Potential Descending Principle, Dynamic Law of Physical Motion and Statistical Theory of Heat

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Outline

I. Dynamic Law of Physical Motion

II. Potential-Descending Principle in Statistical Physics

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IV. Statistical Theory of Heat


I. Dynamic Law of Physical Motion

Guiding Principle of Physics; see Ma-Wang, Mathematical Principles of Theoretical Physics, Science Press, Beijing, pp. 525, 2015

All physical systems obey laws and principles of Nature, and possess the following three properties:

1) For each system, there is a group of functions $u = (u_1, \ldots, u_N)$ describing its states, and the laws and principles obeyed by the system can be expressed by the mathematical models expressed as

   \textit{physical laws = mathematical equations},

   and the state functions $u$ are solutions of the mathematical equations;

2) For the mathematical models, there are functionals $F(u)$ such that $F$ dictate mathematical expressions of the models, which are usually differential equations.
3) Physical systems are governed by symmetries, which essentially determine the mathematical forms of the functionals $F$. 
Let $H, H_1$ be two Hilbert spaces, and $L : H_1 \to H$, $L^* : H \to H_1^*$ be a pair of dual linear bounded operators. Let $F : H \to \mathbb{R}^1$ be a functional, and let

$$\mathcal{N}^* = \{ v \in H \mid L^*v = 0 \} \neq \{0\}.$$  

**Definition**

1) For any $u \in H$, let $\delta_{L^*}F(u)$ be the derivative operator of $F$ at $u$ with $L^*$—constraint:

$$\langle \delta_{L^*}F(u), v \rangle_H = \frac{d}{dt}\bigg|_{t=0} F(u + tv) \quad \forall v \in \mathcal{N}^*.$$  

2) The derivative operator of $F$ at $u$ with $L$—constraint, denoted by $\delta_LF(u)$, is defined as follows

$$\langle \delta_LF(u), \varphi \rangle_{H_1} = \frac{d}{dt}\bigg|_{t=0} F(u + tL\varphi) \quad \forall \varphi \in H_1.$$  


Theorem [Variation with $L$–constraints]

1) For $\delta_{L^*}F(u)$, there is a $\varphi \in H_1$ such that

\[
\delta_{L^*}F(u) = \delta F(u) + L\varphi.
\]

2) For $\delta_L F(u)$, we have

\[
\delta_L F(u) = L^* \delta F(u).
\]

Here $\delta F(u)$ is the normal derivative operator.
Dynamic Law of Physical Motion (Ma-Wang, 2017)

There are two types of physical motion systems: the dissipative systems and the conservation systems. For each physical motion system, there are a set of state functions \( u = (u_1, \cdots, u_N) \), a functional \( F(u) \), and a differential operator \( \mathcal{L} \), which is either \( \mathcal{L} = L \) or \( \mathcal{L} = L^* \) for some differential operator \( L \), such that the following statements hold true:

- \( -\delta_{\mathcal{L}} F(u) \) is the derived force of the system;
- \( F \) is \( SO(n) \) (\( n = 2, 3 \)) invariant;
- for an isolated system, the dynamic equation can be expressed in the form

\[
\frac{du}{dt} = -A\delta_{\mathcal{L}} F(u),
\]

where \( A \) is the coefficient matrix, \( A \) is symmetric and positive definite if and only if the system is a dissipative system, and \( A \) is anti-symmetry if and only if the system is a conservation system;
• for a system coupling different subsystems, the motion equations of (6) become

\[
\frac{du}{dt} = -A\delta_{\mathcal{L}}F(u) + B(u),
\]

where \( B(u) \) represents the symmetry-breaking.
The Boussinesq equations are written as

\[
\frac{\partial u}{\partial t} + (u \cdot \nabla)u - \rho_0^{-1}[\nu \Delta u + \nabla p] = -gk\rho(T),
\]

(8)

\[
\frac{\partial T}{\partial t} + (u \cdot \nabla)T - \kappa \Delta T = 0,
\]

\[
\text{div} u = 0,
\]

where \(\nu, \kappa, g\) are constants, \(u = (u_1, u_2, u_3)\) is the velocity field, \(p\) is the pressure function, \(T\) is the temperature function, \(T_0\) is a constant representing the lower surface temperature at \(x_3 = 0\), and \(k = (0, 0, 1)\) is the unit vector in the \(x_3\)-direction.

As before, we take the linear constraint operator \(L = -\nabla\) with dual \(L^* = \text{div}\). Let

\[
\Phi(u, T) = \int_{\Omega} \left[ \frac{\mu}{2} |\nabla u|^2 + \frac{\kappa}{2} |\nabla T|^2 \right] \, dx.
\]
Then the Boussinesq equations of (8) are written as

\[
\begin{align*}
\frac{du}{dt} &= -\frac{1}{\rho_0} \frac{\delta L^*}{\delta u} \Phi(u, T) + B(u, T), \\
\frac{dT}{dt} &= -\frac{\delta}{\delta T} \Phi(u, T),
\end{align*}
\]

which is in the form of (6) with coefficient matrix \( A = \text{diag}(1/\rho_0, 1) \). The term \( B(u, T) \) is given by

\[
B(u, T) = g\rho_0 k\rho(T),
\]

which breaks the symmetry of the functional \( \Phi(u, T) \), caused by the coupling between momentum equations and the temperature equation. Also, the incompressibility condition is built into the construction of the basic function space, which we omit the details.
II. Potential-Descending Principle in Statistical Physics

- A thermodynamic system is described by order parameters (state functions), control parameters, and thermodynamic potential, which is a functional of the order parameters.

- All thermodynamic potentials are expressed in terms of conjugate pairs. The most commonly considered conjugate thermodynamic variables are
  1) the temperature $T$ and the entropy $S$, and
  2) $f$ the generalized force and $X$ the generalized displacement.

Typical examples of $(f, X)$ include (the pressure $p$, the volume $V$), (applied magnetic field $H$, magnetization $M$), (applied electric field $E$, electric polarization $P$).
• Let \( U \) be the internal energy. Then for a completely closed thermodynamic system, the first law states:

\[
dU = TdS + fdX. \tag{10}
\]

Here \((T, f)\) are the order parameters and \((S, X)\) are the control parameters.

• For an isothermal process, we need to use the Helmholtz free energy:

\[
F = U - TS. \tag{11}
\]

In fact, (11) is the Legendre transformation such that the Helmholtz free energy \( F \) is a functional of \( S \) and \( f \). In other words, \((S, f)\) are order parameters, and \((T, X)\) are control parameters. Consequently,

\[
F = F(S, f; \lambda), \quad \lambda = (T, X),
\]
and the equilibrium state enjoys

\begin{equation}
\frac{\delta F}{\delta S} = 0, \quad \frac{\delta F}{\delta f} = 0.
\end{equation}

- **Gibbs free energy.** When the system has the thermal and mechanical exchanges with the external, i.e., the thermal process is in the constant temperature $T$ and generalized force $f$, the corresponding potential is the Gibbs free energy:

\begin{equation}
G = F - fX, \quad F \text{ the Helmholtz free energy}.
\end{equation}

For the Gibbs potential, the order parameters are $(S, X)$, and the control parameters are $\lambda = (T, f)$,

\[ G = G(S, X; \lambda), \]

and the equilibrium state satisfies

\begin{equation}
\frac{\delta G}{\delta S} = 0, \quad \frac{\delta G}{\delta X} = 0.
\end{equation}
Potential-Descending Principle (MW17a)

For each thermodynamic system, there are order parameters $u = (u_1, \cdots, u_N)$, control parameters $\lambda$, and the thermodynamic potential functional $F(u; \lambda)$. For a non-equilibrium state $u(t; u_0)$ of the system with initial state $u(0, u_0) = u_0$,

1) the potential $F(u(t; u_0); \lambda)$ is decreasing: $\frac{d}{dt} F(u(t; u_0); \lambda) < 0 \quad \forall t > 0$;

2) the order parameters $u(t; u_0)$ have a limit: $\lim_{t \to \infty} u(t; u_0) = \bar{u}$;

3) there is an open and dense set $\mathcal{O}$ of initial data in the space of state functions, such that for any $u_0 \in \mathcal{O}$, the corresponding $\bar{u}$ is a minimum of $F$, which is called an equilibrium of the thermodynamic system:

$$\delta F(\bar{u}; \lambda) = 0.$$
1. The potential-descending principle leads to both the first and second laws of thermodynamics

For the equilibrium state, PDP says that \( \frac{\delta}{\delta u} F(\bar{u}; \lambda) = 0 \), and then

\[
\frac{dF(\bar{u}, \lambda)}{dt} = \frac{\delta}{\delta u} F(\bar{u}; \lambda) \frac{du}{dt} + \frac{\partial F}{\partial \lambda} d\lambda = \frac{\partial F(\bar{u}; \lambda)}{\partial \lambda} d\lambda,
\]

which is the first law of thermodynamics.

For a given non-equilibrium thermodynamic state \( u(t) \), the PDP tells us that

\[
\frac{dF}{dt} = \frac{\delta}{\delta u} F(u(t); \lambda) \frac{du}{dt} < 0 \quad \Longrightarrow \quad \frac{\delta}{\delta u} F(u(t); \lambda) du < 0.
\]

Hence

\[
dF(u(t), \lambda) = \frac{\delta}{\delta u} F(u(t); \lambda) du + \frac{\partial F}{\partial \lambda} d\lambda < \frac{\partial F}{\partial \lambda} d\lambda,
\]

which is the second law of thermodynamics.
Also, as an example, we consider an internal energy of a thermodynamic system, classical theory asserts that the first and second laws are given by

\[
dU \leq \left( \frac{\partial U}{\partial S} \right) dS + \left( \frac{\partial U}{\partial X} \right) dX,
\]

where the equality represents the first laws, describing the equilibrium state, and inequality presents second law for non-equilibrium state. However, there is a hidden assumption in (15) that at the equilibrium, there is a free-variable in each of the conjugate pairs \((T, S)\) and \((f, X)\). In the internal energy system, \(S\) and \(X\) are free variables. Namely,

\[
\frac{\partial U}{\partial T} \leq 0, \quad \frac{\partial U}{\partial f} \leq 0,
\]

where, again, the equality is for equilibrium state and the strict inequality is for non-equilibrium state. This assumption is mathematically equivalent to the minimal-potential principle (or potential-descending principle).
2. **PDP is a first principle of statistical mechanics.** Namely, PDP leads to all three distributions:

\[
a_n = \begin{cases} 
\dfrac{N}{Z} g_n e^{-\varepsilon_n/kT} & \text{Maxwell-Boltzmann distribution} \\
\dfrac{g_n}{e^{(\varepsilon_n-\mu)/kT} - 1} & \text{Bose-Einstein distribution} \\
\dfrac{g_n}{e^{(\varepsilon_n-\mu)/kT} + 1} & \text{Fermi-Dirac distribution}
\end{cases}
\]

(16)

Partition functions with \( \alpha = -\dfrac{\mu}{kT} \) and \( \beta = \dfrac{1}{kT} \):

\[
Z = \begin{cases} 
\sum_n g_n e^{-\beta \varepsilon_n} & \text{classical system} \\
\prod_n \left( 1 \mp e^{-\alpha - \beta \varepsilon_n} \right) \mp g_n & \text{Bose (Fermi) system}
\end{cases}
\]

(17)
Consider an isolated classical system with following arrangement of number of particles on different energy levels:

\[ \varepsilon_1 < \varepsilon_2 < \cdots < \varepsilon_{N_E}, \]
\[ g_1 \quad g_2 \quad \cdots \quad g_{N_E}, \]
\[ a_1 \quad a_2 \quad \cdots \quad a_{N_E}, \]

where \( g_n \) represents the degeneracy of the energy level \( \varepsilon_n \).

The aim is then to find the relations between \( \varepsilon_n \) and \( a_n \)

\[ a_n = f(\varepsilon_n, T) \quad \text{for } 1 \leq n \leq N_E \]

under constraint:

\[ N = \sum_n a_n = \text{constant}, \quad E = \sum_n a_n \varepsilon_n = \text{constant}. \]
• The temperature $T$ is a control parameter, and consequently, its thermodynamic potential functional is

\begin{equation}
F = E - ST, \tag{21}
\end{equation}

where $E$ is the total energy, and $S = k \ln W$ is the entropy.

• PDP shows that the distribution $\{a_n\}$ at the thermodynamic equilibrium solves the following minimal potential variational equations of the potential functional (21):

\begin{equation}
\frac{\delta}{\delta a_n} \left[ -kT \ln W + \alpha_0 \sum_n a_n + \beta_0 \sum_n a_n \varepsilon_n \right] = 0, \tag{22}
\end{equation}

where $\alpha_0$ and $\beta_0$ are the Lagrangian multipliers of constraints (20).
The multiplicity function $W$ is given by

\begin{equation}
W = \frac{N!}{\prod_n a_n!} \prod_n g_{n}^{a_{n}},
\end{equation}

The remaining part of the proof is trivial.
3. Let $F(u, \lambda)$ be the thermodynamic potential of a thermodynamic system with order parameters $u$ and control parameters $\lambda$. Then PDP gives rise to the following dynamic equation:

\begin{equation}
\frac{du}{dt} = -\delta F(u, \lambda).
\end{equation}

This equation offers a complete description of the irreversibility of the system.
III. Irreversibility in Thermodynamic Systems

• PDP offers a clear description of the irreversibility of thermodynamical systems. Consider a non-equilibrium initial state $u_0$, the PDP amounts to saying that the potential is decreasing:

$$\frac{d}{dt}F(u(t; u_0); \lambda) < 0 \quad \forall t > 0.$$  

This shows that the state of the system $u(t; u_0)$ will never return to its initial state $u_0$ in the future time. This is exactly the irreversibility.

• Entropy $S$ is a state function, which is the solution of basic thermodynamic equations. Thermodynamic potential is a higher level physical quantity than entropy, and consequently, is the correct physical quantity, rather than the entropy, for describing irreversibility for all thermodynamic systems.
IV. Statistical Theory of Heat

Motivations

• For a thermodynamic system, the thermal energy $Q_0$ is given by

(25) \quad Q_0 = ST, \quad S = k \ln W,$

where $k$ is the Boltzmann constant, and $W$ is the number of microscopic configurations of the system. It is then clear that

(26) \text{in modern thermodynamics, there is simply no physical heat carrier in both the temperature $T$ and the entropy $S$, and hence there is no physical carrier for thermal energy } Q_0 = ST.$
Historically, the caloric theory of heat was developed for such a purpose.

Basically, the caloric theory says that heat is made up of a fluid called caloric that is massless and flows from hotter bodies to colder bodies. It was considered that caloric was a massless gas that exists in all matter, and is conserved. However the transfer between heat and mechanical work makes the caloric theory obsolete.
● **Photon Cloud structure of electrons.**

– The recent developments in particle physics reveal the photon cloud structure of electrons: there is an attracting shell region of weak interaction between the naked electron and photons.

– Since photons carry weak charges, they are attached to the electron in the attracting shell region forming a cloud of photons.
– A macroscopic system is immersed in a sea of photons (mediators). When a photon enters the attracting shell region of an electron, it will be absorbed by the electron.

– An electron emits photons as its velocity changes, which is called the bremsstrahlung. Also, when the orbiting electron jumps from higher energy level to a lower energy level, it radiates photons.

– Hence electrons in the system are constantly in a state of absorbing and emitting photons, resulting changes on their energy levels:

\[
\text{(27) in the microscopic world, electrons and photons form a natural conjugate pair of physical carriers for emission and absorption.}
\]
In view of thermal energy $Q_0 = ST$, heat is attributed to the conjugate relation between temperature and entropy. Hence by (27), a theory of heat has to make connections between the two conjugate relations:

$$conjugation \text{ between } electrons \text{ and } photons$$

$$\downarrow$$

$$conjugation \text{ between } temperature \text{ and entropy.}$$

The new theory of heat provides precisely such a connection:

at the equilibrium of absorption and radiation,
– the average energy level of the system maintains unchanged, and represents the temperature of the system;
– at the same time, the number (density) of photons in the sea of photons represents the entropy (entropy density) of the system.
Main ingredients of the new theory of heat

1. **Energy level formula of temperature.** We derive the following energy level formula of temperature using the MB, FD, BE distributions:

\[
\begin{align*}
    kT &= \begin{cases} 
        \sum_n \left(1 - \frac{a_n}{N}\right) \frac{a_n \varepsilon_n}{N(1 + \beta_n \ln \varepsilon_n)} & \text{for classical systems,} \\
        \sum_n \left(1 + \frac{a_n}{g_n}\right) \frac{a_n \varepsilon_n}{N(1 + \beta_n \ln \varepsilon_n)} & \text{for Bose systems,} \\
        \sum_n \left(1 - \frac{a_n}{g_n}\right) \frac{a_n \varepsilon_n}{N(1 + \beta_n \ln \varepsilon_n)} & \text{for Fermi systems.}
    \end{cases}
\end{align*}
\]

Here \(\varepsilon_n\) are the energy levels of the system particles, \(N\) is the total number of particles, \(g_n\) are the degeneracy factors (allowed quantum states) of the energy level \(\varepsilon_n\), and \(a_n\) are the distributions, representing the number of particles on the energy level \(\varepsilon_n\).
2. **Photon number formula of entropy.** In view of (28), since entropy $S$ is an extensive variable, we need to characterize entropy as the number of photons in the photon gas between system particles, or the photon density of the photon gas in the system. Also, photons are Bosons and obey the Bose-Einstein distribution.

\[
S = kN_0 \left[ 1 + \frac{1}{kT} \sum_n \frac{\varepsilon_n a_n}{N_0} \right],
\]

where $\varepsilon_n$ are the energy levels of photons, and $a_n$ are the distribution of photons at energy level $\varepsilon_n$. $N_0 = \sum_n a_n$ is the total number of photons between particles in the system, and $\sum_n \frac{\varepsilon_n a_n}{kT}$ represents the number of photons in the sense of average energy level.

This new entropy formula is equivalent to the **Boltzmann entropy formula** $S = k \ln W$. However, their physical meanings have changed: the new formula (30) provides explicitly that

\[
\text{(31) the physical carrier of heat is the photons.}
\]
3. Temperature theorem.

- There are minimum and maximum values of temperature with $T_{\text{min}} = 0$ and $T_{\text{max}}$;

- When the number of photons in the system is zero, the temperature is at absolute zero; namely, the absence of photons in the system is the physical reason causing absolute zero temperature;

- (Nernst Theorem) With temperature at absolute zero, the entropy of the system is zero;

- With temperature at absolute zero, all particles fills all lowest energy levels.
4. **Thermal energy formula.** Thanks to the entropy formula (30), we derive immediately the following thermal energy formula:

\[
Q_0 = ST = E_0 + kN_0T,
\]

where \( E_0 = \sum_n a_n \varepsilon_n \) is the total energy of *photons* in the system, \( \varepsilon_n \) are the energy levels of photons, and \( a_n \) are the distributions of photons at energy level \( \varepsilon_n \), and \( N_0 \) is the number of photons in the system.
• Photons are Bosons and obey the Bose-Einstein distribution. In this case, since the total number of photons is not fixed, the chemical potential \( \mu = 0 \). Then the BE distribution and the partition function are written as

\[
a_n = \frac{g_n}{e^{(\epsilon_n - \mu)/kT} - 1}, \quad Z_B = \prod_n [1 - e^{-\epsilon_n/kT}]^{-g_n}.
\]

• By the entropy formula: \( S = k \left[ \ln Z_B - \beta \frac{\partial}{\partial \beta} \ln Z_B \right] \), we obtain that

\[
S = k \sum_n \left[ g_n \ln \frac{e^{\epsilon_n/kT}}{e^{\epsilon_n/kT} - 1} + \frac{g_n}{e^{\epsilon_n/kT} - 1} \cdot \frac{\epsilon_n}{kT} \right] \\
= k \sum_n \left[ g_n \ln \left(1 + \frac{a_n}{g_n}\right) + \frac{a_n \epsilon_n}{kT} \right].
\]

• Since \( a_n \ll g_n \), which implies that \( \ln \left(1 + \frac{a_n}{g_n}\right) \simeq \frac{a_n}{g_n} \), and the result follows.