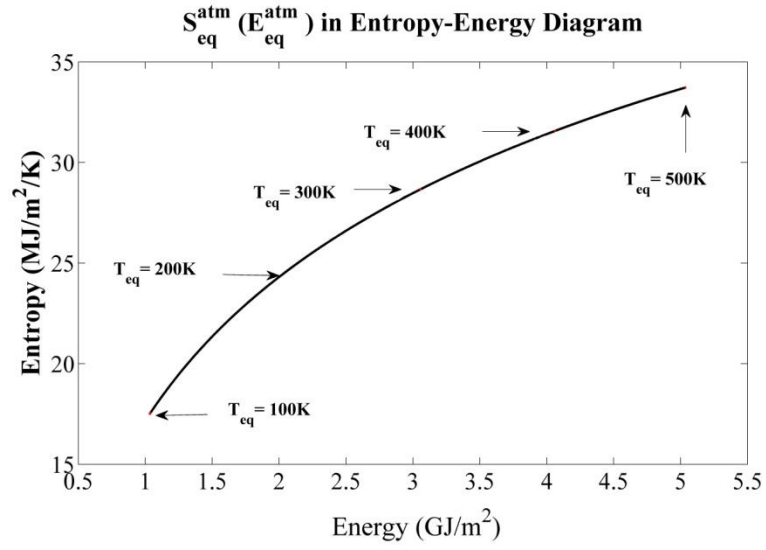
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632 **Fig. 6** The behavior of the function $S_{eq}^{atm}(E_{eq}^{atm})$ with T_{eq} increasing from 100 K to 500 K.

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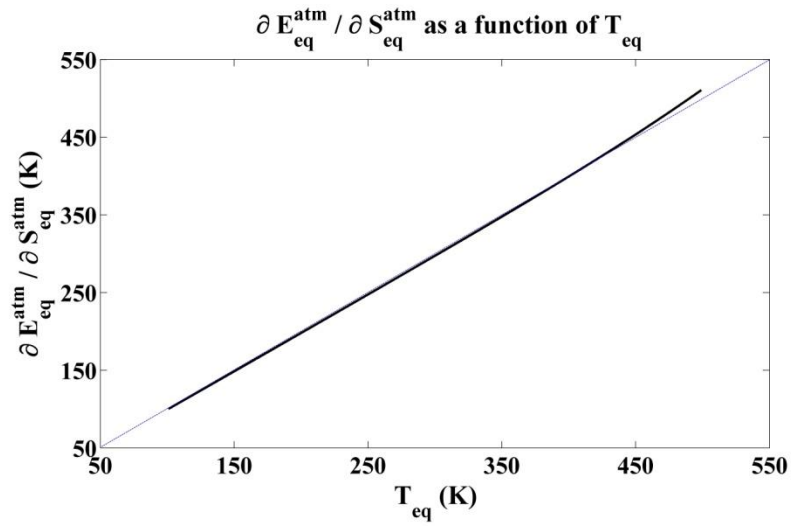
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648 **Fig. 7** The behavior of the gradient $\partial S_{eq}^{atm} / \partial E_{eq}^{atm}$ with T_{eq} ranging from 100 K to 500 K.

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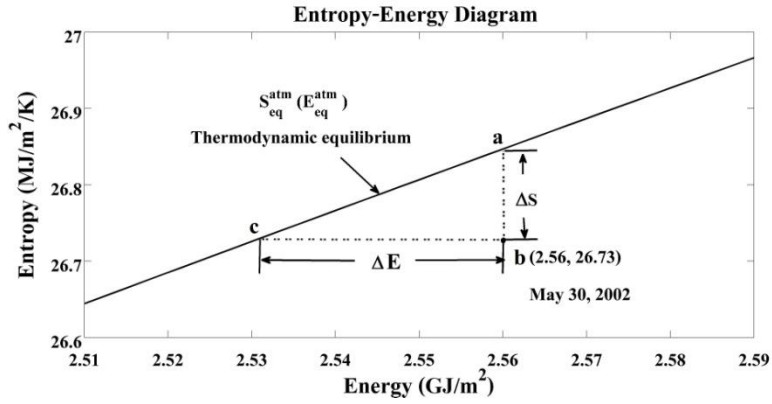
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661 **Fig. 8** The thermodynamic condition, (E^{atm}, S^{atm}) , of the atmosphere on May 30, 2002

662 displayed in an Entropy-Energy Diagram. The ΔE in the figure represents the maximum work,

663 W_{max} , that can be performed in a thermally reversible process; ΔS represents the maximum

664 increase in entropy, $(\Delta S)_{max}$, that can arise in a thermally irreversible process with zero work.

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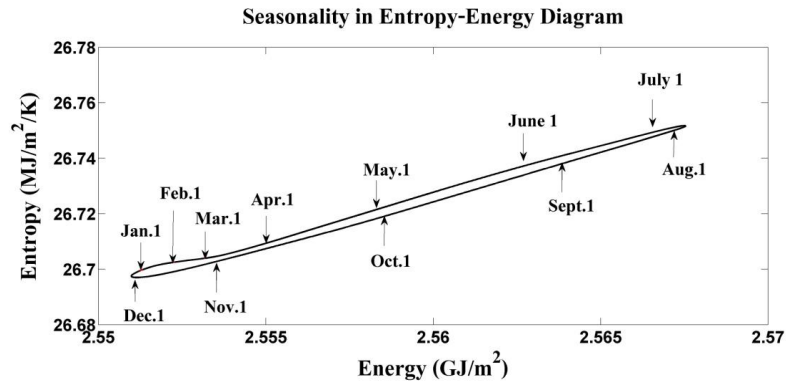
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675 **Fig. 9** The seasonality of the thermodynamic conditions, (E^{atm}, S^{atm}) , of the atmosphere in an
 676 Entropy-Energy Diagram.

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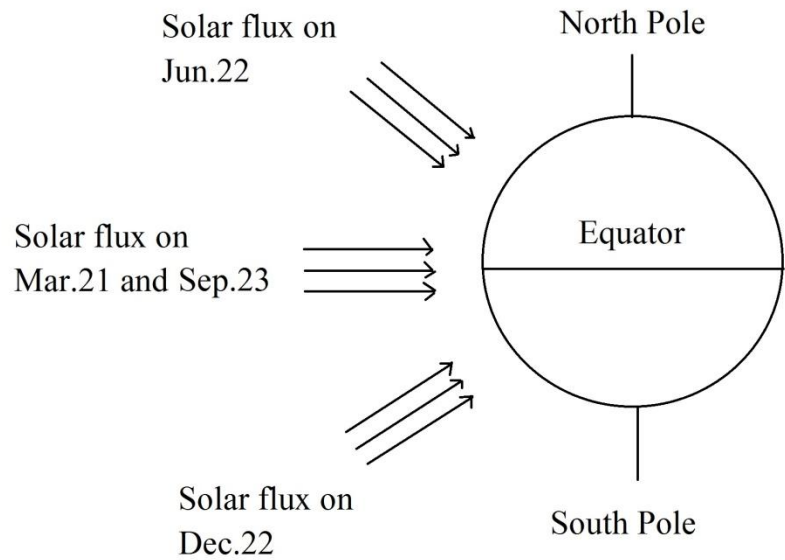
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686 **Fig. 10** Schematic illustration of solar radiation.

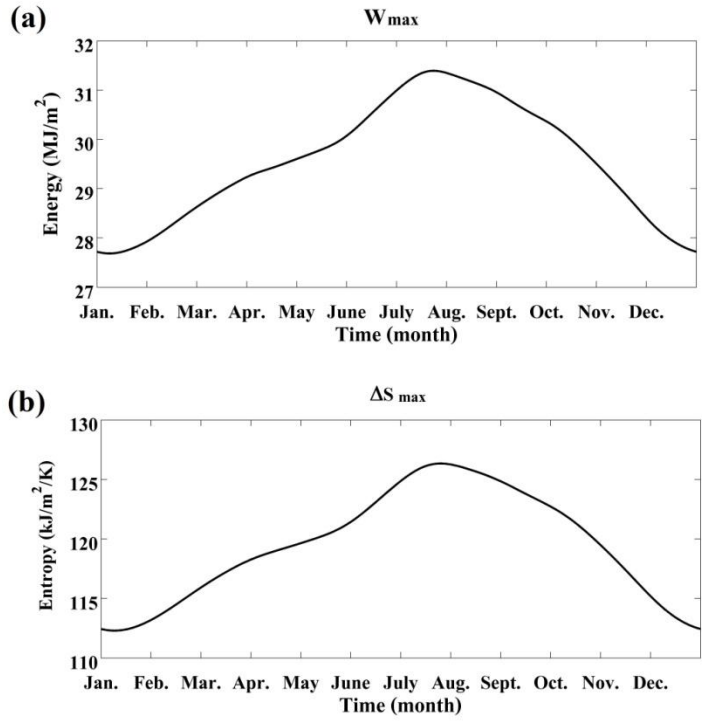
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693 **Fig. 11** The seasonalities of W_{max} and $(\Delta S)_{max}$ based on an average of data for the past 32 years.

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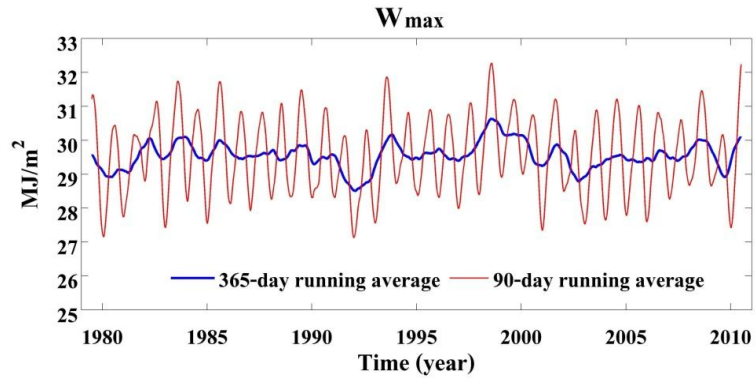
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702 **Fig. 12** Variation of W_{max} from January 1979 to December 2010.

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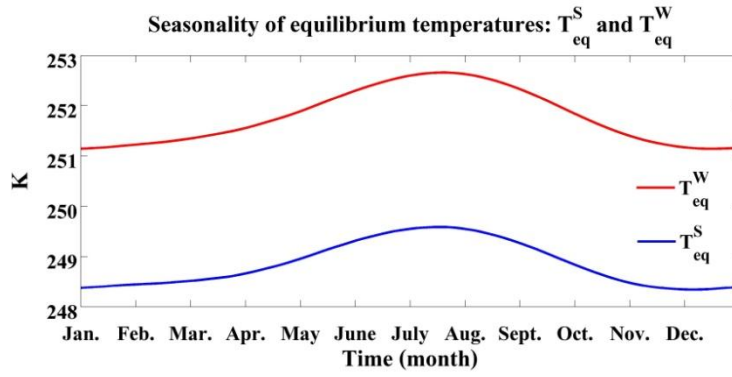
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716 **Fig. 13** The seasonalities of the equilibrium temperatures, T_{eq}^S and T_{eq}^W , based on an average of

717 data for the past 32 years.

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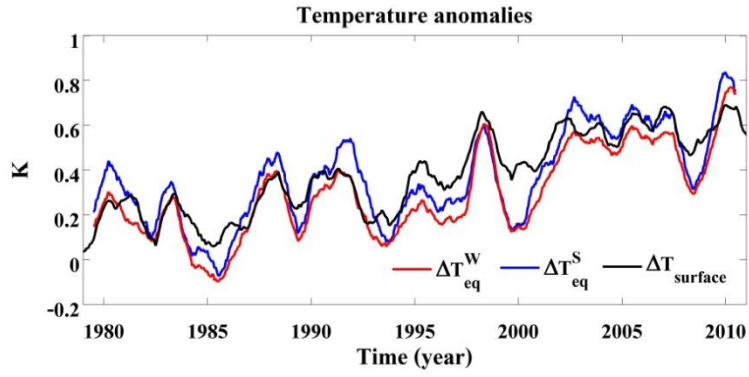
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733 **Fig. 14** Variation of ΔT_{eq}^S , ΔT_{eq}^W and $\Delta T_{surface}$ from January 1979 to December 2010.

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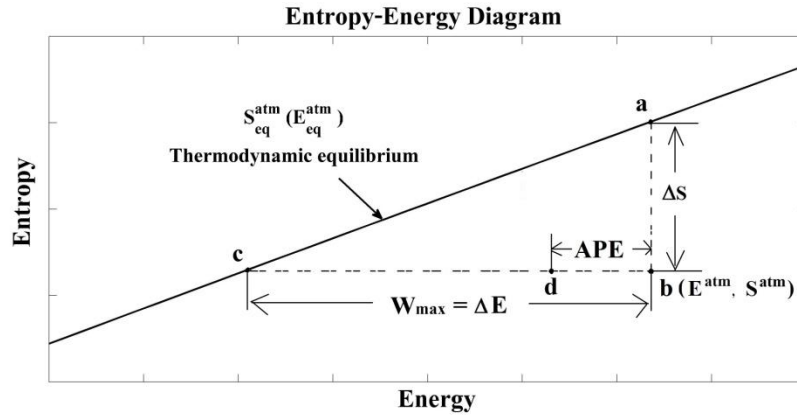
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749 **Fig. 15** Schematic illustration of the relationship between APE and W_{max} . The distance between

750 b and d represents APE , and the distance between b and c represents W_{max} .

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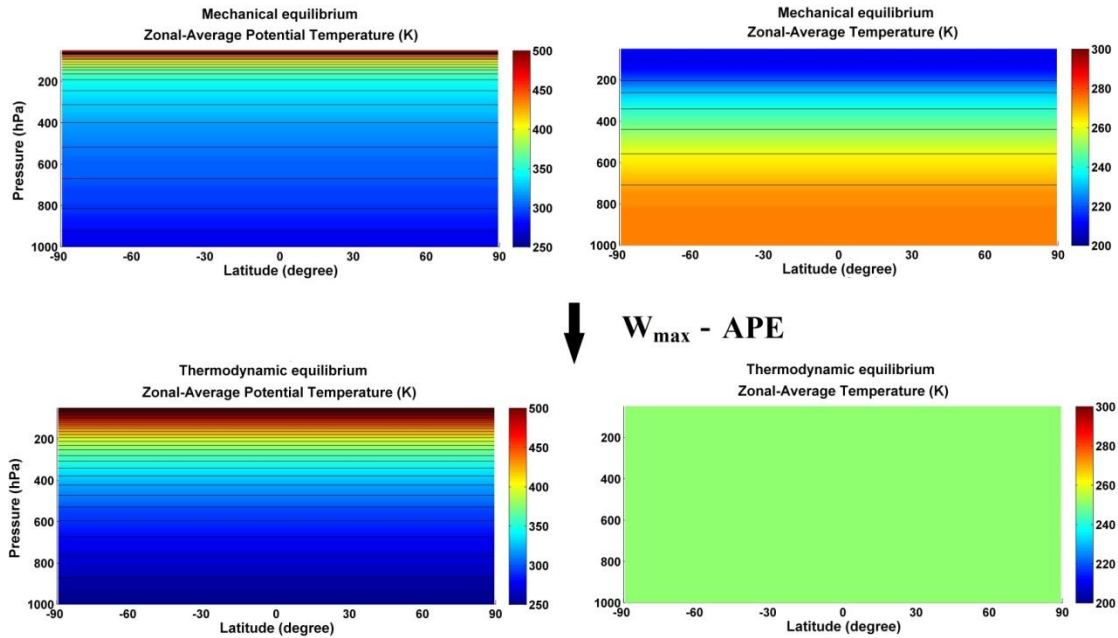
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764 **Fig. 16** Schematic illustration of $(W_{max} - APE)$. The upper panels display zonal-average
 765 potential temperatures, θ , and zonal-average temperatures, T , for the associated reference state
 766 proposed by Lorenz. The lower panels present zonal-average potential temperatures, θ , and
 767 zonal-average temperatures, T , for the associated thermodynamic equilibrium state.