

Research Letter

Soft-Material Dissipative Formation by a Kramers-Type Picture

Adam Gadomski

Institute of Mathematics and Physics, University of Technology and Life Sciences, 85796 Bydgoszcz, Poland

Correspondence should be addressed to Adam Gadomski, agad@utp.edu.pl

Received 17 July 2007; Accepted 5 November 2007

Recommended by Eldon Case

We consider a model soft-material formation in dimension d (a degree of freedom) undergoing an entropic drive, deeply rooted in first law of thermodynamics as well as in entropy production, namely, dissipation rate. It turns out that for such entropy-driven (dissipative) process, two strategies of making the formation orderly can be seen. In low-temperature limit, one may promote curvature-controlled, surface-tension involving scenario, usually characteristic of polycrystals and bubbles. In high-temperature limit, there can be a chance for creating order by establishing viscoelastic phase separation, promoting some microstress field's microrheological action that somehow renormalizes the system toward ordering. The latter, in turn, is very characteristic of protein and/or colloid network formations. This altogether implies that a disordering thermodynamic factor, such as the entropy can typically be, is able to effectively promote ordering by respective energy dissipation, in particular for soft-matter rearrangements and clusterings with weak interactions among the basic material's units, namely, "soft" grains.

Copyright © 2007 Adam Gadomski. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

1. INTRODUCTION

How can order effectively arise from disorder? This is a key (quite philosophical) question that is plausible to appear in materials physics, especially within the framework of nonequilibrium statistical thermodynamics because this physics discipline is well equipped with measures of both order (toward enthalpy, H) and disorder (toward entropy, S) altogether based on the definition of the free (Gibbs) energy, namely, $G = H - TS$ with T -absolute temperature.

In this short note, however, we do not want to embark on such general question posed above but rather we are going to consider this problem based upon one specific example called a d -dimensional matter agglomeration at mesoscopic level of its organization. Thus, we are based on soft-matter aggregation which we will further simply name soft-material formation throughout. The notion of soft matter involved herein means that we are going to typically talk about dispersive systems, such as colloid or protein formations in which the interaction energies are of order of a few $k_B T$ (k_B -Boltzmann constant, T -temperature), thus they are intriguingly weak, preferentially in the realm of van der Waals attraction [1].

Although many soft-material formations of protein and/or colloid, possibly ordered nature [1, 2], also organic

crystalline coatings [3], leading to a soft-material output in a fluctuation-driven context, can markedly differ in detail while being formed during both nucleation as well as growth stages, they all seem to have a certain generic property in common. Namely, they basically undergo, within their mostly dissipative context, the two-state Kramers-type thermally activated barrier-crossing picture [4]. Such a two-state picture of crossing over an energy barrier can, if necessary, also contribute to uncovering some material formation mechanisms over more hilly or corrugated (protein-like) energetic landscapes/funnels, since it becomes eventually a well-drawn (though simplified) picture showing up the main kinetic passage between initial (nucleation) and final (mature growing or cessation to grow) stages. The overall scenario can be realized over a finite number of dynamically emerging intermediate stages, such as dense-liquid formation during protein crystallization [1], or experimentally accessible emergence of liquid-liquid phase separation during formation of crystals made of organic molecules [3]. In dissipative conditions [5], such as supersaturated solution or melt, in which the interaction energy is typically of the order of a few $k_B T$, the presence of such intermediate states can mostly contribute to the width and shape of the energetic barrier [2, 4] but may by no means spoil the general view of the Kramers-like scenario of a typical model soft-material

formation that always involves the two-state contribution(s) when passing between two consecutive (typically neighboring) physical stages of interest, separated by a well-defined energetic barrier [4, 6].

2. THEORETICAL FRAMEWORK

Nonequilibrium thermodynamics (NT) is a powerful theoretical and conceptual framework often proved to be useful when describing (dis)ordered matter rearrangements, preferentially soft-matter aggregations at a level of mesoscale [5, 7–10], ranging between micro- and nanometer size scale. It is deeply rooted in the first law of thermodynamics for open Gibbs ensembles, $TdS(x, t) = -\mu(x, t)f(x, t)dx$, where by assuming, for the sake of clarity, isothermal conditions, $T = \text{const}$, an infinitesimal change in system's entropy, $dS(x, t)$, yields a chemical-potential ($\mu(x, t)$) mediated, an equal small change in the number of rearranging units ("building blocks"), $f(x, t)dx$, having a number density, $f(x, t)$, which is a state or reaction coordinate (x) and time (t) dependent physical quantity [5]. The above is justified for the internal energy of the system remaining unchanged, namely $dU = 0$, as well as when the (external-force) work can thoroughly be neglected, $dW = pdV = 0$ under a constant pressure p , additionally assumed that the system is able to suffer from some very small changes in volume, customary designated by dV . (Such conditions, when causing to generate internal stress' field, are said to be of microrheological character.)

A mesoscopic technique applied to NT (abbreviated by MNET, cf. [5, 7]) makes readily use of the first NT-law in a variational form, $T\delta S(x, t) = -\int \mu(x, t)\delta f(x, t)dx$, also applies the Gibbs entropy-production (dissipation) equation [7, 9], and then effectively utilizes the Kramers-type two-state picture [4] with, in principle [3, 4], a single activation barrier crossing, where Φ -barrier height, to be surmountable by a matter (rearranging-units) flux, $J(x, t)$, which in turn fulfils Neumann-type (reflecting very suitable for the Kramers' picture) boundary conditions at both valleys (states), x_L and x_R , respectively, $J(x = x_L, t) = J(x = x_R, t) = 0$, of the "energetic" hill of effective height $\Phi \equiv \Phi(x)$ [5]. This MNET technique, offering an entropy-driven (small dissipation) picture, yields in a clear way, albeit under one relevant assumption about locality of quasi-equilibrium states [5, 7, 9–11] the Smoluchowski-type matter flux [9], $J(x, t) = -D(x, t)(\partial f(x, t)/\partial x) - C(x, t)(d\Phi/dx)f(x, t)$, with the Onsager coefficients, $D(x, t)$ (diffusion function) and $C(x, t)$ (drift function) being linearly (mutually) dependent on each other, since $C(x, t) = (1/k_B T)D(x, t)$ is expected to hold [5, 9]. The latter appears to be the fluctuation-dissipation condition, being here firmly re-established for the soft matter rearrangement of interest. (Note that it is a simple analog for a standard Einstein-Smoluchowski formula, interconnecting system's diffusivity and viscosity, when the former is, however, defined in a position space.)

For the soft-material formations of interest the key assumption, giving rise to simple-minded type of interaction among the rearranging units, that is, building blocks of the aggregate, would be the one, which, as in colloids or proteins

[1–3, 6], involves their surfaces, and their promoting (catalyzing) role in creating any formation of the model soft material [1, 7, 9]. Thus, identifying x with the volume of the unit but in a d -dimensional (degrees-of-freedom involving) space [5, 7, 9], one has to firmly state that $D(x, t) \propto x^{(d-1)/d}\varepsilon(t)$, where $\varepsilon(t) \approx \text{const}$ should read just for clarity of our presentation, especially in a late-time domain, $t \gg 0$ [10], although for some biopolymer material formations, such as those of polycrystalline, herein of spherulitic or cylindrolitic types, its time-dependent both degree of crystallinity and adsorption-involving role(s) cannot be easily postponed, especially within the prevailing fluctuation-influenced context of the formation; on the contrary, $\varepsilon(t)$ behaves typically powerfully in time [10]. Let us, however, notice quite formally here that $x^{(d-1)/d}$ represents the magnitude of the soft-grain surface [9], that is, the surface of the material's unit (soft grain) scales powerfully with a dimensionality-dependent exponent, namely $(d - 1)/d$.

3. RESULTS AND DISCUSSION IN BRIEF

Such a Smoluchowski-type (dissipative) system described above, the formal expression of which must lead to plugging eventually $J(x, t)$ in a local continuity equation (conservation law), $\partial f(x, t)/\partial t + \partial J(x, t)/\partial x = 0$ [5, 7–10], is able to produce an emergent [12, 13] (self-organized both in unit's size and time domains) behavior, which however, cannot be easily seen in a customary form of strips, (magnetic) bubbles, rings, or other geometrically characterized, often orderly mesophases, typical of nanoscale realizations [12], but is solely reflected by power laws, such as $l(t) \sim t^{\eta(d)}$ [7, 9, 10], for some $t \gg 0$, which is merely of special interest from technological point of view [1–5]; herein, $l(t)$ a characteristic (average) length of the building block, namely, a molecular cluster, the exponent $\eta(d)$ typically involves a $(d+1)$ -account, which is a certain signature of random close-packing, thus leading to inherent amorphization of the obtained material output since the process is entropic (dissipative) by its very nature [7, 10, 11]. It may even lead to a solid conjecture to be formulated, namely that the thermodynamic description of the formations in terms of the Gibbs entropy-production equation as well as the (global) mass conservation law, typically resulting in a material formation in a matter-fluctuation-driven context [10], would lead to the same kinetic equation of Smoluchowsky type (cf. [7, 9, 10] and references therein). Moreover, the main characteristic observables of so designed model system, such as the number of units (soft grains), its total volume, the reduced variance of the unit's volume fluctuations, and finally, a characteristic linear size of the unit, such as $l(t)$ introduced above, scale powerfully with time, very likely in the same algebraic manner as the internal microstress field, or equivalently, the creep compliance can do [9]. In addition, the observables readily discriminate between two basic material outputs of so described matter aggregations: the low-temperature, and its high-temperature counterpart [9]. The discrimination relies mostly on encountering certain different forms of the thermodynamic potential, $\Phi(x)$, which in turn shows up either no unit curvature's influence in case

of loosely packed material formations, or some obvious involvement of the curvature when the packing is appropriately increased [11]. It is of special value if one is able, by effectively employing the sol-gel-type transition concept, to increase temperature T , this way, after exceeding some (percolation) threshold [1, 13], to cause the drift function $C(x, t)$ to vanish uniformly [9], what leads to entering a “purely” diffusional regime by the system [6, 8], described by a “reduced” matter flux $J_D(x, t) = -D(x, t)\partial f(x, t)/\partial x$ [5, 9], that is, of generalized Fickian form. This is the situation described as a formation of loosely packed microstructure [7, 9, 11].

This diffusional regime, characteristic of loosely packed units, is then characterized by another potential Φ , that is, a contribution to the Kramers barrier, but of qualitatively different type than the one governing the nondiffusional (mixed) regime of matter rearrangement defined by full flux $J(x, t)$ [5–9]. To be more specific, it suffices to state that for loosely packed formations the barrier is a linear function of $l(t)$ at a given time instant t whereas it becomes always nonlinear in $l(t)$ if the packing enters high-value regime [7–9]. Such a thermodynamic and kinetic behaviors of emergent and quite self-organized propensity [6–12] may serve as an affective model for deciphering some existing paradigms of the mentioned-above soft-matter formations [1–9], in particular, when pointing to optimal matter aggregations in $d = 2$ (see Langmuir-Blodgett films as a landmark example), which is of clear interest of nanotechnology (quantum dots, wires, etc.) [8], biotechnology (coatings) [3, 14] as well as of modern thin-film techniques, see [7, 9] and references therein. It is interesting to realize that in $d = 2$ such model (high-temperature) soft-matter formation formally predicts the Lifshitz-Slyozov phase-separation behavior with the characteristic exponent $\eta(d) \approx 1/3$. For further reading see also [7, 9, 10], where (a) random close-packing or efficient quasi-amorphization strategy for the aggregations due to $(d + 1)$ -account has thoroughly been discussed; (b) curvature and mechanical microstress involvement, presumably accompanied by viscoelastic phase separation [15, 16], have extensively been utilized for low- and high-temperature orderly matter rearrangements, respectively; for direct application of the offered description to nanostructures compare [8] and [7, 9].

4. CONCLUSION

In the last years, there is a vivid debate on disparate matter aggregations, merely encountered in colloid-type realizations [1, 2]. The emerging rearrangements are either nature’s by-products, such as protein (poly)crystals and aggregates [2, 3, 6], or they are achievements of rapidly expanding modern-era technology, such as the one applied in pharmaceutical industry in which crystallization of drugs is of primary interest [3]. Moreover, growing nanotechnological applications also offer some in-perspective utilitarian end-products named often nanostructures, specifically nanoarrays or nanowires, and the likes, that may preferentially—similarly to colloidal low-dimensional micelles [2, 7]—emerge in an entropic (dissipative) context, that is, when no quantum tunnelling across the resulting (Kramers-type) energy barrier occurs [4], and

under a global constraint that entropy production in the system results naturally in effective yielding the material output [8–10], see some remarks above.

To conclude, we see that it is very important to propose such a timely short communication that reveals in a self-consistent manner the two-state perennially alive picture by Dutch physicist Kramers of thermally activated barrier crossing [4, 15] as a valuable tool for describing the soft-material formation, whether orderly [1, 3, 6] or not [9, 11, 13], by means of an enhanced (due to either curvature-enhanced transport mechanism [7, 9, 14, 16] or viscoelasticity [2, 3, 9, 16], that means typically structural-order creating enthalpy-oriented factors, that is, in protein formations [17]) diffusion along a reaction coordinate [6, 8, 15], x , where this coordinate does not imply—as in the classical Smoluchowski-type picture [9]—the position of a building block, namely, some molecular cluster, being a constitutive piece of the material [12], but is going to be recognized as another relevant stochastic and thermodynamically, equally relevant variable, here specifically: the volume of the building block [7, 9, 10]. Clearly, according to the basic rules of MNET [5, 15], having its qualitative roots in the famous theory of dissipative structures [5, 7] by Prigogine and Glansdorff, there is an advantageous freedom in properly selecting x which goes in parallel with the number of freedom degrees, d , a system of interest can eventually explore. Some limitation, in turn, will be expected when the assumption about quasi-equilibria [15] as well as the linear fluctuation-dissipation rule of $D(x, t) \propto C(x, t)$ (see above) are to be violated [5, 9, 11], which can occur when escaping from mesoscopic and entering readily the submesoscopic level of the nonequilibrium-thermodynamic description [14].

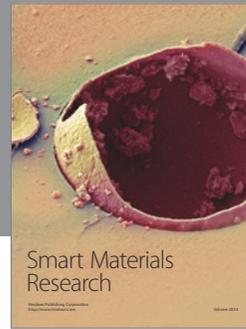
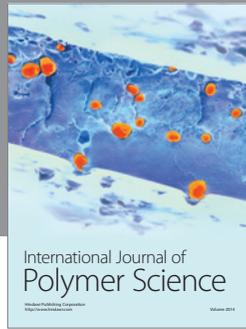
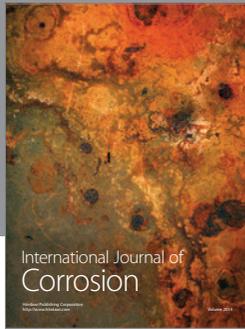
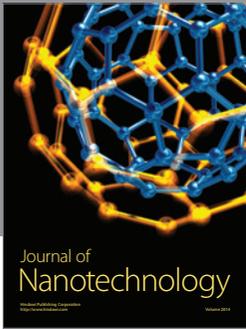
ACKNOWLEDGMENT

This work is sponsored in part by MNil (Poland).

REFERENCES

- [1] R. Holyst, “Some features of soft matter systems,” *Soft Matter*, vol. 1, no. 5, pp. 329–333, 2005.
- [2] P. G. Vekilov, “Two-step mechanism for the nucleation of crystals from solution,” *Journal of Crystal Growth*, vol. 275, no. 1–2, pp. 65–76, 2005.
- [3] S. Veesler, L. Lafferrere, E. Garcia, and Ch. Hoff, “Phase transitions in supersaturated drug solution,” *Organic Process Research & Development*, vol. 7, no. 6, pp. 983–989, 2003.
- [4] P. Hänggi, P. Talkner, and M. Borkovec, “Reaction-rate theory: fifty years after Kramers,” *Reviews of Modern Physics*, vol. 62, no. 2, pp. 251–341, 1990.
- [5] D. Reguera, J. M. Rubí, and A. Pérez-Madrid, “Fokker-Planck equations for nucleation processes revisited,” *Physica A*, vol. 259, no. 1–2, pp. 10–23, 1998.
- [6] P. G. Vekilov and J. I. D. Alexander, “Dynamics of layer growth in protein crystallization,” *Chemical Reviews*, vol. 100, no. 6, pp. 2061–2089, 2000.
- [7] A. Gadomski and J. M. Rubí, “On the two principal curvatures as potential barriers in a model of complex matter agglomeration,” *Chemical Physics*, vol. 293, no. 2, pp. 169–177, 2003.

-
- [8] D. E. Jesson, T. P. Munt, V. A. Shchukin, and D. Bimberg, "Tunable metastability of surface nanostructure arrays," *Physical Review Letters*, vol. 92, no. 11, Article ID 115503, 4 pages, 2004.
- [9] A. Gadomski, J. M. Rubí, J. Łuczka, and M. Ausloos, "On temperature- and space-dimension dependent matter agglomerations in a mature growing stage," *Chemical Physics*, vol. 310, no. 1–3, pp. 153–161, 2005.
- [10] A. Gadomski, "Stochastic approach to the evolution of some polycrystalline (bio) polymeric complex systems," *Chemical Physics Letters*, vol. 258, no. 1–2, pp. 6–12, 1996.
- [11] R. Zallen, *Physics of Amorphous Solids*, chapter 4, John Wiley & Sons, New York, NY, USA, 1983.
- [12] R. B. Laughlin, D. Pines, J. Schmalian, B. P. Stojković, and P. Wolynes, "The middle way," *Proceedings of the National Academy of Sciences of the United States of America*, vol. 97, no. 1, pp. 32–37, 2000.
- [13] D. L. Cox and D. Pines, "Complex adaptive matter: emergent phenomena in materials," *Materials Research Bulletin*, vol. 30, no. 6, pp. 425–432, 2005.
- [14] B. J. Reynwar, G. Illya, V. A. Harmandaris, M. M. Müller, K. Kremer, and M. Deserno, "Aggregation and vesiculation of membrane proteins by curvature-mediated interactions," *Nature*, vol. 447, no. 7143, pp. 461–464, 2007.
- [15] D. Reguera, J. M. Rubí, and A. Pérez-Madrid, "Kramers-type picture for crystal nucleation," *Journal of Chemical Physics*, vol. 109, no. 14, pp. 5987–5993, 1998.
- [16] H. Tanaka and Y. Nishikawa, "Viscoelastic phase separation of protein solutions," *Physical Review Letters*, vol. 95, no. 7, Article ID 078103, 4 pages, 2005.
- [17] N. Combe, P. Jensen, and A. Pimpinelli, "Changing shapes in the nanoworld," *Physical Review Letters*, vol. 85, no. 1, pp. 110–113, 2000.



Hindawi

Submit your manuscripts at
<http://www.hindawi.com>

