Anomalous Latent Heat in Nonequilibrium Phase Transitions

A. E. Allahverdyan and K. G. Petrosyan

Yerevan Physics Institute, Alikhanian Brothers Street 2, Yerevan 375036, Armenia

(Received 27 November 2005; published 13 February 2006)

We study first-order phase transitions in a two-temperature system, where due to the time-scale separation all the basic thermodynamical quantities (free energy, entropy, etc.) are well defined. The sign of the latent heat is found to be counterintuitive: it is positive when going from the phase where the temperatures and the entropy are higher to the one where these quantities are lower. The effect exists only out of equilibrium and requires conflicting interactions. It is displayed on a lattice gas model of ferromagnetically interacting spin-1/2 particles.

PACS numbers: 64.60.Cn, 05.70.Ln

The theory of equilibrium phase transitions is an established field with known achievements in describing transformations of various states of the matter [1,2]. Concepts borrowed from this theory apply for some nonequilibrium transitions that get equilibrium features on the macroscopic scale [3–5]. Less is known, however, about phase transition scenarios that are impossible in equilibrium.

Here we study such a truly nonequilibrium phase transition scenario realized in the steady state of a two-temperature system. Since the components of the system are in local equilibrium, the quantities like entropy, internal energy, and free energy are well defined. In spite of that, the system shows a counterintuitive type of first-order phase transition, where the latent heat is positive (anomalous latent heat) when transforming a high temperature (higher entropy) phase to the low temperature (lower entropy) one; i.e., in the first phase the energy is larger. This is a nonequilibrium effect. It is well known, even from the everyday physics, that for equilibrium transitions the latent heat is negative [1]. This plays a crucial role in the heat balance of the Earth and in the weather formation, since nearly 70% of the energy transferred from the Earth’s surface is due to the latent heat consumed during the vaporization at the surface and released during the vapor condensation in the atmosphere [6].

First we shall recall the thermodynamics of two-temperature systems with different time scales [7–9]. In contrast to the usual equilibrium case, the anomalous latent heat is not forbidden here. We then work out a simple model of mean-field Ising ferromagnet demonstrating the sought effect. A necessary condition for its existence is the presence of conflicting interactions.

Consider a pair of coupled stochastic variables $s$ and $f$ with Hamiltonian $H(s, f)$, which interact with different thermal baths at temperatures $T_s$ and $T_f$, respectively ($s$ and $f$ can denote a set of variables). For $T = T_s = 1/\beta$, the stationary probability distribution $P(s, f)$ of the system is Gibbsian: $P(s, f) \propto e^{-\beta H(s, f)}$. For $T \neq T_s$ we can derive the stationary $P(s, f)$ if the variables have different characteristic times: $s$ is slow, while $f$ is fast (adiabatic limit). This derivation together with corrections coming from a large, but finite time-scale difference was given in [8] based on stochastic equations of motion. Here we recall the heuristics [7–10]. On the times relevant for $f$, $s$ is fixed, and the conditional probability $P(f|s)$ is Gibbsian:

$$P(f|s) = \frac{1}{Z(s)} e^{-\beta H(s, f)} , \quad Z(s) = Tr_{f} e^{-\beta H(s, f)} , \quad (1)$$

where $Tr_f$ is the sum over all values of $f$. The steady-state $P(s)$ is found by noting that on the times relevant for $s$, $\tau$ is already in the conditional steady state. Thus the force $\delta H(s, f)$ acting on $s$ can be averaged over $P(f|s)$:

$$Tr_s [\delta_s H(s, f) P(f|s)] = \delta_s F(s)$$

where $F(s) = -T \ln Z(s)$ is the conditional free energy. The steady $P(s)$ is Gibbsian with the Hamiltonian $F(s)$:

$$P(s) = e^{-\beta F(s)} Z = \frac{Z^{T/T_s}(s)}{Z} , \quad Z = Tr_s e^{-\beta F(s)} , \quad (2)$$

and the common probability is $P(s, f) = P(s) P(f|s)$.

This two-temperature situation admits a (generalized) thermodynamical description, because in the adiabatic limit both variables are in local equilibrium [7–9]. (It has certain analogies with nonequilibrium thermodynamics of the glassy state proposed in [5].) The average energy of the system is $\mathcal{U} = Tr_f [P(s, f) H(s, f)]$, or using (1) and (2)

$$\mathcal{U} = - \frac{1}{n} \frac{\partial}{\partial n} \ln Z , \quad n = \frac{T}{T_s} , \quad (3)$$

where the derivative is taken for fixed $n$. The entropies of $s$ and $f$ are, respectively,

$$S_s = -Tr_s P(s) \ln P(s) , \quad (4)$$

$$S = -Tr_s P(s) [Tr_f P(f|s) \ln P(s|f)] . \quad (5)$$

Equation (4) is the usual definition of entropy. Equation (5) is the conditional entropy; it appears due to the adiabatic limit. The total entropy is the sum of partial ones $S_{\text{tot}} = -Tr_s [P(s, f) \ln P(s, f)] = S + S_s$. Now the steady distributions (1) and (2) are obtained when minimizing the free energy of the slow motion

$$\mathcal{F} = -Tr_s \ln Z . \quad (6)$$
To this end, note from (1)–(5) that the free energy and the entropies are expressed as

$$F = U - TS - T_s S_s, \quad (7)$$

$$S_s = -\partial_{T_s} F |_{T_1}, \quad S = -\partial_T F |_{T_1}, \quad (8)$$

generalizing the usual thermodinamical relations.

Let us now study the first-order phase transitions in this approach. Consider two phases $l$ and $h$. Assume that when $T_s$ decreases below some critical value $T_s^{(c)}$ ($T$ is fixed), the phase $l$ dominates, since its free energy is smaller: $F_l < F_h$. For $T_s > T_s^{(c)}$ the dominating phase is $h$: $F_h > F_l$. At high (low) temperatures $T_s$, $l$ ($h$) is metastable. $F_l = F_h$ at $T_s = T_s^{(c)}$, while other quantities change by jump. Denoting $\delta X = X_l - X_h$, we get

$$\delta U = T_s \delta S_s + T \delta S = -T_s \delta T_s \delta F |_{T_1} - T \partial_T \delta F |_{T_1}, \quad (9)$$

where $\delta U$ is the latent heat of the transition. Note that, in general, both $\delta S_s$ and $\delta S$ are functions of $T_s$ and $T$. In the vicinity of $T_s^{(c)}$, $\delta F = F_l - F_h$ is an increasing function of $T_s$ (for fixed $T$); thus $\delta S_s < 0$. The sign of $\delta S$ is, however, left open, and we cannot conclude that $\delta U < 0$. It may even be positive (anomalous latent heat), provided $\delta S > 0$, that is, provided the system moves from $l$ to $h$ when decreasing $T$ for constant $T_s$.

Things get different if we decrease both $T_s$ and $T$, with constant $n = T/T_s$. Since $\delta F(T_s, nT_s) = F_l - F_h$ has to be an increasing function of $T_s$, we get $\delta U = (\delta T_s + n\delta T) \delta F > 0$, and then (9) shows that $\delta U < 0$, confirming the equilibrium result for $T_s = T$ [1].

Thus for $T_s \neq T$ the anomalous latent heat is not forbidden, provided the transition is not driven by a proportional change of both temperatures. Here is a model demonstrating this effect. Particles are located at the nodes of a lattice embedded into a particle reservoir with chemical potential $\mu = -\alpha < 0$. Each particle carries an Ising spin. At short distances the particles repel each other so that not more than one particle can occupy a single node. The Ising spins interact ferromagnetically. This interaction is active between two nodes only if both are occupied; $s = \{s_i = \pm 1\}_{i=1}^N$ and $f = \{f_i = 0, 1\}_{i=1}^N$ are, respectively, the spins and the occupations of $N$ nodes. We assume all nodes can interact with each other (mean field). The Hamiltonian reads

$$H(s, f) = -\frac{J}{2N} \sum_{i \neq k} f_i f_k s_i s_k + \alpha \sum_i f_i, \quad (10)$$

where $J/(2N) > 0$ is the ferromagnetic coupling constant with $J = O(1)$, as required for the extensivity.

We make two assumptions. (1) $s$ and $f$ couple, respectively, to a spin bath and lattice bath at different temperatures, $T_s = \frac{1}{2}$ and $T = \frac{1}{2}$. (2) $s$ ($f$) is slow (fast), i.e., the relaxation time $\tau_s$ of $s$. These times are driven by the interactions with thermal baths, since $H$ contains only commuting terms; note that in the quantum setting $s_i = s_{i,z}$ and $f_i = \frac{1}{2}(1 + \sigma_{i,z})$, where $s_{i,z}$ and $\sigma_{i,z}$ are the third Pauli matrices.

The above assumptions are motivated by NMR or ESR physics, where for nuclear or electronic spins the spin bath is realized by relatively weak dipole interactions and does, indeed, lead to a temperature different from the lattice one [11]. This spin temperature can be tuned by external fields or by spin cooling and plays an important role in analyzing experiments [11]. The relaxation time $\tau_s$ on which the spin temperature is established is known as $T_2$ time in NMR or ESR, and usually varies between $10^{-4}$ s and 1 s depending on the material. The spin and the lattice temperatures tend to equalize on the $T_1$ time, which for many magnetic materials amounts to minutes or hours [11]. Estimating the relaxation time $\tau_f$ of $f$ via the rotation-vibration mechanism as $10^{-12}$–$10^{-9}$ s [11], we see that our assumptions are based on $\tau_f \ll \tau_s \ll T_1$.

The model is a suitable candidate for displaying the anomalous latent heat, since the two terms in the right-hand side (RHS) of (10) are in conflict: for two lined up spins, $s_i s_k > 0$, the term $-\gamma \sum_i s_i f_i s_k$ tends to increase occupations, $f_i f_k > 0$, while $\alpha \sum_i f_i$ makes this increase costly. The equilibrium ($T_s = T$) version of the model is related to the Blume-Capel model [2]. Similar models were employed for describing solid mixtures [2], reentrance phenomena [12], and glassy physics [13].

Employing $e^{\sum_i s_i f_i} = c e^{\int dm e^{-\beta J m^2 + \beta J \sum_i s_i f_i}}$, where $c = \sqrt[2]{\frac{N!}{\pi}}$, we express from Eqs. (2) and (10), the partition function $Z$ of the model as

$$Z = \left[ \prod_{a=1}^n \right] \int dm_a e^{\int dm_m e^{-\beta J m^2 + \beta J \sum_i s_i f_i}} \frac{\partial}{\partial m_a} F |_{m_a = 0} = \int \mathcal{D}m e^{-\beta J m^2},$$

where $\mathcal{D}m = e^{\sum_a m_a^2}$, and we assumed that $n \equiv \frac{T}{T_s}$ is an integer (replica method); later on we shall make continuation to real $n$. We also defined $\psi(m) = 1 + e^{-\alpha \beta J m^2}$ and

$$\beta_s F(m) = \frac{\beta J}{2} \sum_{a=1}^n m_a^2 - \ln \left[ \sum_{k=1}^a e^{\sum_{a=1}^n \ln(\sigma_{km_a})} \right], \quad (11)$$

$Z$ is calculated by the saddle-point method, where one searches the deepest minimum of $F$ as a function of $m_a$. This minimum is reached for $m_a = m$ (replica symmetry), where $m$ satisfies

$$m = e^{-\alpha \beta J \psi(m)^n - \psi^{-1}(m) m e^{-\beta J m^2}}.$$
Because of the symmetry of the model, Eq. (12) admits two equivalent solutions with ±m. The choice between them is done spontaneously.

The energy $\mathcal{U}$ and the entropies of the spins $S_\pm$ and the occupations $S$ are calculated from Eqs. (3)–(10)

$$\mathcal{U} = \frac{-jm^2}{2} + \frac{\alpha}{z(m)} \sum_{k \pm 1} \phi^{n-1}(km)e^{\beta Jkm},$$

$$S_\pm = \ln z(m) - \frac{n}{z(m)} \sum_{k \pm 1} \phi^n(km) \ln \phi(km),$$

$$S = \beta \mathcal{U} + \frac{1}{z(m)} \sum_{k \pm 1} \phi^n(km) \ln \phi(km) - \frac{\beta jm^2}{2},$$

where $z(m) = \sum_{k \pm 1} \phi^n(km)$. The two terms in the RHS of (15) are equal, respectively, to the spin-spin interaction energy $\frac{\beta}{N} \langle \sum_i f_i \rangle^2$ and $\alpha N$, where $\mathcal{N} = \sum_i \langle f_i \rangle$ is the average number of particles.

In the derivation of (15)–(17) we assumed that the system is in the ferromagnetic phase: $m \neq 0$. For the paramagnetic phase $m = 0$ one has from (13)

$$\mathcal{U} = \frac{\alpha}{e^{\alpha\beta} + 1}, \quad S_\pm = \ln 2,$$

$$S = \frac{\alpha \beta}{e^{\alpha\beta} + 1} + \ln(1 + e^{-\alpha\beta}).$$

The phase diagram of the model is constructed in terms of three independent adimensional parameters:

$$a = \alpha/J, \quad \theta_s = T_s/J, \quad \theta = T/J.$$ (18)

Let us start with few particular cases. For $\theta \to 0$ we get from (13) (assuming $m \geq 0$)

$$\beta_s \mathcal{F} = \frac{m^2}{2\theta_s} - \ln\left[1 + \zeta(m - a) + \zeta(a - m) e^{(m - a) / \theta_s}\right].$$ (19)

$$m = (1 + e^{(a - m) / \theta_s})^{-1} \left[1 - \zeta(a - m)\right],$$ (20)

where $\zeta(x)$ is approximated by the step function: $\zeta(x) = 1(0)$ for $x > 0$ ($x < 0$). We see that $m \neq 0$ only for $a < 1$. However, only for $a < 0.5$, Eq. (20) predicts first-order phase transition to the ferromagnet at $\theta_s = \theta_s^{(c)}$. Above $\theta_s^{(c)}$ there are no particles in the system, $\mathcal{N} = 0$, since the energy cost for consuming a particle from the particle reservoir is too high (due to $T \to 0$). At $\theta_s = \theta_s^{(c)}$ a finite fraction of particles is consumed from the particle reservoir making up the ferromagnetic phase, which appears as a metastable state at a higher critical temperature $\theta_s^{(c)} > \theta_s^{(c)}$. There is no first-order transition for $a > 0.5$, though for $1 > a > 0.5$ the ferromagnet can exist as a metastable phase.

In a different limit $\alpha = 0$ we get from (13)

$$\frac{\mathcal{F}}{\mathcal{J}} = \frac{m^2}{2} - \theta_s \ln \cosh\left(\frac{m}{2\theta_s}\right) - \theta \ln \cosh\left(\frac{m}{2\theta}\right).$$ (21)

$$2m = \tanh\left(\frac{m}{2\theta_s}\right) + \tanh\left(\frac{m}{2\theta_s}\right).$$ (22)

Now there are only second-order phase transitions for the same reason as for the usual (Curie-Weiss) mean-field ferromagnet: $\partial^2_m \mathcal{F}$ can never turn to zero for $m \neq 0$. The phase diagram on the $\theta_s$-$\theta$ plane amounts to the ferromagnet (paramagnet) located below (above) the line,

$$\theta_s^{-1} + \theta_s^{(c)} = 4.$$ (23)

The same Eqs. (21) and (22) without the terms containing $\theta$ apply for $\theta \to \infty$. Here $f_i$ fluctuate so strongly that the influence of $\alpha$ disappears.

A necessary condition for second-order transition is the local instability of the paramagnet: $\partial^2_m \mathcal{F}|_{m=0} = 0$, i.e.,

$$\theta_s = \left[1 + e^{a/\theta}(2 + e^{a/\theta} - a^{-1})\right]^{-1}.$$ (24)

We could continue this reasoning and develop the Ginzburg-Landau expansion, but here it is easier to study (12) and (13) directly. For $a > 0.5$ there is only the second-order phase transition to ferromagnet at temperatures given by (24). Equation (14) shows that $m$ can increase by lining up the spins with or without increasing the occupations. For $a > 0.5$ the second way works, since it is too costly to absorb particles from the reservoir. Indeed, slightly below the transition the difference in the average number of particles is small: $\Delta \mathcal{N} \approx m^2 \ll m$; see (15).

For $0.38 < a < 0.5$ the phase diagram is of the type presented in Fig. 1. Now there are first-order phase transitions from the paramagnet to the ferromagnet. Recall Eqs. (19) and (20) for understanding their mechanism. The transition (phase coexistence) line is found by solving (14), looking for the deepest minima of $\mathcal{F}(m)$, and requir-

![FIG. 1. The phase diagram on the $T - T_s$ plane; $x = 0.45$. P and F refer to the paramagnet and ferromagnet, respectively. Bold line: first-order phase transitions. Normal line: second-order phase transitions. For $T \to \infty$ this line monotonically saturates at $T_s = 0.25$ J, as seen from (23). Dashed line: the instability line of the paramagnet. On the AC segment the latent heat is anomalous.](image-url)
ing the continuous change of the free energy: \( \mathcal{F}(m) = \mathcal{F}(0) \). The ferromagnet corresponds to \( \mathcal{F}(m) < \mathcal{F}(0) \) (recall the saddle-point method). Other quantities of interest change by jump. The ferromagnet first appears as a metastable phase above the first-order transition line, while the paramagnet survives as metastable till the dashed line in Fig. 1. Thus, in the vicinity of the first-order transition line, both phases are locally stable. This bistability implies hysteresis and memory: when changing the temperature the final state of the system (paramagnet or ferromagnet) depends on its initial state. Since both \( m \) and \( \mathcal{N} \) increase in the ferromagnet, \( m \) jumps to a nonzero value not simply due to lining up the existing spins, but also due to absorption of additional particles from the reservoir.

On the AC segment the system moves from the paramagnet to the ferromagnet upon increasing \( T \) or decreasing \( T_s \). Thus, \( S_s \) is smaller in the ferromagnet, while \( S \) is larger there: \( \delta S_s < 0 \) and \( \delta S > 0 \); see (9). This is necessary for the existence of the anomalous latent heat effect; see (9) and below. On the AB segment the latent heat is anomalous: when decreasing \( T_s \) for a fixed \( T \) the system moves towards the ferromagnet, and its internal energy increases. This is due to a positive energy brought about by the particles coming from the reservoir; see (15). The maximal magnitude of the effect reached in the middle of the AC segment is \( \delta U \sim J/20 \). Recall that the transition to the ferromagnet is induced by the tendency of the spin interaction energy to decrease. The latent heat \( \delta U \) is a consequence of this tendency that for \( \delta U > 0 \) overcomes its cause. On the whole first-order transition line the total entropy jump is negative: \( \delta S_{\text{tot}} = \delta S + \delta S_s < 0 \). Expectedly the ferromagnet is more ordered than the paramagnet.

At the point \( B \) the latent heat is zero, while the BC segment shows an anomalous latent heat in a different scenario: upon decreasing \( T \) the system goes to the paramagnet, where the energy is higher. The main difference between the two scenarios is that now the low-\( T \) phase (paramagnet) has higher total entropy \( S_{\text{tot}} \): a first-order transition to a higher entropy phase is induced by decreasing the temperature \( T \). This is impossible in equilibrium.

An example of the phase diagram for \( a < 0.38 \) is presented in Fig. 2. The qualitative shape of the ferromagnet-paramagnet boundary is given by (23). The transitions to the ferromagnet are always induced when decreasing either temperature: there is no anomalous latent heat here. During the first-order transitions the particle number still increases: \( \delta \mathcal{N} > 0 \), but now this brings to decreasing entropy \( \delta S < 0 \). In the present low-\( a \) regime the occupations are slaved by the spins so that the incoming particles arrange their entropy in the way dictated by the spin-spin interaction energy. For \( T = 0 \), the first-order transitions gradually disappear.

In conclusion, we found first-order phase transitions with an unexpected sign of the latent heat: it is positive when going from high temperature (high entropy) phase to the low temperature (low entropy) one. Two conditions are necessary for this: global nonequilibrium (two different temperatures), though the local equilibrium is kept and leads to a slightly generalized thermodynamics, and conflicting interactions. The effect was displayed on the model of lattice gas whose particles carry ferromagnetically interacting Ising spins. In this model the spins equilibrate at a temperature different from the lattice one, and there is a conflict between the spin-spin interaction and the chemical potential.

The effect seems to be generic, since we found it in many other situations, e.g., in the present model, but with fast spins and slow occupations, models with multiparticle interactions, Ising spin-link ferromagnet, etc.

We thank Theo Nieuwenhuizen for discussions. A. E. A. was supported by CRDF Grant No. ARGP-2647-YE-05. K. G. P. was supported by ISTC Grant No. A-820.

\[ \text{Fig. 2. The same as in Fig. 1, but now } \alpha = 0.245 \text{ J.} \]

\[ \text{[7] R. Landauer and J. Woo, Phys. Rev. A 6, 2204 (1972).} \]