A MEAN FIELD ANALYSIS OF THE FLUID/SOLID PHASE TRANSITION

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Abstract. We study the fluid/solid phase transition via a mean field model using the language of large dense random graphs. We show that the entropy density, for fixed particle and energy densities, is minus the minimum of the large deviation rate function for graphs with independent edges. We explicitly compute this minimum for small energy density and a range of particle density, and show that the resulting entropy density must lose its analyticity at some point. This implies the existence of a phase transition, associated with the heterogeneous structure of the energy ground states.

1. Introduction

We will adapt an old random graph model of Strauss [S] to provide a mean field model of the fluid/solid transition of equilibrium matter, in particular to model how high density can produce the internal (crystalline) structure of solids out of a homogeneous fluid. The energy ground state in the model exhibits a range of different structures as the particle density varies, and we use this feature to show there is a phase transition between the structures, near the energy ground state. We are forced to use a mean field model as there is still no convincing model of the basic phenomenon of a distinct solid phase; see [A, Br, Uh, AR1]. A side issue is the use of recent analyses of dense graphs to provide a mathematical framework for the asymptotics of mean field models.

The following is the usual route for understanding the thermodynamic phases of a noble gas such as argon, using classical statistical mechanics and a Lennard-Jones, rotation symmetric, 2-body interaction potential V, depending on separation r by $V(r) = c_1 r^{-12} - c_2 r^{-6}$, with $c_1, c_2 > 0$; see Figure 1. This phenomenological interaction contains the desired features that the (neutral) atoms repel strongly at small separation due to their electron clouds, and deform at intermediate separation, providing a weak attraction responsible for the 'molecular bonds' in the solid phase. The two basic phase transitions, the gas/liquid and fluid/solid, are drawn schematically in Figure 2; neither can be proven for this model, and indeed it has yet to be proven even that the energy ground state is crystalline. (The appropriate crystal has been proven to be the unique ground state in 1 dimension [GR] and to be a ground state in 2 dimensions [T].)

Other, less-realistic models supply a convincing theoretical argument for a gas/liquid transition for such materials. This was first achieved by the well known mean field model of van der Waals, in which the attraction between particles is simplified by ignoring the separation. See [LMP] for recent history of the model and improvements beyond mean field. These models reproduce the basic features of the transition as first order, with coexisting disordered phases of different energy and particle density, ending in a critical point.

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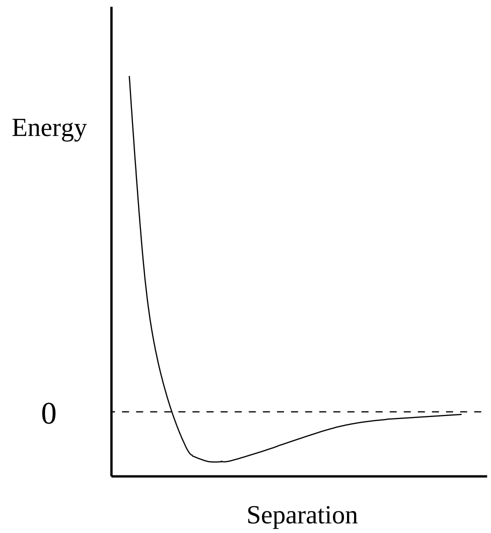

FIGURE 1. The Lennard-Jones interaction potential

We note that not just for noble gases but for most materials the gas/liquid transition is associated with an attractive force between the molecules. For argon the Lennard-Jones potential is reasonable, but for molecules which utilize other types of bonds in the solid phase a more complicated modeling would be desired. In contrast, the fluid/solid transition, at least when the pressure is varied at fixed high temperature, is normally associated with the repulsion of the two electron clouds, independently of the detailed interaction associated with the outer electrons. The hard sphere model [Low], in which the only interaction is a simple hard core—two particles separated by less than the hard core distance produce infinite energy—is then appropriate quite generally, at least for roundish molecules. Simulation of the hard sphere model seems to show only a densely packed face centered cubic crystal ([BFMH, W]); the less-dense crystals which appear at lower pressure in some materials presumably are in part due to other features of the interaction, as in the simple cubic crystals of ionic solids such as table salt. And of course the hard sphere model does not show a gas/liquid transition since it does not include an attractive force. But the model does exhibit the basic phenomenon whereby (crystalline) structure is produced at high density.

Unfortunately our knowledge of the hard sphere model [Low], and more generally the creation of crystalline structure at high density, is based almost completely on computer simulation [A, Br, Uh]. We will try to remedy this via an analogue of the van der Waals result, a mean field analysis but now for the fluid/solid transition. We will adapt a model of Strauss [S], with particles represented by edges in an abstract graph and the (total) energy of a graph being the number of triangular subgraphs, providing a repulsion. (There is no attraction in our model; see however [PN, CD, RY] and references therein for a similar approach using attraction to model a gas/liquid transition.) Our argument depends on several recent results on the asymptotics of large graphs. We begin with notation; see [LS1, LS2, Lov, BCLSV, LS3, CD, CV] for background.

Consider the set $\hat{G}^n$ of simple graphs G with set $V(G)$ of (labelled) vertices, edge set $E(G)$ and triangle set $T(G)$, where the cardinality $|V(G)| = n$. ('Simple' means the edges are undirected and there are no multiple edges or loops.) Let $Z^{n,\delta}_{e,t}$ be the microcanonical

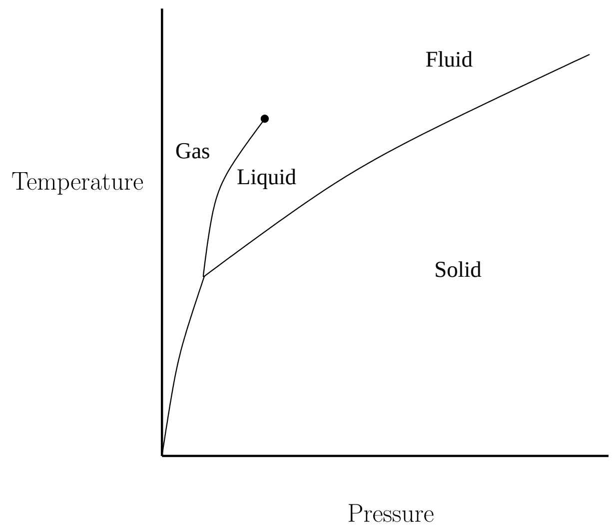

Figure 2. A schematic pressure/temperature phase diagram

partition function, the number of such graphs such that:

$$e(G) \equiv \frac{|E(G)|}{\binom{n}{2}} \in (e-\delta, e+\delta) \quad \text{and} \quad t(G) \equiv \frac{|T(G)|}{\binom{n}{3}} \in (t-\delta, t+\delta). \tag{1}$$

Graphs in $\cup_{n\geq 1}\hat{G}^n$ are known to have edge and triangle densities, (e,t), dense in the region R in the e,t-plane bounded by three curves, $c_1 : (e, e^{3/2}),\ \ 0 \leq e \leq 1$, the line $l_1 :\ (e, 0),\ \ 0 \leq e \leq 1/2$ and a certain scalloped curve $(e, f(e)),\ \ 1/2 \leq e \leq 1$, lying above the curve $(e, e(2e-1),\ \ 1/2 \leq e \leq 1$, and meeting it when $e = e_k = k/(k+1),\ \ k \geq 1$; see [PR] and references therein, and Figure 3.

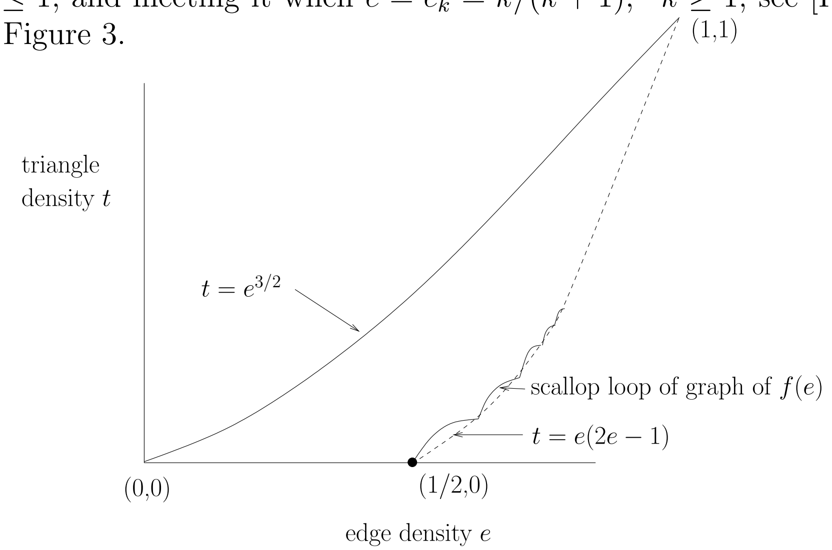

Figure 3. The microcanonical phase space R, outlined in solid lines

We are interested in the density of graphs in R, more precisely in the entropy, the exponential rate of growth of the density as n grows, as follows. First consider

$$s^{n,\delta}_{e,t} = \frac{\ln(Z^{n,\delta}_{e,t})}{n^2}, \text{ and } s_{e,t} = \lim_{\delta\to 0^+} \lim_{n\to\infty} s^{n,\delta}_{e,t}. \tag{2}$$

We will measure the growth rate by the entropy density $s_{e,t}$, and the main question of interest for us is the existence of phase transitions (*i.e.* lack of analyticity of $s_{e,t}$) near the lower boundary of R in Figure 3. The lower boundary consists of the scalloped curve together with the 'first scallop', the line from $(0,0)$ to $(1/2,0)$.

The analysis of phase transitions in traditional models with short range interactions requires the mathematical tools of the infinite volume limit. In this mean field graph setting appropriate tools have been developed recently under the title of 'graph limits', utilizing 'graphons', as we sketch next.

2. Graphons

Consider the set $\mathcal{W}$ of all symmetric, measurable functions

$$g : (x,y) \in [0,1]^2 \to g(x,y) \in [0,1]. \tag{3}$$

Think of each axis as a continuous set of vertices of a graph. For a graph $G \in \hat{G}^n$ one associates

$$g^G(x,y) = \begin{cases} 1 & \text{if } (\lceil nx \rceil, \lceil ny \rceil) \text{ is an edge of } G \\ 0 & \text{otherwise,} \end{cases} \tag{4}$$

where $\lceil y \rceil$ denotes the smallest integer greater than or equal to y. For $g \in \mathcal{W}$ and simple graph H we define

$$t(H,g) \equiv \int_{[0,1]^\ell} \prod_{(i,j)\in E(H)} g(x_i,x_j)\, dx_1 \cdots dx_\ell, \tag{5}$$

where $\ell = |V(H)|$, and note that for a graph G, $t(H,g^G)$ is the density of graph homomorphisms $H \to G$:

$$\frac{|\mathrm{hom}(H,G)|}{|V(G)|^{|V(H)|}}. \tag{6}$$

We define an equivalence relation on $\mathcal{W}$ as follows: $f \sim g$ if and only if $t(H,f) = t(H,g)$ for every simple graph H. Elements of $\mathcal{W}$ are called "graphons", elements of the quotient space $\tilde{\mathcal{W}}$ are called "reduced graphons", and the class containing $g \in \mathcal{W}$ is denoted $\tilde{g}$. The space $\tilde{\mathcal{W}}$ is compact in the metric topology with metric:

$$\delta_{\blacksquare}(\tilde{f},\tilde{g}) \equiv \sum_{j\ge 1} \frac{1}{2^j} |t(H_j,f) - t(H_j,g)|, \tag{7}$$

where $\{H_j\}$ is a countable set of simple graphs, one from each graph-equivalence class. Equivalent functions in $\mathcal{W}$ differ by a change of variables in the following sense. Let Σ be the space of measure preserving bijections σ of $[0,1]$, and for f in $\mathcal{W}$ and $\sigma \in \Sigma$, let $f_\sigma(x,y) \equiv f(\sigma(x),\sigma(y))$. Then $f \sim g$ if and only if $g = f_\sigma$ for some $\sigma \in \Sigma$. Note that if each vertex of a finite graph is split into the same number of 'twins', each connected to the same vertices, the result stays in the same equivalence class, so for a convergent sequence $\tilde{g}^{G_j}$ one may assume $|V(G_j)| \to \infty$.

The value of this formalism here is that one can use large deviations on graphs with independent edges [CV] to give an optimization formula for $s_{e,t}$, which allows us to analyze $s_{e,t}$ near the energy ground states, the lower boundary of R in Figure 3. We do this next.

3. The entropy is minus the minimum of the rate function

We next use the large deviations rate function for graphs with independent edges [CV].

Theorem 3.1. *For any possible pair (e,t), $s_{e,t} = -\min I(g)$, where the minimum is over all graphons g with $e(g)=e$ and $t(g)=t$, where*

$$e(g) = \int_0^1\int_0^1 g(x,y)\,dx\,dy, \qquad t(g) = \int_0^1\int_0^1\int_0^1 g(x,y)g(y,z)g(z,x)\,dx\,dy\,dz$$

and the rate function is

$$I(g) = \int_0^1\int_0^1 I_0(g(x,y))\,dx\,dy, \text{ where } I_0(u) = \frac{1}{2}\left[u\ln(u) + (1-u)\ln(1-u)\right]. \tag{8}$$

Proof. Actually, the entropy $s_{e,t}^{n,\delta}$ is not a-priori well-defined. All we know is that lim inf and lim sup of $\ln(Z)/n^2$ exist as $n\to\infty$. However, we will show that both of them approach $-\min I(g)$ as $\delta \to 0^+$.

We need to define a few sets. Let U_δ be the set of graphons g with $(e(g),t(g))$ strictly within δ of (e,t), i.e. the preimage of an open ball of radius δ in (e,t)-space, and let F_δ be the preimage of the closed ball of radius δ. Let $\tilde{U}_\delta$ and $\tilde{F}_\delta$ be the corresponding sets in $\tilde{\mathcal{W}}$. Let $|U_\delta^n|$ and $|F_\delta^n|$ denote the number of graphs with n vertices whose checkerboard graphons (4) lie in U_δ or F_δ. The large deviation principle, Theorem 2.3 of [CV], implies that:

$$\limsup_{n\to\infty} \frac{\ln|F_\delta^n|}{n^2} \le -\inf_{\tilde g \in \tilde F_\delta} I(\tilde g), \tag{9}$$

which also equals $-\inf_{g\in F_\delta} I(g)$, and that

$$\liminf_{n\to\infty} \frac{\ln|U_\delta^n|}{n^2} \ge -\inf_{\tilde g \in \tilde U_\delta} I(\tilde g), \tag{10}$$

which also equals $-\inf_{g\in U_\delta} I(g)$. This yields a chain of inequalities

$$-\inf_{U_\delta} I(g) \le \liminf \frac{\ln|U_\delta^n|}{n^2} \le \limsup \frac{\ln|U_\delta^n|}{n^2} \le \limsup \frac{\ln|F_\delta^n|}{n^2} \le -\inf_{F_\delta} I(g) \le -\inf_{U_{\delta+\delta^2}} I(g) \tag{11}$$

As $\delta\to 0^+$, the limits of $-\inf_{U_\delta} I(g)$ and $-\inf_{U_{\delta+\delta^2}} I(g)$ are the same, and everything in between is trapped.

So far we have proven that

$$s_{e,t} = -\lim_{\delta\to 0^+}\inf_{U_\delta} I(g). \tag{12}$$

Next we must show that the right hand side is equal to $-\min_{F_0} I(g)$. By definition, we can find a sequence of reduced graphons $\tilde g_\delta \in \tilde U_\delta$ such that $\lim_{\delta\to 0} I(\tilde g_\delta) = \lim\inf_{U_\delta} I(g)$. Since $\tilde W$ is compact, these reduced graphons converge to a reduced graphon $\tilde g_0$, represented by a graphon $g_0 \in F_0$. Since I is lower-semicontinuous [CV], $I(g_0) \le \lim I(g_\delta)$, so $\min_{F_0} I(g) \le \lim\inf_{U_\delta} I(g)$. (We write min rather than inf since $\tilde F_0$ is compact.) However, $\min_{F_0} I(g)$ is at least as big as $\inf_{U_\delta} I(g)$, since $F_0 \subset U_\delta$. Thus $\min_{F_0} I(g) = \lim_{\delta\to 0}\inf_{U_\delta} I(g)$. □

4. Minimizing the rate function on the boundary

From now on we will work exclusively with graphons rather than with actual graphs. From Theorem 3.1, all questions boil down to "minimize the rate funciton over such-and-such region". The first region we study is the lower boundary of (e,t)-space, beginning with the first (flat) scallop:

Theorem 4.1. *If $e \le 1/2$ and $t = 0$, then $\min_{F_0} I(g)$ is achieved at the graphon*

$$g_0(x,y) = \begin{cases} 2e & \text{if } x < \frac{1}{2} < y \text{ or } y < \frac{1}{2} < x; \\ 0 & \text{otherwise.} \end{cases} \tag{13}$$

Furthermore, any other minimizer is equivalent to g_0, corresponding to the same reduced graphon.

Proof. Since $t(g)$ is identically zero, the measure of the set $\{(x,y) \in [0,1]^2 | g(x,y) = 0\}$ is at least $1/2$. Otherwise, the graphon $\bar{g}(x,y) = \begin{cases} 1 & \text{if } g(x,y) > 0; \\ 0 & \text{otherwise,} \end{cases}$ would have no triangles and would have edge density greater than $1/2$, which is impossible. So we restrict attention to graphons that are zero on a set of measure at least $1/2$. From the convexity of I_0, we know that the minimum of I among such graphons must be zero on a set of measure $1/2$ and must be constant on the rest . Thus g_0 is a minimizer.

Now suppose that g is another minimizer. Since g is zero on a set of measure $1/2$ and is $2e$ on a set of measure $1/2$, $\bar{g}$ is 1 on a set of measure $1/2$, and so describes a graphon with edge density $1/2$ and no triangles. This means that $\bar{g}$ describes a complete bipartite graph with the two parts having the same measure. That is, $\bar{g}$ is equivalent to the graphon that equals 1 if $x < \frac{1}{2} < y$ or $y < \frac{1}{2} < x$ and is zero everywhere else. But then $g = 2e\bar{g}$ is equivalent to g_0. ☐

The situation on the curved scallops is slightly more complicated. Pick an integer $t > 1$. (The case $t = 1$ just gives us our first scallop.) If $e \in \left[1 - \frac{1}{t}, 1 - \frac{1}{t+1}\right]$, then any graph G with edge density e and the minimum number of triangles has to take the following form (see [PR] for the history). Let

$$c = \frac{t + \sqrt{t(t - e(t+1))}}{t(t+1)}. \tag{14}$$

There is a partition of $\{1, \ldots, n\}$ into t pieces, the first $t-1$ of size $\lfloor cn \rfloor$ and the last of size between $\lfloor cn \rfloor$ and $2\lfloor cn \rfloor$, such that G is the complete t-partite graph on these pieces, plus a number of additional edges within the last piece. ($\lfloor y \rfloor$ denotes the largest integer greater than or equal to y.) These additional edges can take any form, as long as there are no triangles within the last piece.

This means that, after possibly renumbering the vertices, the graphon for such a graph can be written as an uneven $t \times t$ checkerboard obtained from cutting the unit interval into pieces $V_k = [(k-1)c, kc]$ for $k < t$ and $V_t = [(t-1)c, 1]$, with the checkerboard being 1 outside the main diagonal, 0 on the main diagonal except the upper right corner, and corresponding to a zero-triangle graph in the upper right corner.

Limits of such graphons in the metric must take the form

$$g(x,y) = \begin{cases} 1 & x < kc < y \text{ or } y < kc < x \text{ for an integer } k < t; \\ 0 & (k-1)c < x, y < kc \text{ for some integer } k < t; \\ \text{unspecified} & x, y > (t-1)c, \end{cases} \tag{15}$$

with

$$\iiint\limits_{[(t-1)c,1]^3} g(x,y)g(y,z)g(z,x)\,dx\,dy\,dz = 0, \tag{16}$$

and with $\iint\limits_{[0,1]^2} g(x,y)\,dx\,dy = e$. Minimizing $I(g)$ on such graphons is easy, since all but the upper right corner of the graphon is fixed. Applying Theorem 4.1 to that corner, we get

Theorem 4.2. *If $e > 1/2$ and t is the smallest value possible, then the minimum of $I(g)$ on F_0 is achieved by the graphon*

$$g_0(x,y) = \begin{cases} 1 & x < kc < y \text{ or } y < kc < x \text{ for an integer } k < t; \\ p & (t-1)c < x < [1+(t-1)c]/2 < y \text{ or } (t-1)c < y < [1+(t-1)c]/2 < x; \\ 0 & \text{otherwise,} \end{cases} \tag{17}$$

where

$$p = \frac{4c(1-tc)}{(1-(t-1)c)^2} \tag{18}$$

is a number chosen to make $\iint_{[0,1]^2} g(x,y)\,dx\,dy = e$. Furthermore, any other minimizer is equivalent to g_0.

5. Minimizing near the first scallop

Now that we know the minimizer *at* the boundary, we perturb it to get a minimizer *near* the boundary.

Theorem 5.1. *Pick $e < 1/2$ and ϵ sufficiently small. Then the graphon*

$$g(x,y) = \begin{cases} 2e - \epsilon & x < \frac{1}{2} < y \text{ or } y < \frac{1}{2} < x \\ \epsilon & \text{otherwise,} \end{cases} \tag{19}$$

minimizes the rate function to second order in perturbation theory among graphons with $e(g) = e$ and $t(g) = e^3 - (e-\epsilon)^3$. For pointwise small variations δg of g, the second variation in $I(g)$ is bounded from below by $\frac{1}{2}\iint\limits_{[0,1]^2} (\delta g(x,y))^2\,dx\,dy$.

Proof. We first consider the first variation in $I(g)$ for general graphons and derive the Euler-Lagrange equations. It is easy to check that our specific g satisfies these equations. We then consider the second variation in $I(g)$. Note that the function I_0 satisfies

$$I_0'(u) = \frac{1}{2}[\ln(u) - \ln(1-u)], \qquad I_0''(u) = \frac{1}{2}\left[\frac{1}{u} + \frac{1}{1-u}\right] \geq 2. \tag{20}$$

To find the Euler-Lagrange equations with the constraints that $(e(g), t(g))$ are equal to fixed values (e_0, t_0), we use Lagrange multipliers and vary the function $I(g) + \lambda_1(e(g) - e_0) + \lambda_2(t(g) - t_0)$. To first order, the variation with respect to g is

$$\delta I(g) = \int_0^1\int_0^1 I_0'(g(x,y))\delta g(x,y)\,dx\,dy + \lambda_1 \int_0^1\int_0^1 \delta g(x,y)\,dx\,dy \tag{21}$$

$$+3\lambda_2 \int_0^1\int_0^1 h(x,y)\delta g(x,y)\,dx\,dy, \tag{22}$$

where we have introduced the auxiliary function

$$h(x,y) = \int_0^1 g(x,z)g(y,z)\,dz. \tag{23}$$

Setting $\delta I(g)$ equal to zero, we get

$$I_0'(g(x,y)) = -\lambda_1 - 3\lambda_2 h(x,y). \tag{24}$$

Our particular $g(x,y)$ satisfies this equation with

$$3\lambda_2 = \frac{I_0'(2e-\epsilon) - I_0'(\epsilon)}{2(e-\epsilon)^2}. \tag{25}$$

Next we expand δt and δI to second order in δg, ignoring $O((\delta g)^3)$ terms.

$$\begin{aligned}
\delta I = {} & \iint I_0'(g(x,y))\delta g(x,y)dx\,dy \\
& +\frac{1}{2}\iint I_0''(g(x,y))(\delta g(x,y))^2 dx\,dy \\
= {} & \iint(-\lambda_1 - 3\lambda_2 h(x,y))\delta g(x,y)dx\,dy \\
& +\frac{1}{2}\iint I_0''(g(x,y))(\delta g(x,y))^2 dx\,dy \\
= {} & -\lambda_1\delta e - \lambda_2 \delta t + 3\lambda_2 \iiint g(x,y)\delta g(x,z)\delta g(y,z)\,dx\,dy\,dz \\
& +\frac{1}{2}\iint I_0''(g(x,y))(\delta g(x,y))^2\,dx\,dy \\
= {} & 3\lambda_2 \iiint g(x,y)\delta g(x,z)\delta g(y,z)dx\,dy\,dz \\
& +\frac{1}{4}\iint I_0''(g(x,y))\delta g(x,y)^2 dx\,dy + \frac{1}{4}\iint I_0''(g(x,y))\delta g(x,y)^2 dx\,dy,
\end{aligned} \tag{26}$$

since

$$\delta t = 3\iint h(x,y)\delta g(x,y)dx\,dy + 3\iiint g(x,y)\delta g(x,z)\delta g(y,z)dx\,dy\,dz + O((\delta g)^3), \tag{27}$$

and since we are holding $e(g)$ and $t(g)$ fixed. We have split the $\iint I''\delta g^2$ term into two pieces, as we will be applying different estimates to each piece.

Since $h(x,y)$ and $I''(g)$ are piecewise constant, all of our integrals break down into integrals over different quadrants. Let R_1 and R_2 be the following subsets of $[0,1]^2$:

$$R_1 = \{x, y < 1/2\} \cup \{x, y > 1/2\}, \qquad R_2 = \{x < 1/2 < y\} \cup \{y < 1/2 < x\}. \tag{28}$$

For each z, we define the functions $f_1(z) = \int_0^{1/2} \delta g(x,z)dx$ and $f_2(z) = \int_{1/2}^1 \delta g(x,z)dx$. The second variation in I is then

$$\begin{aligned}
& \frac{1}{4}\iint\limits_{[0,1]^2} I_0''(g)\delta g(x,y)^2 dx\,dy + \frac{I_0''(\epsilon)}{4}\iint\limits_{R_1} \delta g(x,y)^2 dx\,dy + \frac{I_0''(2e-\epsilon)}{4}\iint\limits_{R_2} \delta g(x,y)^2 dx\,dy \\
+ & \ 3\lambda_2 \int_0^1 dz \left[\epsilon \iint\limits_{R_1} \delta g(x,z)\delta g(y,z) dx\,dy + (2e-\epsilon)\iint\limits_{R_2} \delta g(x,z)\delta g(y,z)dx\,dy\right] \\
= & \ \frac{1}{4}\iint\limits_{[0,1]^2} I_0''(g(x,y))\delta g(x,y)^2 dx\,dy + \frac{I_0''(\epsilon)}{4}\iint\limits_{R_1} \delta g(x,z)^2 dx\,dz + \frac{I_0''(2e-\epsilon)}{4}\iint\limits_{R_2} \delta g(x,z)^2 dx\,dz \\
& +3\lambda_2 \int_0^1 \epsilon\left[f_1(z)^2 + f_2(z)^2)\right] + 2(2e-\epsilon)f_1(z)f_2(z)\,dz
\end{aligned} \tag{29}$$

Note that by Cauchy-Schwarz,

$$\int_0^{1/2} (\delta g(x,z))^2 dx \ \geq \ 2\left(\int_0^{1/2} \delta g(x,z)dx\right)^2 = 2f_1(z)^2 \tag{30}$$

$$\int_{1/2}^1 (\delta g(x,z))^2 dx \ \geq \ 2\left(\int_{1/2}^1 \delta g(x,z)dx\right)^2 = 2f_2(z)^2. \tag{31}$$

Since $I_0''(\epsilon)$ and $I_0''(2e-\epsilon)$ are positive, δI is bounded from below by

$$\begin{aligned}
& \frac{1}{4}\iint\limits_{[0,1]^2} I_0''(g(x,y))\delta g(x,y)^2 dx\,dy + \frac{I''(\epsilon)}{2}\left[\int_0^{1/2} f_1(z)^2 dz + \int_{1/2}^1 f_2(z)^2 dz\right] \\
+ & \ \frac{I_0''(2e-\epsilon)}{2}\left[\int_0^{1/2} f_2(z)^2 dz + \int_{1/2}^1 f_1(z)^2 dz\right] \\
+ & \ 3\lambda_2 \int_0^1 dz\left[\epsilon(f_1(z)^2 + f_2(z)^2) + 2(2e-\epsilon)f_1(z)f_2(z)\right]
\end{aligned} \tag{32}$$

Collecting terms and applying equation (25), this bound becomes

$$\begin{aligned}
\frac{1}{4}\iint\limits_{[0,1]^2} I_0''(g(x,y))\delta g(x,y)^2 dx\,dy \ & + \ \int_0^{1/2} dz[c_1 f_1(z)^2 + c_2 f_2(z)^2 + 2c_3 f_1(z)f_2(z)] \\
& + \ \int_{1/2}^1 dz[c_1 f_2(z)^2 + c_2 f_1(z)^2 + 2c_3 f_1(z)f_2(z)],
\end{aligned} \tag{33}$$

where

$$c_1 \ = \ \frac{I_0''(\epsilon)}{2} + \frac{\epsilon(I_0'(2e-\epsilon) - I_0'(\epsilon))}{2(e-\epsilon)^2} \tag{34}$$

$$c_2 \ = \ \frac{I_0''(2e-\epsilon)}{2} + \frac{\epsilon(I_0'(2e-\epsilon) - I_0'(\epsilon))}{2(e-\epsilon)^2} \tag{35}$$

$$c_3 \ = \ \frac{(2e-\epsilon)(I_0'(2e-\epsilon) - I_0'(\epsilon))}{2(e-\epsilon)^2}. \tag{36}$$

Note that all coefficients are positive, and that $c_2 > 1$. As $\epsilon \to 0$, c_1 goes to $+\infty$ as $1/\epsilon$, while c_3 only diverges as $-\ln(\epsilon)$. Since $c_1 c_2 > c_3^2$ for small ϵ, the integrand for each z is positive semi-definite, so the integral over z is non-negative, and we obtain

$$\delta I \geq \frac{1}{4} \iint I_0''(g) \delta g^2 \geq \frac{1}{2} \iint \delta g(x,y)^2, \tag{37}$$

where we used the fact that $I_0''(u) \geq 2$ for all u. □

Any global minimizer must be $O(\epsilon)$ close to g_0, and hence $O(\epsilon)$ close to our specified perturbative minimizer. This means that the only way for them to differ is through a complicated bifurcation of minimizers at g_0, despite the uniform bounds on δI as we approach the boundary.

Corollary 5.2. *Assuming our perturbative solution is the global minimizer, there is a phase transition near the boundary point* $(1/2, 0)$ *between the first and second scallop.*

Proof. Our perturbative solution yields a formula for the entropy:

$$s_{e,t} = \frac{-1}{2}[I_0(\epsilon) + I_0(2e - \epsilon). \tag{38}$$

This formula for the entropy cannot be extended analytically beyond $e = (1+\epsilon)/2$, as $\partial^2 s/\partial e^2$ diverges as $e \to (1+\epsilon)/2$. However, $e = (1+\epsilon)/2$ corresponds to $t = (\epsilon^3 + 3\epsilon)/4 = [(2e-1)^3 + 3(2e-1)]/4$, which is in the interior of (e,t) space. (Since the graphon $g(x,y)$ is nowhere zero, it differs in form from the graphons describing graphs with minimal t.) Thus $s_{e,t}$ must fail to be analytic in some neighborhood of the first scallop. □

6. Conclusion

Our goal is to understand why materials develop a solid phase at high density (pressure) or low energy (temperture). As discussed in the introduction, this is presumably due to the repulsive part of the interaction. Simplifying the Lennard-Jones potential, the interaction $\tilde{V}(r) = r^{-12}$ for separation r should give the desired effect. We have been working in the microcanonical ensemble, so for this model the main problem would be to show why, at high particle density, the energy ground state is crystalline and that this survives at low but not minimum energy density.

This has been a famous unsolved problem for many years [A, Br, Uh, AR1]. We have taken an unusual path here, working in a model in which there are energy ground states of different type as one varies the particle density. (A simple model with this property using short range forces in one spatial dimension is the 'shift model' [NR]. Of course the crystal structures do not survive to higher energy density in one dimensional models such as this.)

Many real materials display a range of crystal structures. Most materials (ignoring quasicrystals) must have a close packed crystal structure at high particle density, but many are looser packed at lower density, for instance simple cubic for table salt. This feature of varying crystal structure is useful for us because there is then a phase transition between the different crystal structures *near energy minimization*, the lower edge of the phase space in Figure 2. This is useful because the analysis can focus on a perturbation of the energy ground state, instead of states far away, where the crystal melts to a fluid.

This is the path we have taken in our mean field model. We have shown that our (bipartite) graphon g minimizes the entropy density to second order in perturbation theory, among states sufficiently close to the low density end of the energy ground state. Assuming it is the global minimizer we saw that entropy would have to lose analyticity as the density of the state approaches the tripartite regime. We expect that a more complicated analysis could be extended to create appropriate graphon perturbations g^k, $g \geq 1$ near each of the higher density (multipartite) regimes, with a transition near each scallop intersection.

Intuitively we have given evidence for a mechanism whereby as particle density is increased, near the energy ground state, the system progressively transitions through finer and finer structure; for large particle density most configurations would consist of many interacting 'parts', in a crude approximation to how the unit cells in a crystal behave.

We have used the graph limit formalism, and the large deviation theorem for independent-edge graphs, to prove our results. The graphon formalism is a powerful and flexible tool for analyzing mean field models, for instance modeling the fluid/solid phase transition as we have done here. To see its power one can contrast the sharpness of results obtained with ([CD, RY]) and without ([PN]) the graphon formalism, on very similar models but with attractive forces and modeling the gas/liquid transition.

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