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Thermodynamics in Paintings: A Physics-Based Review

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Abstract
Thermodynamic phenomena critically influence the creation, degradation, and conservation of classical oil paintings. This review synthesizes key principles - heat transfer, thermal expansion, energy conservation and entropy, phase transitions, and Arrhenius-type reaction kinetics, and examines their manifestation in traditional painting materials (pigments, binders, varnishes, supports). We discuss how temperature gradients induce mechanical stresses across stratified paint layers, leading to craquelure, delamination, and flow in thermoplastic media. Case studies illustrate (1) heat-darkening of oil films in fire-damaged works and its partial reversal via photobleaching, and (2) catastrophic instability of 19th-century bitumen-containing glazes that soften and creep near room temperature. We then review scientific conservation tools grounded in thermodynamics—active infrared thermography for subsurface defect detection, thermogravimetric and calorimetric analyses (TGA/DSC) for material characterization, and mechanical testing combined with finite-element modeling to predict crack initiation under environmental cycling. Finally, we explore preventive strategies informed by thermodynamic modeling, from climate-controlled display environments and microclimate vitrines to optimized backing and framing systems. By framing paintings as dynamic thermodynamic systems, this review underscores the necessity of physics-based approaches for understanding material behavior and guiding effective preservation of our pictorial heritage.

Keywords: Thermodynamics, Heat transfer, Phase transitions, Reaction kinetics, Oil paint polymerization, Thermal aging, Infrared thermography, Thermogravimetric analysis (TGA/DSC), Environmental control in conservation

1. Introduction

Classical oil paintings are complex multi-layered structures highly sensitive to environmental conditions. Decades of conservation research have shown that fluctuations in temperature and relative humidity (RH) can induce mechanical stresses and chemical changes in paintings, affecting their stability and appearance [1]. Museums and conservation institutes have established environmental guidelines for paintings – generally recommending moderate, stable climates – to minimize thermally or hygroscopically induced damage [2]. However, defining "acceptable" ranges for temperature and RH involves understanding the thermodynamics of paint and canvas materials [1][3] . This technical review synthesizes key findings on how thermodynamic principles govern the deterioration or preservation of classical paintings. It covers the effects of environmental fluctuations, the mechanical behavior of traditional painting materials under varying climate conditions, and the chemical thermodynamics of paint drying and aging. By integrating historic studies and recent advances, we aim to provide a cohesive understanding of the physical and chemical processes – from macroscopic crack formation to molecular reactions – that occur in painted artworks over time.

2. Environmental Effects on Paintings

The surrounding environment plays a critical role in the longevity of artworks. High temperatures (especially >30 °C) combined with high RH can soften paint and varnish layers, leading to increased dirt adhesion and potential deformation [2] . Conversely, low RH causes organic layers (like wood panels and glue-based components) to contract and become brittle, often resulting in crack formation. Pioneering studies by Mecklenburg and Tumosa demonstrated that even normal climate variations can generate substantial internal stress in canvas paintings: as RH drops, glue sizing layers shrink and induce tensile forces, while at high RH, canvas fibers swell and slacken [3]. These cyclic stress fluctuations contribute to craquelure (network of cracks) and flaking paint. Early guidelines for museums advocated very tight climate control (e.g. 50% ± 5% RH) to avoid such damage. By the 1990s, conservation scientists began to systematically determine acceptable environmental ranges by measuring how paintings respond to slow thermodynamic changes. For example, Erhardt *et al.* analyzed museum climate data and object response to propose that slightly broader RH ranges could be tolerated by many objects without immediate damage, as long as extreme fluctuations were avoided [1]. Similarly, a Smithsonian Museum Conservation Institute report by Mecklenburg (2011) quantified safe temperature/RH envelopes for collections based on materials research, emphasizing that both overly dry and overly damp conditions can be harmful in different ways [4].

One major risk of environmental stress is the development of cracks in the paint or ground layers. If a painting is suddenly exposed to low RH (e.g. during a cold, dry winter), the hide glue in the ground layer can lose moisture and shrink. This shrinkage can exert high tensile stress on the paint above, sometimes exceeding the paint film's elongation at break, causing the paint to crack [3]. Mechanical tests and modeling confirm this failure mechanism: in Mecklenburg's classic 1991 study, restrained canvas samples with typical gesso and paint layers were cycled through humidity changes, and significant stresses were recorded at low RH, correlating with the formation of new cracks in the brittle ground [3]. On the other hand, at high humidity the same glue layer absorbs moisture and swells, which can lead to delamination or "tenting" of paint if the expansion is constrained. Thus, both extremes of RH are dangerous – a fact that underpins modern preventive conservation strategies.

Temperature influences act in tandem with humidity. Cooling a painting can embrittle binding media and reduce the capacity of materials to deform without cracking. In fact, at sufficiently low temperatures, any painting can fracture if jarred or stressed [13] .However, cooler storage (within reason) also slows down harmful chemical reactions such as oxidation or hydrolysis, illustrating the trade-off between mechanical and chemical stability [13]. Heat, in contrast, accelerates deterioration and can cause differential expansion of layers. Thermal expansion mismatches between the canvas, ground, and paint can create shear stresses. If a painting is heated by direct sunlight or hot display lights on one side, temperature gradients will form across its cross-section. Research has shown that an unprotected canvas on an external wall, with its front warmer than its reverse, suffers internal RH fluctuations because the cooler backside causes condensation or high RH near the back (while the front is at ambient RH) [12]. Such microclimate effects can promote mold or localized stress. To mitigate this, conservators often install *backing boards* or insulation on painting verso. A sealed backing board can buffer against abrupt RH changes and dust, but it also creates an enclosed air gap that needs consideration of thermodynamics

[9] [12]. Padfield *et al.* used sensors in mock-up frames to show that a poorly ventilated space behind a painting can experience large RH swings if the wall behind is cold and the enclosure is not thermally insulated [12]. Interestingly, their 2019 experiments revealed that adding a hygroscopic material (like cardboard or cotton canvas) as a backing can paradoxically de-stabilize the microclimate if there is a temperature gradient: the absorbent backboard competes with the painting for moisture, leading to complex RH behavior within the sealed layer [12]. This finding updates earlier assumptions that any moisture-buffering backboard is always beneficial; it turns out that when a painting's back is cooler than its front, a hygroscopic buffer at the back will take up and release moisture out-of-phase with the canvas, potentially exacerbating stress on the painting [12]. The safest approach is to eliminate temperature gradients (for instance, by spacing the painting away from cold walls or adding thermal insulation behind the backing board) [12]. Risk analysis by Michalski has similarly highlighted that the efficacy of backing boards depends on climate context: in cold climates, thermal insulation is crucial, whereas in damp climates, an air-tight moisture barrier might be more important [11].These insights underscore that preventing damage requires controlling both humidity *and* temperature fluctuations – truly a thermodynamic challenge.

Conservation engineers have also studied *microclimate vitrine* systems as a solution. Sozzani (1997) described an economical design using the picture frame itself as a sealed housing with silica gel to buffer humidity [9] .Such enclosures significantly slow moisture exchange between the painting and the room, thus smoothing out rapid changes. Experiments showed that when a painting is enclosed and the enclosure climate is stabilized, even daily heating and cooling cycles have less effect on the painting's internal RH [9]. Likewise, Ligterink and Di Pietro (2007) investigated the so-called "stretcher bar effect," where areas of canvas directly over stretcher bars tend to crack less. They attributed this to the wood acting as a thermal insulator and humidity buffer, reducing the amplitude of micro-environmental changes near the bars [8] . In their study, small RH differences were measured across a canvas on a cold wall: regions over the wooden strainer were protected from the full drop in temperature and thus maintained a higher local RH compared to exposed canvas areas, which explains the differential crack patterns historically noted in paintings [8]. These findings have practical implications. For example, the *Cologne approach* to stretching canvas (as discussed by Portsteffen) emphasizes maintaining even tension and possibly using auxiliary supports that minimize environmental gradients across the canvas [10].

Overall, maintaining a stable, moderate environment remains one of the most effective preventative measures for painting conservation. Scientific understanding of thermodynamic responses – gleaned from both field observations and laboratory simulations – has led to more nuanced guidelines. Rather than one-size-fits-all rules, conservators now evaluate factors like a painting's materials and history when defining safe environmental parameters [1][13].The trend is towards *proofed fluctuations*: allowing some range (e.g. RH 40–60%) if a painting has shown it can safely acclimate, but avoiding sudden or extreme shifts. Case studies have documented that many well-constructed panel and canvas paintings can tolerate gradual seasonal changes, but they are vulnerable to abrupt thermo-hygrometric shocks [1][3].
This section has outlined the macroscopic thermodynamic effects – how heat and moisture inputs from the environment translate into physical stresses in a painting. We now turn to the materials themselves: how do the components of a painting behave mechanically under these conditions?

3. Mechanical Behavior of Painting Materials

Classical paintings typically consist of a fabric or wood support, animal glue size, a mineral ground (gesso) layer, and multiple pigment-rich paint layers bound with drying oil, sometimes topped with varnish. Each component has distinct mechanical properties that are temperature- and RH-dependent. Understanding these properties is essential for predicting how paintings respond to environmental stress. Researchers have employed tensile testing, bending tests, and more recently dynamic mechanical analysis to characterize these materials. Early work by Hedley in the 1970s examined how conservation treatments alter canvas behavior: he found that impregnating a linen canvas with a beeswax-resin lining significantly increased its tensile strength and reduced its extensibility [5] . While lining was intended to stabilize damaged paintings, this stiffening effect could make a painting less able to accommodate expansions/contractions, potentially shifting where and how cracks form. Around the same time, the need to test real painting samples (not just bare canvas) led to innovations like the biaxial tensile tester developed by Young and Hibberd [6] . They mounted small painting fragments on a rig that could apply tension in two directions simultaneously, simulating the way a painting on a stretcher is stressed in-plane. Their 1999 study demonstrated that canvas supported paintings show anisotropic behavior: the weave direction (warp/weft) influences stiffness, and paintings can bear more load along the canvas threads than on the bias [6] . Biaxial testing also revealed that adding layers (size, ground, paint) dramatically increases overall stiffness compared to raw canvas, but at the cost of making the system more brittle [6] . These findings quantitatively supported conservators' empirical knowledge that a taut, well-prepared canvas is strong yet can be vulnerable to cracking if overstressed.

More recent work has delved deeper into each layer's contribution. Janas et al. (2022) performed comprehensive tensile tests on samples of canvas, canvas plus glue size, and canvas with size and gesso ground under various humidity conditions [14] .The presence of an animal glue sizing was found to raise the elastic modulus of the canvas composite by an order of magnitude, effectively making the canvas much stiffer and less anisotropic [14] . Adding a typical chalk/glue ground layer further increased stiffness (in their study, up to ~2 GPa at low RH) and also eliminated the directional dependency, because the ground forms a continuous, relatively isotropic layer on top of the fabric [14] . However, as RH increased from 30% to 90%, all samples showed marked softening: the modulus dropped as the hygroscopic glue and gesso absorbed moisture and plasticized [14] . This explains why paintings become more "slack" or deformable in damp conditions and conversely become quite rigid in very dry conditions. Significantly, Janas et al. observed that cracks in the gesso layer occurred at very small strains (on the order of a few thousandths), highlighting that the ground can fracture even under minor dimensional changes [14]. This aligns with real-world observations: the network of fine cracks (craquelure) often originates in the brittle ground or paint during the first drying and aging of the painting, and can later propagate with environmental cycling.

Paint films themselves evolve mechanically as they age. Fresh oil paint is relatively flexible, but as it dries and undergoes chemical curing (oxidation and polymerization), it hardens. After years and decades, oil paint can become quite brittle. A recent study by Janas and colleagues examined oil paints from a reference collection that had been naturally aged for ~30 years, measuring their tensile properties and shrinkage [15] . They found that aged oil paints were significantly stiffer (higher elastic modulus) and could sustain much less elongation before breaking compared to their early dried state [15] . Some paints had become more brittle than the glue-chalk ground, meaning the paint would crack under stress before the ground does [15] . Intriguingly, the team also measured the cumulative shrinkage of these oil paints over time. As paints age, ongoing slow oxidation and solvent-loss can cause them to shrink further, even without environmental moisture changes. The study reported that long-term dried oil paints had experienced enough shrinkage to potentially exceed their strain-at-break – implying that even in stable conditions, an old oil layer can spontaneously crack if it is restrained by a non-shrinking substrate (like a rigid ground or panel) [15] . This phenomenon was evidenced by X-ray microtomography of a historical panel painting: cracks were found in an oil paint layer that had developed simply due to the paint's own shrinkage against an unyielding ground below, independent of external RH fluctuations [15] . It modifies the classic picture of environmental damage by adding that intrinsic material aging can generate stresses.

All these mechanical studies feed into predictive fracture models. Modern finite element simulations incorporate the measured properties of each layer to predict when and where cracks will form under certain climate scenarios. For example, Lee et al. (2022) created a detailed finite element model of a multi-layer oil painting on canvas to investigate crack formation under severe drying (desiccation) conditions [16] . Their simulation included separate layers – linen canvas, glue size, ground, and paint – with nonlinear mechanical properties. When the model painting was exposed to an extreme drop from 90% RH to 10% RH, the analysis predicted three types of damage: bulging of the canvas near the corners (due to differential contraction), cracking in the ground layer, and some plastic deformation in the paint [16] . Notably, the model showed that cracks would likely initiate in the lower layers (glue size or ground) rather than the paint surface, especially near rigid constraints like the corners or edges of the stretcher [16] . These cracks might remain hidden under intact paint for some time. The study provides a possible explanation for the often observed phenomenon of cracks that suddenly appear in paintings: micro-cracks can develop in the ground during a period of environmental stress, but the paint layer above doesn't immediately flake. With repeated stress cycles or additional deterioration, the cracks can propagate up through the paint, eventually becoming visible [16] . Furthermore, the simulation by Lee and co-workers supported the "stretcher effect": in their full-frame model, significantly fewer cracks formed toward the center of the canvas because the inward bowing of the stretcher relieved some tension in the middle, making extreme RH-induced cracks more of a perimeter problem [16] .

Beyond the computational models, empirical observation and art historical research have contributed insights into crack patterns. For instance, art scientist Spike Bucklow performed a formal analysis of craquelure patterns on historical paintings, finding that certain crack characteristics (size, network orientation) correlated with the painting's age and origin, since they result from original techniques and long-term environmental history [17] . The thermodynamic history of a painting – essentially the record of all the heat, humidity, and loading it has experienced – is partly "written" in its crack patterns. While Bucklow's study was aimed at developing a stylistic and diagnostic tool, it reinforces that understanding crack formation is a multidisciplinary challenge involving mechanics, chemistry, and even statistics [17] .

In summary, the mechanical behavior of painting materials under thermodynamic stress is now better understood than ever. Through tensile tests, we know the strength and flexibility limits of canvases, glues, and paints under different climate conditions. Through high-resolution monitoring and modeling, we have identified where cracks are likely to start and how they propagate. All this mechanical knowledge serves two purposes: it informs conservation decisions (like how to reinforce a weak painting or how slow climate changes should be to avoid shock), and it complements chemical studies of degradation, which we will discuss next. The intersection of physical forces and chemical changes is ultimately where "thermodynamics in paintings" plays out most vividly.

4. Thermodynamics of Paint Drying and Aging

Oil paint is essentially a reactive chemical system that, after application, undergoes a long curing process followed by gradual aging. Thermodynamics governs these processes at the molecular level. Drying oils, such as linseed oil, cure by autoxidation – a reaction with oxygen from the air that is exothermic (releasing heat) and results in polymerization of the oil's fatty acids. The kinetics and thermodynamics of oil polymerization have been studied in both art and industrial contexts. Important factors include the oil composition, pigment interactions, and the use of metal driers (catalysts like lead or cobalt soaps added to paint to accelerate drying). Pizzimenti et al. (2025) recently conducted a comprehensive study on how different driers impact the curing of commercial oil paints, using techniques like Differential Scanning Calorimetry (DSC) and infrared spectroscopy [22] . They observed that the presence of certain metal driers (e.g., cobalt tallate, zirconium carboxylates) not only speeds up the curing (oxidation) rate but also influences the thermodynamic profile of the reaction – for example, altering the heat flow during the curing exotherm and the glass transition temperature of the resulting polymer network [22] . Paints with efficient driers tend to cure more completely (consuming more unsaturated bonds) and form a more cross-linked network, which is thermodynamically more stable (lower free energy) but often mechanically stiffer and more brittle. In contrast, paints without such catalysts may retain a higher fraction of unreacted components and remain softer for a longer time. This explains why historically some pigments (like lead white or red lead, which supply their own heavy-metal driers) yield paints that harden relatively quickly and robustly, whereas others like ivory black or zinc white without added driers can remain tacky or brittle [13] [22] .

The exothermic drying reaction in oil paints is not just an academic concern; it has real consequences. In thick paint layers or in rags soaked with drying oil (as in studio or industrial settings), the heat released can build up, leading to a risk of spontaneous combustion. While a thin paint film on a canvas is unlikely to overheat itself to ignition, the thermogenesis does contribute to the paint's curing dynamics. It also means that ambient temperature influences the rate – higher temperatures accelerate the autoxidation (in line with the Arrhenius principle), which is why paintings in warm conditions tend to "age" faster in terms of drying and cross-linking than those in cooler climates [13] . However, higher temperature can also lead to defects like wrinkling of paint films, as the top layer may skin over and trap heat or volatile products beneath.

As oil paints age, complex chemical reactions continue to occur: hydrolysis of triglycerides, formation of free fatty acids, reaction of those acids with metal ions from pigments to form metal soaps, and ongoing radical oxidation leading to chain scission or additional cross-links. Many of these processes are thermodynamically driven or can be understood via thermodynamic concepts (e.g. equilibrium of fatty acids between metal ions and the organic matrix). Izzo et al. (2021) provide a critical review of metal soap formation in oil paintings, outlining how metal carboxylates (soaps) precipitate or migrate in paint films over time [20] . They note that heavy-metal pigments like lead and zinc readily react with fatty acids liberated from the oil binder to form soaps, especially under conditions of high humidity or in the presence of acetic or other acids [20] . These soap formation reactions can be favored because they produce a lower-energy, more crystalline solid (the metal soap) from a higher-energy combination of free ion and free acid. Unfortunately, while thermodynamically favorable, the creation of metal soaps within a paint layer can lead to visible and structural issues: opaque aggregates, efflorescence, increased transparency of paint, or even protrusions and paint delamination when soaps migrate and aggregate into blobs. From a thermodynamic perspective, once enough mobile fatty acid is present, the reaction will proceed until one of the reactants is depleted or until the system reaches a new equilibrium of phases (oil network + crystalline soaps) [20] . Conservation scientists use techniques like FTIR and XRD to detect these soap crystals and assess their extent. Preventive care (like controlling temperature, humidity, and avoiding pollutant gases) can slow the processes, but fundamentally these are spontaneous aging reactions that are part of an oil painting's natural maturation.

Analytical studies have also focused on correlating the molecular structure of aged paints with their mechanical and visual properties. Sanches et al. (2017) applied Dynamic Mechanical Thermal Analysis (DMTA) to 19th-century oil paint formulations (specifically chrome yellow paints) to probe how molecular composition affects viscoelastic behavior [19]. Their work showed that paints with different additives or fillers (e.g., calcium carbonate vs. barium sulfate in chrome yellow) exhibited different glass transition temperatures and stiffness, reflecting differences in the polymer network formed and the presence of residual mobile components [19]. A higher cross-link density, which might result from certain pigment-catalyzed drying processes, typically leads to a higher glass transition temperature and a more brittle paint at room conditions. On a thermodynamic level, increased cross-linking lowers the system's entropy and can create an internal stress if the reaction is constrained (since the network would shrink but is held in place by the canvas/ground). This again ties into the shrinkage stresses mentioned in Section 2. The interplay of chemistry and mechanics is evident: a paint that becomes chemically more ordered and cross-linked (thermodynamically "settled") often becomes mechanically less forgiving.

One fascinating intersection of art and thermodynamics was the attempt to use thermodynamic simulation for art dating and authentication. Zilbergleyt, a physicist, proposed a method to simulate the long-term chemical degradation of pigments and binders using thermodynamic and kinetic data, essentially predicting how a painting's chemistry evolves over centuries [23]. In a 2005 Physics World report, it was noted that his simulations of pigment interactions (for example, cadmium sulfide darkening or lead white reacting to form soaps) showed good agreement with observed changes in old paintings [23]. The idea is that if one can model the entropy increase or free-energy minimization processes in a given paint mixture over time, one could estimate the painting's age or whether it had been artificially aged. While this approach is still speculative and not widely adopted in practice, it underlines a core concept: classical paintings are not static objects but evolving thermodynamic systems. They continuously exchange energy and matter with their environment (absorbing moisture, reacting with oxygen, light-induced reactions, etc.), and they inexorably move toward states of equilibrium (though very slowly).

From a conservation perspective, the goal is to slow down these thermodynamic drives – to keep a painting in a kind of "meta-stable" state as long as possible. Lowering temperature can slow chemical reactions (hence recommendations to store paintings in cool conditions, balancing against the brittleness issue) [13] . Controlling RH can prevent the input of excessive moisture or desiccation that would trigger mechanical or chemical responses. Using inert barrier layers (e.g., protective varnishes or enclosures with inert gas) can reduce the influx of reactive oxygen or pollutants, thereby reducing the thermodynamic potential for oxidative reactions. In recent years, researchers like Mecklenburg, Bratasz, and others have argued for sustainable climate control – not simply keeping one rigid set point, but tailoring the microclimate to what the painting can tolerate, based on its known material properties and history [13] . This evidence-based approach relies on data from both mechanical tests and chemical analyses, many of which were discussed in this review.

5. Conclusion

Thermodynamics – in the broad sense of energy, moisture, and chemical change – is at the heart of how paintings age. Classical oil paintings can be viewed as thermodynamic systems comprised of multiple phases and materials, each responding to environmental parameters. Mechanical damage such as warping, cracking, and delamination often originates from thermally or hygroscopically induced stress, while chemical degradation such as embrittlement, discoloration, or metal soap formation arises from spontaneous reactions driven by the materials seeking lower-energy states. Through pioneering works over the past decades, scientists have quantified these processes: from the force generated by a shrinking glue layer [3] , to the glass transition of an oil paint [19], to the heat released by its curing reactions [22] . This knowledge enables conservators to make informed decisions, like choosing appropriate climate settings, backing methods, or treatments that respect the artwork's material limits. There is a continuous feedback between theory and practice – for instance, when new research showed that slightly relaxed RH controls might be safe for certain robust objects, some museums adjusted their guidelines to both protect the art and reduce energy usage [1] . On the other hand, when simulations warn that unseen micro-cracks could be forming under certain conditions, conservators may implement more cautious handling or microclimate enclosures for vulnerable paintings [16]. In essence, preserving a painting is an exercise in applied thermodynamics: minimizing free energy changes, preventing entropy increase in the form of damage, and buffering external influences. As technology advances, we gain new tools (like microclimate monitoring, chemical sensors, and modeling software) to foresee and counteract detrimental thermodynamic processes in artworks. By compiling the insights from material science, mechanics, and chemistry, this review highlights that effective conservation of classical paintings must embrace a technically informed approach – one that treats each painting as a dynamic system and strives to maintain its delicate equilibrium over time. The references below, ranging from fundamental research studies to conservation guidelines, provide a framework for understanding and continuing this interdisciplinary effort to safeguard our painted heritage.

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