Nonuniversality in low-volume-fraction Ostwald ripening

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May 20, 2006

Abstract

We study Ostwald ripening in the regime of small volume fraction and consider spatially periodic systems whose size is smaller than the screening length. Within the snapshot perspective we obtain an explicit characterization of the leading-order deviation to the classical mean-field theory by Lifshitz, Slyozov and Wagner (LSW). Using this representation, we show that the corrections are not universal, in the sense that the mean value has a strong dependence on geometry, and arbitrarily large fluctuations can happen with finite probability.

Keywords: Ostwald ripening, monopole approximation

AMS Subject classification: 35B27, 74N20, 82C26

1 Introduction

Late–stage phase separation in a dilute off–critical binary mixture is driven by competitive growth of the particles of the minority phase to reduce their total surface energy. This phenomenon, known as Ostwald ripening, has been traditionally studied by the mean-field theory by Lifshitz, Slyozov and Wagner (LSW) [8, 12], which is appropriate in the limit of vanishing volume fraction ϕ. Both experiment and numerical simulations have shown significant deviations from the LSW results [4, 3, 9].

First-order corrections to the LSW theory have been intensively studied in the applied literature (see e.g. [10, 11, 5] for reviews and references). More recently, a mathematically rigorous result which establishes the scaling of the lowest order correction in finite systems was given in [6]. It was shown that the first-order correction to the LSW theory shows a crossover from a $\phi^{1/3}$ scaling to a $\phi^{1/2}$ scaling when the system size becomes larger than the so-called screening length which describes the effective interaction range of a particle. More precisely, the deviation of the surface-energy decay rate from the mean-field prediction has been considered as a measure for the deviation of the coarsening rate. It has been established that for supercritical systems (systems larger than the screening length), this quantity is with large probability negative and scales as $\phi^{1/2}$. In the case of subcritical systems (systems smaller than the screening length) it was only shown in [6] that the average value of the deviation behaves as $\phi^{1/3}N^{-1/3}$, N being the particle number, and a one-sided bound with the same scaling was given. We show here that this result is optimal, in the sense that the energy decay rate can have large fluctuations (in the opposite direction). Furthermore, we show that the average of the deviation from mean-field theory is geometry dependent, at least in a periodic setting.

2 Set up and main results

2.1 Overview

The coarsening process can be described by the Mullins-Sekerka evolution and for small volume fraction ϕ this is well approximated by the monopole approximation [1, 2, 13]. Here, one phase is represented by spherical particles with centers $\{X_i\}_{i=1,\dots,N}$ and radii $\{R_i\}_{i=1,\dots,N}$ which are distributed in a domain $\Omega \subset \mathbb{R}^3$. The growth rates of the particle volumes

$$B_i \ := - \frac{d}{dt}[\frac{1}{3} R_i^3] \ = - \ R_i^2 \frac{dR_i}{dt} \,,$$

are given for each time as a solution of the linear system

$$\frac{1}{R_i} = u_\infty + \frac{B_i}{R_i} + \sum_{j\neq i} \frac{B_j}{|X_i - X_j|} \,, \qquad \sum_i B_i = 0 \,. \tag{2.1}$$

The constant u_∞ is called the "mean–field" and is determined by the constraint that the total volume of the particles is conserved, which is equivalent to $\sum B_i = 0$ (see e.g. [5, 6] for a more detailed presentation of the model and a summary of the related literature). The identity (2.1) gives an exact evolution equation for the empirical distribution of particle radii, and is the starting point of the present analysis.

In their classical mean-field theory, Lifshitz, Slyozov and Wagner [8, 12] simplified (2.1) by neglecting the interaction term. This gives

$$\frac{1}{R_i} = u_\infty^{LSW} + \frac{B_i^{LSW}}{R_i}, \qquad \sum_i B_i^{LSW} = 0,$$

which has the explicit solution

$$B_i^{LSW} = 1 - R_i\, u_\infty^{LSW} \quad \text{and} \quad u_\infty^{LSW} = \frac{N}{\sum_i R_i},$$

hence $u_\infty^{LSW} = 1/\bar{R}$, where $\bar{R} := \frac{1}{N}\sum_i R_i$ is the mean radius in the system. LSW predicted for the corresponding evolution equation for the particle size distribution universal self-similar large-time asymptotics. This implies universal growth laws for typical length scales and a universal particle radius distribution. Experiments and numerical simulations of the evolution equation (2.1) show however larger growth rates and broader size distributions than the ones given by the LSW theory. This is not surprising, since in the LSW theory the local interaction between particles is neglected. The LSW theory overestimates the distance over which diffusion takes place and thus underestimates coarsening rates.

We are interested in the deviation of the coarsening rate given by the monopole approximation from the LSW theory. To that aim we take in the following the so-called snap-shot perspective, that is we consider a finite system $\{(X_i, R_i)\}_{i=1,\dots,N}$, where X_i and R_i are independently distributed. Then we analyze the joint distribution of $\{(X_i, R_i, B_i)\}$, where the growth rates B_i are determined as a solution of the monopole approximation. In particular we are interested in how $\{B_i\}$ deviate from the LSW truncation $\{B_i^{LSW}\}$.

As a measure for the deviation from the LSW theory we consider here as in [6] the relative deviation in the rate of change of the surface energy. More precisely, if $E := \frac{1}{2N}\sum R_i^2$ is the surface energy, then the decay rate is given by

$$\dot{E} = -\frac{1}{N}\sum_i \frac{B_i}{R_i},$$

whereas the LSW theory gives $\dot{E}^{LSW} = -N^{-1}\sum B_i^{LSW}/R_i$. Within the Mullins-Sekerka evolution (2.1) the surface energy is decreasing, and correspondingly $\dot{E} \le 0$ for all realizations $\{(X_i, R_i)\}$. Also $\dot{E}^{LSW} \le 0$, but we expect that for most realizations $\dot{E} - \dot{E}^{LSW} \leq 0$ since the LSW theory should underestimate the coarsening rate. Three of us estimated the relative deviation $\frac{\dot{E}-\dot{E}^{LSW}}{|\langle \dot{E}^{LSW}\rangle|}$ in the preceding paper [6]. It turns out that the scaling of the deviation depends on a certain intrinsic length scale, the so-called screening length. The latter describes the effective range of particle interactions and reflects the analogous effect to the classical Debye-Hückel screening. In a system with particles of average radius $\langle R\rangle$ and typical neighrest-neighbor distance $\langle d\rangle$ the screening length ξ is determined by the capacity density of the particles via $\xi^2 = \frac{\langle d\rangle^3}{4\pi\langle R\rangle}$. For a finite system with N particles and consequently system size $\sim \langle d\rangle N^{1/3}$ this means that the system is much smaller than the screening length if $\langle d\rangle N^{1/3} \ll \xi$ or in other words if $N \ll \left(\frac{\langle d\rangle}{\langle R\rangle}\right)^{3/2} \sim \phi^{-1/2}$. We call such a system subcritical as opposed to super-critical systems which are characterized by $N \gg \phi^{-1/2}$. We have shown in [6] that with large probability

$$\frac{\dot{E} - \dot{E}^{LSW}}{|\langle \dot{E}^{LSW}|\rangle} \sim -\phi^{1/2}$$

if $N \gg \phi^{-1/2}$. (For the precise statement see Theorem 2.2 of [6].) For subcritical systems, that is if

$$\lim_{N\to\infty} N^2\phi(N) = 0\,, \tag{2.2}$$

the result of [6] (cf. Theorem 2.1) was only that with large probability

$$\frac{\dot{E} - \dot{E}^{LSW}}{|\langle \dot{E}^{LSW}\rangle|} \geq -C\frac{\phi^{1/3}}{N^{1/3}}.$$

The goal of the present paper is to show that the latter result is in some sense optimal. We completely characterize, for periodic boundary conditions, the distribution of $\frac{\dot{E}-\dot{E}^{LSW}}{|\dot{E}^{LSW}|}$. Our result implies in particular that for any $M > 0$ there is a positive probability that

$$\frac{N^{1/3}}{\phi^{1/3}}\frac{\dot{E} - \dot{E}^{LSW}}{|\langle \dot{E}^{LSW}\rangle|} \geq M > 0.$$

In addition we show that the sign of the expected value $\langle \dot{E} - \dot{E}^{LSW}\rangle$ depends on the geometry of the domain.

2.2 Setting

Periodic boundary conditions. We consider a fixed realization of uniformly distributed (in a sense specified below) particle centers $\{X_i\}$ in a unit-volume parallelepiped with periodic boundary conditions. The use of periodic boundary conditions requires to replace in (2.1) the Green's function for the Laplacian in the whole space $1/|X_i - X_j|$ with its periodic analogue, which we now define.

We fix three linearly independent vectors in $\mathbb{R}^3$, denoted by $\{e_1, e_2, e_3\}$, and assume that the unit cell they generate, $\Omega_{\mathcal{L}} = \{\sum x_i e_i : x \in (0,1)^3\}$, has unit volume, i.e. $|\Omega_{\mathcal{L}}| = e_1 \cdot e_2 \wedge e_3 = 1$. We shall denote by $\mathcal{L} = \{\sum z_i e_i : z \in \mathbb{Z}^3\}$ the lattice generated by $\{e_1, e_2, e_3\}$, and by $\mathcal{L}^*$ the reciprocal lattice, generated by the reciprocal vectors f_i, which are defined by the relation $e_i \cdot f_j = 2\pi\delta_{ij}$. To shorten notation we further define $\mathcal{L}^*_0 = \mathcal{L}^* \setminus \{0\}$.

The Green's function for the Laplacian on $\Omega_{\mathcal{L}}$ with periodic boundary conditions can be defined according to

$$G(x) := \lim_{\varepsilon \to 0} \sum_{k \in \mathcal{L}^*_0} \frac{4\pi}{|k|^2} e^{ik \cdot x} e^{-\varepsilon |k|^2} , \tag{2.3}$$

where the arbitrary additive constant has been fixed by requiring that the average of G over the unit cell must be zero. With periodic boundary conditions the problem (2.1) becomes

$$\frac{1}{R_i} = u_\infty + \frac{B_i}{R_i} + \sum_j g_{ij} B_j \, , \qquad \sum_i B_i = 0 \, ,$$

where $g_{ij} = G(X_i - X_j)$ for $i \neq j$, and

$$g_{ii} = G_0 := \lim_{x \to 0} G(x) - \frac{1}{|x|} \, . \tag{2.4}$$

(A finite system can be recovered replacing $g_{ij} = 1/|X_i - X_j|$ for $i \neq j$, and $g_{ii} = 0$.) Since $\sum B_i = 0$, adding a constant to g_{ij} does not change the solution of the equation (in particular, taking $g_{ii} = 0$ and $g_{ij} = G(X_i - X_j) - G_0$ would give an equivalent system which has a more direct correspondence to the non-periodic formulation in (2.1)). The present choice leads to some simplifications in the calculations that follow.

Scaling. We rescale the radii with respect to their typical size $(\phi/N)^{1/3}$, and scale time so that the evolution rates B_i become of order one. The monopole approximation reads, after rescaling,

$$\frac{1}{R_i} = u_\infty + \frac{B_i}{R_i} + \frac{\phi^{1/3}}{N^{1/3}} \sum_j g_{ij} B_j \,, \qquad \sum_i B_i = 0\,. \tag{2.5}$$

We still denote $E := \frac{1}{N}\sum_i R_i^2$, so that

$$\dot{E} = -\frac{1}{N}\sum_i \frac{B_i}{R_i} \qquad \text{and} \qquad \dot{E}^{LSW} = -\frac{1}{N}\sum_i \frac{B_i^{LSW}}{R_i}\,.$$

The ratio $(\dot{E} - \dot{E}^{LSW})/|\dot{E}^{LSW}|$ is unaffected by the scaling. After rescaling, $|\dot{E}^{LSW}| = O(1)$, so it suffices to consider in the following the quantity $\dot{E} - \dot{E}^{LSW}$.

Distribution of centers. We assume that the centers are uniformly distributed in the unit cell, in the sense that for any continuous function $f : \Omega_{\mathcal{L}} \to \mathbb{R}$ one has

$$\lim_{N\to\infty} \frac{1}{N} \sum_i f(X_i) = \int_{\Omega_{\mathcal{L}}} f(x)dx\,, \tag{2.6}$$

and that they are not too close, in the sense that

$$|X_i - X_j| \geq \frac{c_0}{N^{1/3}} \tag{2.7}$$

for some c_0 which does not depend on N. The condition (2.6) implies convergence for two point functions, i.e.

$$\lim_{N\to\infty} \frac{1}{N^2} \sum_{i,j} f(X_i, X_j) = \int_{\Omega_{\mathcal{L}}\times\Omega_{\mathcal{L}}} f(x,y)\,dxdy \tag{2.8}$$

for all continuous $f : \Omega_{\mathcal{L}} \times \Omega_{\mathcal{L}} \to \mathbb{R}$, and analogously for three-point ones. Further, (2.7) will permit us to apply those convergence results also to the Green's function G and to its square, provided the diagonal terms are truncated.

Distribution of radii. We assume that the (rescaled) radii $\{R_i\}$ are independently and identically distributed (i.i.d.) according to a bounded probability density ν with compact support contained in $[0, R_0]$ for some $R_0 > 0$.

Notation. With $\langle\cdot\rangle$ we denote the expected value with respect to the joint probability measure P of the random variables $\{R_i\}$. We also use the abbreviation $\langle R\rangle := \langle R_i\rangle, \langle R^2\rangle := \langle R_i^2\rangle$ etc.. We denote by C a generic constant, which is independent of N and ϕ, but may change from line to line.

2.3 Main results

Theorem 2.1. *Assume that the radii R_i are i.i.d. with $\max R_i \leq R_0$, the X_i are uniformly distributed in the unit cell of $\mathcal{L}$ in the sense of (2.6-2.7), and (2.2) is valid. Then*

$$\frac{N^{1/3}\langle R\rangle^2}{\phi^{1/3}}\left[\dot{E}-\dot{E}^{LSW}\right] \overset{N\gg 1}{\approx} \sigma_R^2\left[\sum_{k\in\mathcal{L}_0^*}\frac{4\pi}{|k|^2}\left((y^{(k)})^2-1\right)+G_0\right] \quad \textit{in law}$$

where $(y^{(k)})_{k\in\mathcal{L}^*}$ are Gaussian random variables with

$$\langle y^{(k)}\rangle = 0 \quad \textit{and} \quad \langle y^{(k)}y^{(l)}\rangle = \delta_{kl},$$

and $\sigma_R^2 = \langle R^2\rangle - \langle R\rangle^2$ is the variance of the distribution of radii.

By $Y_N \overset{N\gg 1}{\approx} Z_N$ in law we mean that for any bounded continuous function f one has

$$\lim_{N\to\infty}\langle f(Y_N)\rangle - \langle f(Z_N)\rangle = 0\,. \tag{2.9}$$

This is sometimes also called convergence in distribution as e.g. in [7]. We remark that Y_N and Z_N need not be defined on the same probability space, they only need to take values in the same space (the domain of f, in our case $\mathbb{R}$).

We also need to extend the convergence expressed in (2.9) to continuous functions f with quadratic growth at infinity. It is well-known that to establish (2.9) for those functions it is sufficient to show that $\langle e^{ikY_N}\rangle - \langle e^{ikZ_N}\rangle \to 0$ as $N\to\infty$ for any $k\in\mathbb{R}$ and that $\langle |Y_N|^p\rangle, \langle |Z_N|^p\rangle$ are uniformly bounded for some $p>2$. In the following it will usually be convenient to show a corresponding estimate for $p=4$.

We draw from this theorem two main consequences, concerning the influence of the geometry (of the lattice $\mathcal{L}$) and the presence of large fluctuations.

Corollary 2.2. *The average value of the leading-order correction*

$$\lim_{N\to\infty}\frac{N^{1/3}\langle R\rangle^2}{\phi^{1/3}}\langle\dot{E}-\dot{E}^{LSW}\rangle = G_0\sigma_R^2$$

depends on the geometry of the chosen lattice $\mathcal{L}$. In particular, the sign of G_0 can be both positive and negative, depending on $\mathcal{L}$.

Corollary 2.3. *For any $M > 0$ there is a finite probability $\rho_M > 0$ that the scaled deviation is larger than M, in the sense that*

$$\lim_{N\to\infty} P\left(\frac{N^{1/3}\langle R\rangle^2}{\phi^{1/3}}|\dot{E} - \dot{E}^{LSW}| \geq M\right) \geq \rho_M > 0\,.$$

The next three sections are devoted to the proof of these results: Theorem 2.1 will be proved in Section 3, Corollary 2.3 in Section 4, and Corollary 2.2 in Section 5.

3 The representation theorem

3.1 Identification of the leading order term

In Chapter 2 of [6] it was shown that the energy decay rate can be given a variational formulation, which in the present notation reads

$$\dot{E} - \dot{E}^{LSW} = \min_{\{\tilde{B}_i : \sum \tilde{B}_i = 0\}} \left\{ \frac{1}{N}\sum_i \frac{(\tilde{B}_i - B_i^{LSW})^2}{R_i} + \frac{\phi^{1/3}}{N^{4/3}}\sum_{i,j} g_{ij}\tilde{B}_i\,\tilde{B}_j \right\}\,.$$

Taking $\tilde{B}_i = B_i^{LSW}$ one immediately sees that

$$\dot{E} - \dot{E}^{LSW} \leq \frac{\phi^{1/3}}{N^{4/3}}\sum_{i,j} g_{ij}\,B_i^{LSW}\,B_j^{LSW}\,.$$

We now show that in the subcritical case, that is if (2.2) is satisfied, this bound is actually an equality to leading order (this can be heuristically understood considering the one-dimensional trivial case $\min_{x\in\mathbb{R}}(x-a)^2 - \varepsilon x^2 = -\varepsilon a^2 + O(\varepsilon^2)$).

Lemma 3.1. *Assume that the radii R_i are i.i.d. with $\max R_i \leq R_0$, the centers X_i satisfy (2.7), and (2.2) holds. Then, for any $\delta > 0$ there is $M > 0$ such that*

$$\lim_{N\to\infty} P\left(\left|\frac{N^{1/3}}{\phi^{1/3}}[\dot{E} - \dot{E}^{LSW}] - \frac{1}{N}\sum_{i,j} g_{ij}B_i^{LSW}B_j^{LSW}\right| \geq M\phi^{1/3}N^{2/3}\right) \leq \delta\,.$$

Proof. We view B and R as vectors in $\mathbb{R}^N$, equipped with the canonical scalar product $v \cdot w = \sum v_i w_i$, and rewrite the linear system (2.5) as

$$B + \varepsilon AB = \underline{\mathbf{1}} - \lambda R\,, \tag{3.1}$$

where $\underline{\mathbf{1}}$ is the vector with components $(\underline{\mathbf{1}})_i = 1$,

$$\varepsilon = \phi^{1/3} N^{2/3}\,, \qquad \text{and} \qquad (Av)_i = \frac{1}{N}\sum_j R_i g_{ij} v_j\,.$$

We further define the vector R^{-1} by $(R^{-1})_i = R_i^{-1}$ and the operator g by

$$(gv)_i = \frac{1}{N}\sum_j g_{ij} v_j\,.$$

The system (3.1) has the solution

$$B = (\mathrm{Id} + \varepsilon A)^{-1}(\underline{\mathbf{1}} - \lambda R) = (\mathrm{Id} + \varepsilon A)^{-1}\left(B^{LSW} - \mu R\right)\,, \tag{3.2}$$

provided that $\varepsilon|A| < 1$, where $B^{LSW} = \underline{\mathbf{1}} - R/\bar{R}$ is the LSW solution. Here $\mu = \lambda - 1/\bar{R}$, and both, μ and λ, are determined by requiring that $\underline{\mathbf{1}} \cdot B = \sum B_i = 0$.

We observe that $|A| \le R_0|g|$, and evaluate the latter. For any $v \in \mathbb{R}^N$,

$$\begin{aligned}
|gv|^2 &= \sum_i (gv)_i^2 = \frac{1}{N^2}\sum_{i,j,k} g_{ij} g_{ik} v_j\, v_k \\
&\le \left(\frac{1}{N}\max_{j',k'}\sum_i |g_{ij'}|\,|g_{ik'}|\right)\left(\frac{1}{N}\sum_{j,k}|v_j|\,|v_k|\right)\,. \\
&\le \left(\frac{1}{N}\max_j \sum_i g_{ij}^2\right)|v|^2\,.
\end{aligned} \tag{3.3}$$

To bound the sum over g_{ij}^2, we observe that the periodic Green's function G differs from the Coulomb interaction with the closest particle only by a term of order one, i.e.,

$$\left| G(X_i - X_j) - \frac{1}{\min\{|X_i - X_j - l| : l \in \mathcal{L}\}} \right| \le C\,.$$

(The constant C depends on the geometry of the lattice, but not on N). Due to (2.7) the effect of the Coulomb interaction can be estimated by the corresponding integral expression, as explained in the Appendix of [6]. We conclude that $|gv|^2 \leq C|v|^2$ and hence $|g| \leq C$ and $|A| \leq CR_0$, and for small ε the operator inverse in (3.2) is well defined.

The energy decay rate takes the form

$$\dot{E} - \dot{E}^{LSW} = -\frac{1}{N}\frac{1}{R} \cdot (B - B^{LSW}) = -\frac{1}{N}\left(\frac{1}{R} - \frac{1}{\bar{R}}\underline{\mathbf{1}}\right) \cdot (B - B^{LSW})$$

where we used that $\underline{\mathbf{1}} \cdot B = \underline{\mathbf{1}} \cdot B^{LSW} = 0$. Now we insert (3.2), multiply by N and separate the term linear in μ from the rest. We obtain

$$N(\dot{E} - \dot{E}^{LSW}) = T_1 + T_2\,,$$

where

$$\begin{aligned} T_1 &= \mu\left(\frac{1}{R} - \frac{1}{\bar{R}}\underline{\mathbf{1}}\right) \cdot \left((\mathrm{Id} + \varepsilon A)^{-1} R\right) \\ T_2 &= -\left(\frac{1}{R} - \frac{1}{\bar{R}}\underline{\mathbf{1}}\right) \cdot \left((\mathrm{Id} + \varepsilon A)^{-1} B^{LSW} - B^{LSW}\right)\,. \end{aligned}$$

In T_1 we expand $(\mathrm{Id} + \varepsilon A)^{-1} = \mathrm{Id} - \varepsilon A(\mathrm{Id} + \varepsilon A)^{-1}$. This amounts to rendering explicitly the leading-oder term of the Taylor expansion in powers of ε. Since $R^{-1} \cdot R = \underline{\mathbf{1}} \cdot R/\bar{R} = N$, the leading-order term cancels and

$$T_1 = -\mu\left(\frac{1}{R} - \frac{1}{\bar{R}}\underline{\mathbf{1}}\right) \cdot \varepsilon A(\mathrm{Id} + \varepsilon A)^{-1} R\,.$$

In T_2 we expand to second order $(\mathrm{Id} + \varepsilon A)^{-1} = \mathrm{Id} - \varepsilon A + \varepsilon A(\mathrm{Id} + \varepsilon A)^{-1}\varepsilon A$. Again, the first term cancels, and we obtain

$$T_2 = \Delta E_1 + T_3\,.$$

Here the first term is linear in ε and takes the form

$$\Delta E_1 = \left(\frac{1}{R} - \frac{1}{\bar{R}}\underline{\mathbf{1}}\right) \cdot \varepsilon A B^{LSW} = \varepsilon B^{LSW} \cdot g B^{LSW}\,,$$

i.e. it is the desired leading-order effect. The remainder is

$$T_3 = -\left(\frac{1}{R} - \frac{1}{\bar{R}}\underline{\mathbf{1}}\right) \cdot \varepsilon A(\mathrm{Id} + \varepsilon A)^{-1}\varepsilon A B^{LSW}\,.$$

We shall now show that the error terms T_1 and T_3 are, with a high probability, negligible. It is convenient to consider the vector

$$V = \bar{R} g B^{LSW} = \bar{R} A^T \left(\frac{1}{R} - \frac{1}{\bar{R}}\underline{\mathbf{1}}\right)\,,$$

and to observe that

$$|\bar{R}AB^{LSW}| \leq R_0|\bar{R}gB^{LSW}| = R_0|V|\,. \tag{3.4}$$

For simplicity we work in the following under the assumption

$$\bar{R} \geq \frac{1}{2}\langle R\rangle \qquad \text{and} \qquad |\varepsilon A| \leq \frac{1}{3}\,. \tag{3.5}$$

The latter implies $|(\mathrm{Id}+\varepsilon A)^{-1}| \leq 3/2$. We shall show later that (3.5) holds with probability close to one if ε is small and N is large.

We start with T_3, which can be written as

$$T_3 = -\frac{1}{\bar{R}}\varepsilon^2 V\cdot(\mathrm{Id}+\varepsilon A)^{-1}AB^{LSW}\,.$$

Therefore (3.5) implies $|T_3| \leq C\varepsilon^2|V|^2$ (here C can depend on $\langle R\rangle$ and R_0).

In order to estimate T_1 we need to determine the correction to the chemical potential μ. We start from (3.2), which gives

$$0 = \underline{\mathbf{1}}\cdot B = \underline{\mathbf{1}}\cdot(\mathrm{Id}+\varepsilon A)^{-1}\left(B^{LSW} - \mu R\right)\,.$$

We expand again to leading order $(\mathrm{Id}+\varepsilon A)^{-1} = \mathrm{Id} - (\mathrm{Id}+\varepsilon A)^{-1}\varepsilon A$. The term $\underline{\mathbf{1}}\cdot B^{LSW} = 0$ cancels. Solving for μ we obtain

$$\mu = -\frac{\underline{\mathbf{1}}\cdot(\mathrm{Id}+\varepsilon A)^{-1}\varepsilon AB^{LSW}}{\underline{\mathbf{1}}\cdot R - \underline{\mathbf{1}}\cdot(\mathrm{Id}+\varepsilon A)^{-1}\varepsilon AR}\,.$$

Since $|\underline{\mathbf{1}}| = N^{1/2}$ and $\underline{\mathbf{1}}\cdot R = N\bar{R}$, using (3.5) we can estimate the denominator by

$$\begin{aligned} |\underline{\mathbf{1}}\cdot R - \underline{\mathbf{1}}\cdot(\mathrm{Id}+\varepsilon A)^{-1}\varepsilon AR| &\geq N\bar{R} - |\underline{\mathbf{1}}|\frac{3}{2}|\varepsilon AR| \\ &\geq \frac{1}{2}N\langle R\rangle - \frac{3}{2}N|\varepsilon A|R_0\,. \end{aligned}$$

Hence if we add to (3.5) the condition

$$|\varepsilon A| \leq \frac{\langle R\rangle}{6R_0} \tag{3.6}$$

then the denominator in the expression for μ is larger than $\frac{1}{4}N\langle R\rangle$, and we can conclude

$$|\mu| \leq C\varepsilon\frac{|AB^{LSW}|}{N^{1/2}\langle R\rangle}\,. \tag{3.7}$$

We finally write T_1 as

$$T_1 = -\frac{1}{\bar{R}}\varepsilon\mu V \cdot \left((\mathrm{Id} + \varepsilon A)^{-1} R\right) .$$

Since $|R| \le N^{1/2} R_0$, using (3.5), (3.7) and (3.4) we obtain

$$|T_1| \le C\varepsilon|\mu||V|R_0 N^{1/2} \le C\varepsilon^2 |V|^2 \frac{R_0^2}{\langle R\rangle^2} .$$

It remains to estimate the norm of V, which in components reads

$$V_i = \frac{1}{N}\sum_j g_{ij}\bar{R}B_j^{LSW} = \frac{1}{N}\sum_j g_{ij}\left(\bar{R} - R_j\right) .$$

Since the R_i are i.i.d., $\langle R_j R_k\rangle = \langle R\rangle^2 + (\langle R^2\rangle - \langle R\rangle^2)\delta_{jk}$. An explicit computation shows that

$$\langle (R_j - \bar{R})(R_k - \bar{R})\rangle = \left(\langle R^2\rangle - \langle R\rangle^2\right)\left(\delta_{jk} - \frac{1}{N}\right) .$$

To see this it suffices to expand the square, and evaluate

$$\begin{aligned} \langle \bar{R}^2\rangle &= \frac{1}{N}\sum_h \langle R_h \bar{R}\rangle = \langle R_j \bar{R}\rangle = \frac{1}{N}\sum_h \langle\langle R_j R_h\rangle \\ &= \langle R\rangle^2 + \frac{1}{N}\left(\langle R^2\rangle - \langle R\rangle^2\right) . \end{aligned}$$

We obtain

$$\begin{aligned} \langle V^2\rangle &= \frac{1}{N^2}\sum_{ijk} g_{ij}g_{ik}\langle \left(R_j - \bar{R}\right)\left(R_k - \bar{R}\right)\rangle \\ &= \left(\langle R^2\rangle - \langle R\rangle^2\right)\left[\frac{1}{N^2}\sum_{ij} g_{ij}^2 - \frac{1}{N^3}\sum_{ijk} g_{ij}g_{ik}\right] \le C . \end{aligned}$$

The uniform bound on the square bracket follows from the same argument as in (3.3). We remark that the key ingredients in the estimate for $|V|$ are (i) that the vector $R_i - \bar{R}$ is well approximated for large N by $R_i - \langle R\rangle$, whose entries have average zero, and (ii) that the operator g averages over many points.

The norm $|V|$ is nonnegative, therefore for any N

$$P(|V| \ge M) \le \frac{C}{M} .$$

Consider finally (3.5) and (3.6). Recalling that $|A| \leq CR_0$, that $\varepsilon \to 0$ as $N \to \infty$, and observing that $\bar{R}$ is approximately normally distributed with variance proportional to $1/N$ since the R_i are i.i.d., we have

$$\lim_{N\to\infty} P\,(\text{All conditions in (3.5) and (3.6) hold}) = 1\,.$$

We conclude

$$\lim_{N\to\infty} P\left(|T_1| + |T_3| \geq \varepsilon^2 M^2\right) \leq \frac{C}{M}\,,$$

hence the thesis. □

In the following we derive a simpler expression for the leading correction term to $\dot{E} - \dot{E}^{LSW}$. We define

$$S = \frac{1}{N}\sum_{i,j} g_{ij}(R_i - \bar{R})(R_j - \bar{R})$$

so that Lemma 3.1 gives that with large probability

$$\dot{E} - \dot{E}^{LSW} = \frac{\phi^{1/3}}{N^{1/3}\bar{R}^2}S + O\left(\frac{\phi^{2/3}N^{1/3}}{\bar{R}^2}\right)$$

(recall that $B_i^{LSW} = 1 - R_i/\bar{R}$). Now we replace the variables R_i by

$$Y_i := R_i - \langle R\rangle\,,$$

which have zero expectation value. Since the Y_i are identically distributed with mean zero, their average (over i) will behave as $N^{-1/2}$ for large N. It is therefore natural to write

$$R_i - \bar{R} = Y_i - \frac{1}{N^{1/2}}\tilde{Y}\,, \qquad \text{where} \qquad \tilde{Y} = N^{1/2}(\bar{R} - \langle R\rangle) = \frac{1}{N^{1/2}}\sum_i Y_i\,.$$

We use this notation in the definition of S and write $S = S_1 + S_2 + S_3$, where

$$\begin{aligned}
S_1 &:= \frac{1}{N}\sum_{i,j} g_{ij}Y_iY_j,\\
S_2 &:= \left(\frac{1}{N^2}\sum_{l,k} g_{kl}\right)\left(\frac{1}{N^{1/2}}\sum_i Y_i\right)^2,\\
S_3 &:= -2\left(\frac{1}{N^{3/2}}\sum_i Y_i \sum_k g_{ik}\right)\left(\frac{1}{N^{1/2}}\sum_j Y_j\right).
\end{aligned}$$

We now show that for large N, and with high probability, only the first term is relevant. This is based on the fact that sums over the discrete Green's function g_{ij} converge to the corresponding integral expression, which by our normalization vanishes.

Lemma 3.2. *Under the same assumptions as in Theorem 2.1 we have for any $M > 0$ that*

$$\lim_{N\to\infty} P\left(|S_2| + |S_3| \geq M \right) = 0$$

and

$$\lim_{N\to\infty} P\left(\left| \frac{N^{1/3}\langle R\rangle^2}{\phi^{1/3}} \left[\dot{E} - \dot{E}^{LSW} \right] - S_1 \right| \geq M \right) = 0\,.$$

Proof. Consider first S_2. The second term is the square of $\tilde{Y}$, which is approximately normally distributed for large N. Therefore for any $\varepsilon > 0$ there is $K_\varepsilon > 0$ such that

$$\lim_{N\to\infty} P\left(\tilde{Y}^2 \geq K_\varepsilon \right) \leq \varepsilon\,.$$

The first term instead converges to zero as $N \to \infty$, by (2.6). Hence for sufficiently large N it is controlled by M/K_ε. This implies that

$$\lim_{N\to\infty} P\left(|S_2| \geq M \right) \leq \varepsilon$$

for any $\varepsilon > 0$, hence the result for S_2.

Now consider S_3. It suffices to show that $\langle S_3^2\rangle \to 0$. Expanding the product we get

$$\begin{aligned}
\langle S_3^2\rangle = \frac{4}{N^2} \Bigg\{ & 2\sum_{i,j} \left(\frac{1}{N} \sum_k g_{ik} \right) \left(\frac{1}{N} \sum_l g_{jl} \right) \langle Y^2\rangle^2 \\
& + \sum_i \left(\frac{1}{N} \sum_k g_{ik} \right)^2 \langle Y^4\rangle + N \sum_i \left(\frac{1}{N} \sum_k g_{ik} \right)^2 \langle Y^2\rangle^2 \Bigg\}\,.
\end{aligned}$$

Since by (2.6–2.8) all sums over the Green's function g converge to zero, and all expectation values of Y^2 are bounded, the right hand side of the previous equation converges to zero. This concludes the proof of the first claim.

To prove the second claim we start from Lemma 3.1, which after scaling and using (2.2) gives for any $M > 0$

$$\lim_{N\to\infty} P\left(\left| \alpha - \frac{1}{\bar{R}^2} S \right| \geq M \right) = 0\,, \qquad \text{where} \qquad \alpha = \frac{N^{1/3}}{\phi^{1/3}} \left[\dot{E} - \dot{E}^{LSW} \right]\,.$$

At the same time, since the $\{R_i\}$ are i.i.d., the central limit theorem gives

$$\lim_{N\to\infty} P(|\bar{R} - \langle R\rangle| \geq M) = 0$$

for any $M > 0$. We now write

$$\langle R\rangle^2\alpha - S_1 = \langle R\rangle^2 \left(\alpha - \frac{S}{\bar{R}^2}\right) + S_2 + S_3 + \frac{\langle R\rangle^2 - \bar{R}^2}{\bar{R}^2} S\,.$$

Each of the first three terms is almost surely bounded by $M/4$ in the limit, for any M. Consider now the last one. Fix a large $K > 0$. Then

$$\begin{aligned}
&P\left(\left|\frac{\langle R\rangle^2 - \bar{R}^2}{\bar{R}^2} S\right| \geq \frac{M}{4}\right) \\
&\leq P\left(|\langle R\rangle^2 - \bar{R}^2| \geq \frac{M}{4K}\right) + P\left(|\bar{R}| < \frac{1}{2}\langle R\rangle\right) + P\left(|S| \geq K\frac{\langle R\rangle^2}{4}\right)\,.
\end{aligned}$$

Taking the limit $N \to \infty$ the first two terms vanish. It remains to show that the last one can be made arbitrarily small by choosing K sufficiently large. To do so, we first show that

$$\begin{aligned}
\langle S_1^2\rangle &= \frac{1}{N^2}\sum_{i,j,k,l} g_{ij}g_{kl}\langle Y_iY_jY_kY_l\rangle \\
&= \left(\langle Y^2\rangle^2 + \frac{1}{N}\langle Y^4\rangle\right) G_0^2 + 2\langle Y^2\rangle^2 \frac{1}{N^2}\sum_{i,j} g_{ij}^2 \leq C
\end{aligned}$$

which implies

$$\lim_{K\to\infty} \limsup_{N\to\infty} P(|S_1| \geq K) = 0\,,$$

and hence the same for S. This concludes the proof. $\square$

3.2 Representation in Fourier space

We now show that by Fourier transformation the fluctuations in the error term are, for large N, characterized by the sum of independent terms.

Lemma 3.3. *In the limit $N \to \infty$, and under the same assumptions as in Theorem 2.1,*

$$\frac{1}{N}\sum_{i,j} g_{ij}Y_iY_j \overset{N\gg 1}{\approx} \sigma_R^2 \left[\sum_{k\in\mathcal{L}_0^*} \frac{4\pi}{k^2}\left((y^{(k)})^2 - 1\right) + G_0\right] \quad \textit{in law}$$

where $(y^{(k)})_{k\in\mathcal{L}^*}$ *are Gaussian random variables with*

$$\langle y^{(k)}\rangle = 0 \quad \textit{and} \quad \langle y^{(k)}y^{(l)}\rangle = \delta_{kl},$$

and $\sigma_R^2 = \langle Y^2\rangle = \langle R^2\rangle - \langle R\rangle^2$ *is the variance of the distribution of radii.*

Proof. By scaling we can assume without loss of generality that $\langle Y^2\rangle = \sigma_R^2 = 1$. We introduce the new variables $y_N^{(k)}$, for k in the reciprocal lattice $\mathcal{L}^*$, as the Fourier coefficients of the distribution

$$\frac{1}{\sqrt{N}}\sum_n Y_n \delta_{X_n}$$

(in the following proof we shall not use the index i to avoid confusion with the imaginary unit). In order to keep all quantities real, it is more convenient to adopt the basis functions

$$e^{(k)}(x) = \cos(x\cdot k) + \sin(x\cdot k) = \Re(1-i)e^{ik\cdot x}\,,$$

which constitute a complete orthonormal system in $L^2(\Omega)$. Precisely, we set

$$y_N^{(k)} = \frac{1}{\sqrt{N}}\sum_n Y_n e^{(k)}(X_n)\,.$$

We need to show that the $y_N^{(k)}$ can be replaced by the uniformly distributed variables $y^{(k)}$. We first show, by mimicking the proof of the central limit theorem, that any bounded subset of the $y_N^{(k)}$ (in particular, those with $|k| < M$ for any M) converge to normally distributed variables. Then we show that the large wavenumbers give a negligible contribution, for large M. The $k = 0$ case needs a separate treatment, due to the divergence of the Green's function at small separations.

We start by establishing that the fourth moments of $y_N^{(k)}$ are uniformly bounded in k and N. Indeed, we have

$$\begin{aligned}\langle (y_N^{(k)})^4\rangle &= \frac{1}{N^2}\sum_n \left(e^{(k)}(X_n)\right)^4 \langle Y^4\rangle \\ &\quad + \frac{3}{N^2}\sum_n\sum_{m\neq n}\left(e^{(k)}(X_n)\right)^2\left(e^{(k)}(X_m)\right)^2\langle Y^2\rangle^2 \\ &\leq \frac{1}{N^2}N2^4\langle Y^4\rangle + \frac{3}{N^2}N^2 2^4\langle Y^2\rangle^2 \leq C\,. \end{aligned} \tag{3.8}$$

We now claim that for any number $M < \infty$

$$(y_N^{(k)})_{\substack{k\in\mathcal{L}^*\\|k|<M}} \overset{N\gg 1}{\approx} (y^{(k)})_{\substack{k\in\mathcal{L}^*\\|k|<M}} \quad \text{in law.} \tag{3.9}$$

Thanks to the bound (3.8), to prove the claim (3.9) it suffices to show that for any finite dimensional vector $(\zeta^{(k)})_{\substack{k\in\mathcal{L}^*\\|k|<M}}$ with $\zeta^{(k)} \in \mathbb{R}$ one has

$$\lim_{N\to\infty} \langle \exp\left(-i \sum_{\substack{k\in\mathcal{L}^*\\|k|<M}} \zeta^{(k)} y_N^{(k)} \right) \rangle = \exp\left(-\frac{1}{2} \sum_{\substack{k\in\mathcal{L}^*\\|k|<M}} (\zeta^{(k)})^2 \right). \tag{3.10}$$

Since $|Y_n| \le R_0$, $\langle Y_n \rangle = 0$, and $\langle Y_n^2 \rangle = 1$, for any $\xi \in \mathbb{R}$ we have

$$\left| \langle \exp(-i\xi Y_n) \rangle - \left(1 - \frac{1}{2}\xi^2\right) \right| \le C|\xi|^3$$

which we use in the form

$$\left| \ln\langle \exp(-i\xi Y_n) \rangle + \frac{1}{2}\xi^2 \right| \le C|\xi|^3 . \tag{3.11}$$

We set $\zeta^{(k)} := 0$ for $|k| \ge M$, and define the smooth function

$$\zeta(x) := \sum_{k\in\mathcal{L}^*} \zeta^{(k)} e^{(k)}(x) .$$

A straightforward computation shows that

$$\frac{1}{\sqrt{N}} \sum_n \zeta(X_n) Y_n = \frac{1}{\sqrt{N}} \sum_n \sum_{k\in\mathcal{L}^*} \zeta^{(k)} e^{(k)}(X_n) Y_n = \sum_{k\in\mathcal{L}^*} \zeta^{(k)} y_N^{(k)} .$$

From the independence of the Y_n's we obtain

$$\langle \exp(-i \sum_{k\in\mathcal{L}^*} \zeta^{(k)} y_N^{(k)}) \rangle = \prod_n \langle \exp(-i \frac{1}{\sqrt{N}} \zeta(X_n) Y_n) \rangle$$

which we write as

$$\ln \langle \exp(-i \sum_{k\in\mathcal{L}^*} \zeta^{(k)} y_N^{(k)}) \rangle = \sum_n \ln \langle \exp(-i \frac{1}{\sqrt{N}} \zeta(X_n) Y_n) \rangle. \tag{3.12}$$

On the other hand, we have for the right-hand side of (3.10)

$$\ln \exp(-\frac{1}{2}\sum_k (\zeta^{(k)})^2) = -\frac{1}{2}\sum_k (\zeta^{(k)})^2 = -\frac{1}{2}\int_{\Omega_{\mathcal{L}}} \zeta(x)^2 dx. \tag{3.13}$$

Hence, it follows from (3.11), (3.12), and (3.13):

$$\begin{aligned}
&\left| \ln \langle \exp(-i\sum_k \zeta^{(k)} y_N^{(k)})\rangle - \ln \exp(-\frac{1}{2}\sum_k (\zeta^{(k)})^2) \right| \\
&= \left| \sum_n \ln \langle \exp(-i\frac{1}{\sqrt{N}}\zeta(X_n)Y_n)\rangle + \frac{1}{2}\int_{\Omega_{\mathcal{L}}} \zeta(x)^2 dx \right| \\
&\le \sum_n \left| \ln \langle \exp(-i\frac{1}{\sqrt{N}}\zeta(X_n)Y_n)\,\rangle + \frac{1}{2}\frac{1}{N}\zeta(X_n)^2 \right| \\
&\quad + \frac{1}{2}\left| \frac{1}{N}\sum_n \zeta(X_n)^2 - \int_{\Omega_{\mathcal{L}}} \zeta(x)^2 dx \right| \\
&\le C\frac{1}{N^{3/2}}\sum_n \zeta(X_n)^3 + \left| \frac{1}{N}\sum_n \zeta(X_n)^2 - \int_{\Omega_{\mathcal{L}}} \zeta(x)^2 dx \right|.
\end{aligned}$$

The first term converges to zero as $N \to \infty$ since it is bounded by $CN^{-1/2} \max |\zeta|$, the second one by the uniform distribution of the centers (see (2.6)). This concludes the proof of (3.10), and hence of (3.12). In turn, (3.12) implies in particular that

$$\sum_{\substack{k\in\mathcal{L}_0^* \\ |k|<M}} \hat{G}^{(k)} \left(y_N^{(k)}\right)^2 \overset{N\gg 1}{\approx} \sum_{\substack{k\in\mathcal{L}_0^* \\ |k|<M}} \hat{G}^{(k)} \left(y^{(k)}\right)^2 \qquad \text{in law,}$$

where $\hat{G}^{(k)} = 4\pi/|k|^2$ represent the Fourier coefficients of G.

To conclude the proof we consider for any $M < \infty$ the term

$$T := \frac{1}{N}\sum_{n,m} g_{nm} Y_n Y_m - \left\{ \sum_{\substack{k\in\mathcal{L}^* \\ k\neq 0, |k|<M}} \hat{G}^{(k)} \left((y_N^{(k)})^2 - 1 \right) + G_0 \right\}. \tag{3.14}$$

We claim

$$\lim_{M\to\infty} \lim_{N\to\infty} \langle T^2 \rangle = 0. \tag{3.15}$$

Fix a large number $\xi \gg 1$, and consider the screened potential defined, in reciprocal space, by

$$\hat{H}_\xi^{(k)} := \frac{4\pi}{|k|^2 + \xi^2}$$

and the corresponding real-space version, defined in analogy to (2.3) by

$$H_\xi(x) := \sum_{k \in \mathcal{L}_0^*} \hat{H}_\xi^{(k)} e^{ik \cdot x}\,.$$

The potential H_ξ is constructed in order to remove the divergence of G in the origin. Precisely, since

$$(\hat{G} - \hat{H}_\xi)^{(k)} = \frac{4\pi\xi^2}{|k|^2(|k|^2 + \xi^2)} \tag{3.16}$$

decays as $|k|^{-4}$ for large $|k|$, in real space the difference $G - H_\xi$ is continuous. We split the first term in (3.14) as follows

$$\begin{aligned} \frac{1}{N}\sum_{n,m} g_{nm} Y_n Y_m &= \frac{1}{N}\sum_{n,m}(G - H_\xi)(X_n - X_m) Y_n Y_m \\ &+ \frac{1}{N}\sum_n \sum_{m \neq n} H_\xi(X_n - X_m) Y_n Y_m \\ &+ (G_0 - (G - H_\xi)(0)) \frac{1}{N}\sum_n Y_n^2\,. \end{aligned} \tag{3.17}$$

(recall that $g_{nn} = G_0$, and $g_{nm} = G(X_n - X_m)$ for $n \neq m$). Since the first term in (3.17) is continuous we use its Fourier series representation,

$$\frac{1}{N}\sum_{n,m}(G - H_\xi)(X_n - X_m) Y_n Y_m = \sum_{k \in \mathcal{L}_0^*} (\hat{G} - \hat{H}_\xi)^{(k)} \left(y_N^{(k)}\right)^2$$

(to prove this it is sufficient to insert in the right-hand side the definition of the $y_N^{(k)}$, and to use that $\hat{G}$ and $\hat{H}_\xi$ are even in k). By setting $x = 0$ in the definition of G and H_ξ we immediately get

$$\sum_{k \in \mathcal{L}_0^*} (\hat{G} - \hat{H}_\xi)^{(k)} = (G - H_\xi)(0).$$

These relations permit to rewrite (3.17) in the form

$$\begin{aligned}\frac{1}{N}\sum_{n,m} g_{nm} Y_n Y_m &= \sum_{k\in\mathcal{L}_0^*} (\hat{G}-\hat{H}_\xi)^{(k)} \left((y_N^{(k)})^2 - 1\right) \\ &+ \frac{1}{N}\sum_n \sum_{m\neq n} H_\xi(X_n - X_m) Y_n Y_m \\ &+ (G-H_\xi)(0)\left(1 - \frac{1}{N}\sum_n Y_n^2\right) + G_0 \frac{1}{N}\sum_n Y_n^2 .\end{aligned}$$

Thus we obtain the following representation for T:

$$\begin{aligned} T &= \sum_{\substack{k\in\mathcal{L}^* \\ |k|\geq M}} (\hat{G}-\hat{H}_\xi)^{(k)} \left((y_N^{(k)})^2 - 1\right) \\ &\quad - \sum_{\substack{k\in\mathcal{L}_0^* \\ |k|< M}} \hat{H}_\xi^{(k)} \left((y_N^{(k)})^2 - 1\right) \\ &\quad + [(G-H_\xi)(0) - G_0]\left(1 - \frac{1}{N}\sum_n Y_n^2\right) \\ &\quad + \frac{1}{N}\sum_n \sum_{m\neq n} H_\xi(X_n - X_m) Y_n Y_m \\ &= T_1 + T_2 + T_3 + T_4. \end{aligned}$$

We will establish (3.15) by showing

$$\lim_{M\to\infty} \limsup_{\xi\to\infty} \limsup_{N\to\infty} \langle T_i^2 \rangle = 0 \quad \text{for } i = 1,2,3,4 . \tag{3.18}$$

We start with T_1 and calculate:

$$\langle T_1^2 \rangle = \sum_{\substack{k\in\mathcal{L}^* \\ |k|\geq M}} \sum_{\substack{l\in\mathcal{L}^* \\ |l|\geq M}} (\hat{G}-\hat{H}_\xi)^{(k)} (\hat{G}-\hat{H}_\xi)^{(l)} \langle \left((y_N^{(k)})^2 - 1\right)\left((y_N^{(l)})^2 - 1\right)\rangle .$$

We now apply the dominated convergence theorem to this sum. First, according to (3.8) we have

$$\langle \left((y_N^{(k)})^2 - 1\right)\left((y_N^{(l)})^2 - 1\right)\rangle \leq C.$$

Hence the integrand is controlled by $(\hat{G}-\hat{H}_\xi)^{(k)} (\hat{G}-\hat{H}_\xi)^{(l)}$, which has a finite sum (see (3.16)). Therefore we can take the pointwise limit. By (3.9) we have for any $k, l \in \mathcal{L}^*$,

$$\lim_{N\to\infty} \langle \Big((y_N^{(k)})^2 - 1 \Big) \Big((y_N^{(l)})^2 - 1 \Big) \rangle = \begin{cases} \langle (y^2-1)^2 \rangle & \text{if } k = l \\ 0 & \text{if } k \neq l. \end{cases}$$

We conclude that

$$\lim_{N\to\infty} \langle T_1^2 \rangle \le C \sum_{\substack{k\in\mathcal{L}^* \\ |k|\ge M}} \Big((\hat{G} - \hat{H}_\xi)^{(k)} \Big)^2 \le C \sum_{\substack{k\in\mathcal{L}^* \\ |k|\ge M}} \frac{1}{|k|^4} \le \frac{C}{M} ,$$

which implies (3.18) for $i = 1$.

The term T_2 is treated analogously. In this case summability follows from the fact that the sum is over $|k| \le M$ and $|\hat{H}_\xi| \le C/\xi^2$. We obtain

$$\lim_{N\to\infty} \langle T_2^2 \rangle \le C \sum_{\substack{k\in\mathcal{L}_0^* \\ |k|<M}} \Big(\hat{H}_\xi^{(k)} \Big)^2 \le C \frac{M^3}{\xi^4} ,$$

which implies that, for any M,

$$\lim_{\xi\to\infty} \lim_{N\to\infty} \langle T_2^2 \rangle = 0 .$$

We now address T_3. A straightforward expansion gives

$$\begin{aligned} \langle \big(1 - \frac{1}{N}\sum_n Y_n^2\big)^2 \rangle &= 1 - \frac{2}{N}\sum_n \langle Y_n^2 \rangle + \frac{1}{N^2}\sum_n \sum_{m\neq n} \langle Y_n^2 \rangle \langle Y_m^2 \rangle + \frac{1}{N^2}\sum_n \langle Y_n^4 \rangle \\ &= \frac{1}{N}(\langle Y^4 \rangle - 1) \\ &\le \frac{C}{N} . \end{aligned}$$

Therefore

$$\langle T_3^2 \rangle = [(G - H_\xi)(0) - G_0]^2 \, \langle \big(1 - \frac{1}{N}\sum_n Y_n^2\big)^2 \rangle \le \frac{C}{N}$$

and thus

$$\lim_{N\to\infty} \langle T_3^2 \rangle = 0 .$$

We finally treat T_4. Since the Y_n are independent, and H_ξ is even,

$$\begin{aligned}
\langle T_4^2 \rangle &= \frac{1}{N^2}\sum_n \sum_{m\neq n} H_\xi(X_n - X_m) \sum_p \sum_{q\neq p} H_\xi(X_p - X_q)\, \langle Y_n Y_m Y_p Y_q \rangle \\
&= \frac{1}{N^2}\sum_n \sum_{m\neq n} H_\xi(X_n - X_m) H_\xi(X_n - X_m)\, \langle Y^2 \rangle^2 \\
&\quad + \frac{1}{N^2}\sum_n \sum_{m\neq n} H_\xi(X_n - X_m) H_\xi(-(X_n - X_m))\, \langle Y^2 \rangle^2 \\
&= \frac{2}{N^2}\sum_n \sum_{m\neq n} H_\xi^2(X_n - X_m).
\end{aligned}$$

We thus obtain from (2.8), and using periodicity of H_ξ,

$$\lim_{N\to\infty} \langle T_4^2 \rangle = 2\int_{\Omega_\mathcal{L}\times\Omega_\mathcal{L}} H_\xi^2(x-y)\, dx\, dy = 2\int_{\Omega_\mathcal{L}} H_\xi^2(x) dx = 2\sum_{k\in\mathcal{L}_0^*} (\hat{H}_\xi^{(k)})^2 \, .$$

The last sum is again estimated by the corresponding integral expression,

$$\sum_{k\in\mathcal{L}_0^*} (\hat{H}_\xi^{(k)})^2 \leq C \int_{\mathbb{R}^3} \frac{1}{(k^2+\xi^2)^2} dk \leq \frac{C}{\xi} \, .$$

This implies $\lim_{\xi\to\infty}\lim_{N\to\infty}\langle T_4^2\rangle = 0$, and concludes the proof of (3.18).

To conclude the proof of the lemma it remains to show that

$$F = \sum_{\substack{k\in\mathcal{L}^* \\ |k|\geq M}} G^{(k)} \left((y^{(k)})^2 - 1 \right)$$

satisfies

$$\lim_{M\to\infty} \langle F^2 \rangle = 0,$$

which is argued similarly to the case of T_1. □

Proof of Theorem 2.1. Theorem 2.1 follows from the combination of Lemma 3.2 and Lemma 3.3. □

4 Implications: positive long tail

Theorem 2.1 allows a simple analysis of the fluctuation properties of the energy decay rate. We now show that in the limit $N \to \infty$ large fluctuations have a nonvanishing probability.

First we prove the following lemma.

Lemma 4.1. *Consider the random variable*

$$Z_K = \pi K^{1/2} \sum_{\substack{k \in \mathcal{L}^* \\ |k|>K}} \frac{1}{|k|^2} \Big((y^{(k)})^2 - 1 \Big) \,,$$

with $\{y_k\}_{k \in \mathcal{L}^*}$ *independent and normally distributed. Then we have*

$$Z_K \overset{K\to\infty}{\longrightarrow} \text{ normalized Gaussian} \qquad \text{in law.}$$

Proof. It is sufficient to show that for any $\xi \in \mathbb{R}$

$$\lim_{K\to\infty} \ln\langle e^{i\xi Z_K} \rangle = -\frac{1}{2}\xi^2 \,, \tag{4.1}$$

and that the fourth moment of Z_K is uniformly bounded.

We start by proving (4.1). By the independence of the $y^{(k)}$ we get

$$\ln\langle e^{i\xi Z_K} \rangle = \sum_{|k|>K} \ln\langle e^{i\xi_k((y^{(k)})^2-1)} \rangle \,, \qquad \text{where} \qquad \xi_k = \frac{\pi K^{1/2}}{|k|^2}\xi \,.$$

The expectation value can be determined explicitly according to

$$\langle e^{i\xi (y^{(k)})^2} \rangle = \frac{1}{(2\pi)^{1/2}} \int_{\mathbb{R}} e^{-\frac{1}{2}(1-2i\xi)y^2} dy = \frac{1}{(1-2i\xi)^{1/2}}$$

(to see this, it is sufficient to integrate along the line $y' = (1-2i\xi)^{1/2}y$ in the complex plane). Inserting this expression, and expanding the result for small ξ_k, we obtain

$$\begin{aligned}
\ln\langle e^{i\xi Z_k} \rangle &= \sum_{|k|>K} \ln \frac{e^{-i\xi_k}}{(1-2i\xi_k)^{1/2}} \\
&= \sum_{|k|>K} -\xi_k^2 + R_k \\
&= -\xi^2 \sum_{|k|>K} \frac{\pi^2 K}{|k|^4} + \sum_{|k|>K} R_k
\end{aligned}$$

where the remainder R_k satisfies $|R_k| \leq 2|\xi_k|^3$, and therefore

$$\left| \sum_{|k|>K} R_k \right| \leq C\xi^3 \int_K^\infty \frac{K^{3/2}}{r^6} r^2 dr \leq C \frac{\xi^3}{K^{3/2}} \,.$$

To estimate the first term, we observe that

$$\lim_{K\to\infty} \sum_{\substack{k\in\mathcal{L}^*\\ |k|>K}} \frac{\pi^2 K}{|k|^4} = \frac{1}{2}\,.$$

(the unit cell of $\mathcal{L}^*$ has volume $(2\pi)^3$, hence the sum is $(2\pi)^{-3}$ times a Riemann sum for the corresponding integral). The limit (4.1) follows.

To conclude the proof of the lemma we only need to show that the fourth moment of Z_K is uniformly bounded. To see this, we evaluate

$$\langle Z_K^4\rangle \le CK^2\left(\sum_{|k|\ge K}\frac{\langle\big((y^{(k)})^2-1\big)^2\rangle}{|k|^4}\right)^2 + K^2\sum_{|k|\ge K}\frac{\langle\big((y^{(k)})^2-1\big)^4\rangle}{|k|^8} \le C\,.$$

This concludes the proof. □

Proof of Corollary 2.3. Consider the term

$$Z := \sum_{k\in\mathcal{L}_0^*}\frac{1}{|k|^2}\,z_k$$

where

$$z_k := \frac{1}{\sqrt{2}}\Big((y^{(k)})^2-1\Big) \quad \text{for } k\in\mathcal{L}^*\,.$$

The following proof of the large-deviation result of Corollary 2.3 is based on the fact that the contributions at small k to sum forming Z have large deviations (much as each single normally-distributed random variable has), and the fact that, being independent, the contributions at large k do not average this out. More precisely, by Lemma 4.1 the large-k contribution to the sum is approximately normally distributed, hence it is nonnegative with probability approximately 1/2.

To make this argument precise, we separate the two contributions

$$Z := \sum_{\substack{k\in\mathcal{L}_0^*\\ |k|\le K}}\frac{1}{|k|^2}\,z_k + \sum_{\substack{k\in\mathcal{L}^*\\ |k|>K}}\frac{1}{|k|^2}\,z_k.$$

(here K is a fixed number to be chosen below). According to Lemma 4.1 the second term converges, as $K\to\infty$, to a scaled Gaussian with zero average.

Hence for sufficient large K it is nonnegative with probability at least $1/4$. Further, for sufficiently large K one has

$$\frac{(2\pi)^3}{4\pi K}\sum_{\substack{k\in\mathcal{L}_0^*\\|k|\le K}}\frac{1}{|k|^2}\ge\frac{1}{2}$$

(the choice of K does not depend on M). We compute

$$\begin{aligned}P\Big(\sum_{\substack{k\in\mathcal{L}_0^*\\|k|\le K}}\frac{1}{|k|^2}z_k\ge M\Big) &\ge P\Big(\sum_{\substack{k\in\mathcal{L}_0^*\\|k|\le K}}\frac{1}{|k|^2}z_k\ge\frac{2(2\pi)^3}{4\pi K}M\sum_{\substack{k\in\mathcal{L}^*\\|k|\le K,\,k\neq 0}}\frac{1}{|k|^2}\Big)\\ &\ge\prod_{\substack{k\in\mathcal{L}_0^*\\|k|\le K}}P\left(z_k\ge\frac{4\pi^2M}{K}\right).\end{aligned}$$

This is the product of a fixed number of terms, which are all identical and nonnegative. Therefore the latter expression is positive for any M. Combining with the previous estimate, we conclude that for every M there is a number ρ_M such that

$$P(Z\ge M)\ge\rho_M\,.$$

which is the thesis. □

5 Implications: dependence on geometry

We focus here on some properties of the constant G_0 defined in (2.4), which characterizes the average value of the fluctuation. The sum (2.3) defining G does not converge absolutely for $\varepsilon = 0$. In order to evaluate it it is convenient to separate the long-range and the short-range parts, a method usually called Ewald decomposition. There are many ways to do that, the simplest being to use a Gaussian weight function. More precisely, we fix some $\alpha > 0$ and write $G = G_{\mathrm{SR}} + G_{\mathrm{LR}}$, where

$$G_{\mathrm{LR}}(x)=\sum_{k\in\mathcal{L}_0^*}\frac{4\pi e^{-\alpha|k|^2}}{|k|^2}e^{ik\cdot x}$$

and

$$G_{\mathrm{SR}}(x)=\lim_{\varepsilon\to 0}\sum_{k\in\mathcal{L}_0^*}\hat\phi_\varepsilon(k)e^{ik\cdot x}\,,\qquad \hat\phi_\varepsilon(k)=4\pi\frac{1-e^{-\alpha|k|^2}}{|k|^2}e^{-\varepsilon|k|^2}\qquad(5.1)$$

(we denote by "long range" the contributions which are long range in real space, hence short range in reciprocal space). The sum defining $G_{\rm LR}$ converges fast. The sum defining $G_{\rm SR}$ does not converge absolutely for $\varepsilon = 0$, but the kernel $\hat{\phi}_\varepsilon$, seen as a function defined on $\mathbb{R}^3$, is smooth around the origin and indeed its Fourier transform decays rapidly.

Lemma 5.1. *The definition (5.1) is equivalent to*

$$G_{\rm SR}(x) = \sum_{y\in\mathcal{L}} \frac{1}{|x+y|}\,\mathrm{erfc}\left(\frac{|x+y|}{2\alpha^{1/2}}\right) - 4\pi\alpha\,.$$

Here $\mathrm{erfc}(x) = 1 - \mathrm{erf}(x)$, where $\mathrm{erf} : \mathbb{R} \to \mathbb{R}$ is the error function

$$\mathrm{erf}(x) = \frac{2}{\pi^{1/2}}\int_0^x e^{-t^2}\,dt\,.$$

Remark 5.2. *Taking the limit $|x| \to 0$ of the previous expression gives*

$$\lim_{x\to 0} G_{\rm SR}(x) - \frac{1}{|x|} = \sum_{y\in\mathcal{L}\setminus\{0\}} \frac{1}{|y|}\,\mathrm{erfc}\left(\frac{|y|}{2\alpha^{1/2}}\right) - 4\pi\alpha - \frac{1}{(\alpha\pi)^{1/2}}\,. \tag{5.2}$$

Proof. We start from the Fourier transform

$$\phi_\varepsilon(x) = \frac{1}{(2\pi)^3}\int_{\mathbb{R}^3} e^{ik\cdot x}\hat{\phi}_\varepsilon(k)dk$$

of $\hat{\phi}_\varepsilon$ (for an analytic expression, see below) and its lattice sum,

$$\Phi_\varepsilon(x) = \sum_{y\in\mathcal{L}} \phi_\varepsilon(x+y)\,.$$

Convergence of the series will follow from the explicit computations below. The function Φ_ε is $\mathcal{L}$-periodic, and in $L^2(\Omega_\mathcal{L})$. Its Fourier series is given by $\hat{\phi}_\varepsilon(k)$: indeed, for $k \in \mathcal{L}^*$ we get

$$\int_{\Omega_\mathcal{L}} \Phi_\varepsilon(x)e^{-ik\cdot x}dx = \int_{\mathbb{R}^3} \phi_\varepsilon(x)e^{-ik\cdot x}dx = \hat{\phi}_\varepsilon(k)\,.$$

By the inversion theorem for Fourier series we get

$$\sum_{k\in\mathcal{L}^*} \hat{\phi}_\varepsilon(k)e^{ik\cdot x} = \Phi_\varepsilon(x)$$

where the sum also includes the $k=0$ point, where $\hat{\phi}_\varepsilon(0)=4\pi\alpha$. Comparing with the definition (5.1) we get

$$G_{\mathrm{SR}}(x)=\lim_{\varepsilon\to 0}\Phi_\varepsilon(x)-\hat{\phi}_\varepsilon(0)=\lim_{\varepsilon\to 0}\sum_{y\in\mathcal{L}}\phi_\varepsilon(x+y)-4\pi\alpha\,.$$

We now have

$$\begin{aligned}\phi_\varepsilon(x)&=\frac{4\pi}{(2\pi)^3}\int_{\mathbb{R}^3}e^{ik\cdot x}e^{-\varepsilon|k|^2}\frac{1-e^{-\alpha|k|^2}}{|k|^2}\,dk\\&=\frac{2}{\pi}\int_0^\infty\frac{\sin(r|x|)}{r|x|}\left(1-e^{-\alpha r^2}\right)e^{-\varepsilon r^2}\,dr\,,\end{aligned}$$

which can be computed explicitly, e.g. by using Fourier transform and the integration rule:

$$\begin{aligned}\phi_\varepsilon(x)&=\frac{1}{|x|}\Big(\operatorname{erf}\frac{|x|}{2\varepsilon^{1/2}}-\operatorname{erf}\frac{|x|}{2(\alpha+\varepsilon)^{1/2}}\Big)\\&=\frac{1}{|x|}\frac{2}{\sqrt{\pi}}\int_{\frac{|x|}{2(\alpha+\varepsilon)^{1/2}}}^{\frac{|x|}{2\varepsilon^{1/2}}}e^{-t^2}\,dt\\&=\frac{1}{|x|}\Big(1-\operatorname{erf}\frac{|x|}{2\alpha^{1/2}}\Big)+O(\varepsilon).\end{aligned}$$

The resulting function converges exponentially to zero for large x. In the $|x|\to 0$ limit we instead get $\phi_0(x)\simeq|x|^{-1}-(\alpha\pi)^{-1/2}$. □

We have written the Green's function entirely in terms of fast-converging lattice sums. Before computing the first few terms explicitly, we show how the remainder can be estimated quantitatively. Since we shall need to apply the following estimate to both $\mathcal{L}$ and $\mathcal{L}^*$, whose unit cell does not have unit volume, we formulate it for a general lattice, without normalization.

Lemma 5.3. *Let $g:(0,\infty)\to(0,\infty)$ be a nonincreasing function, $a\in\mathbb{R}^3$, and $\mathcal{L}$ a lattice on $\mathbb{R}^3$ with unit cell Ω. Then,*

$$\sum_{x\in\mathcal{L}+a,\ |x|\geq s}g(|x|)\leq\frac{4\pi}{|\Omega|}\int_{s-\operatorname{diam}\Omega}^\infty\left(t+\frac{1}{2}\operatorname{diam}\Omega\right)^2g(t)dt\,.$$

Remark 5.4. *As a special case, if $\mathcal{L}=l\mathbb{Z}^3$ is a cubic lattice and $s=3l$,*

$$\begin{aligned}\sum_{x\in\mathcal{L}+a,\ |x|\geq 3l}g(|x|)&\leq\frac{4\pi}{l^3}\int_{(3-\sqrt{3})l}^\infty\left(t+\frac{\sqrt{3}}{2}l\right)^2g(t)dt\\&\leq\frac{12\pi}{l^3}\int_{(3-\sqrt{3})l}^\infty t^2g(t)dt\,.\end{aligned}\tag{5.3}$$

Proof. Let $\Omega(x)$ be the translation of the unit cell Ω which is centered in x, and extend g to negative arguments so that it remains monotone, e.g. by setting it equal to $g(0)$. By monotonicity for any x

$$g(|x|) \leq \frac{1}{|\Omega|} \int_{\Omega(x)} g\left(|y| - \frac{1}{2}\operatorname{diam}\Omega\right) dy\,.$$

Summing over the lattice we get

$$\sum_{x\in\mathcal{L}+a,\ |x|\geq s} g(|x|) \leq \frac{1}{|\Omega|} \int_{|y|\geq s-\frac{1}{2}\operatorname{diam}\Omega} g\left(|y| - \frac{1}{2}\operatorname{diam}\Omega\right) dy\,.$$

Going to spherical coordinates, and changing variables in the radial direction from $|y|$ to $t = |y| - \operatorname{diam}\Omega/2$, this becomes the thesis. $\square$

Lemma 5.5. *For a cubic lattice $G(x) \geq G_0$ everywhere, hence $G_0 < 0$.*

Proof. We first compute a bound on G_{LR}, using that $\mathcal{L} = \mathbb{Z}^3$ and $\mathcal{L}^* = 2\pi\mathbb{Z}^3$. The part of the sum with $|k| \geq 3\cdot 2\pi$ is controlled using (5.3). The 6 terms with $|k| = 2\pi$ are computed explicitly. The terms with $2\pi < |k| < 3\cdot 2\pi$ are estimated by their number (which is 86) times the largest one (which is $g(2\pi\sqrt{2})$). We get

$$\begin{aligned}
|G_{\mathrm{LR}}(x)| &\leq 6\frac{4\pi e^{-4\pi^2\alpha}}{4\pi^2} + 86\frac{4\pi e^{-8\pi^2\alpha}}{8\pi^2} + \frac{12\pi}{(2\pi)^3}\int_{(3-\sqrt{3})2\pi}^{\infty} 4\pi e^{-\alpha t^2} dt \\
&\leq \frac{6}{\pi}e^{-4\pi^2\alpha} + \frac{43}{\pi}e^{-8\pi^2\alpha} + \frac{3}{(\alpha\pi)^{1/2}}\operatorname{erfc}\left(2\pi\alpha^{1/2}(3-\sqrt{3})\right) \\
&=: X_\alpha
\end{aligned}$$

We now estimate the sum entering G_{SR} for small $|x|$. This is done with the same method, but without separating the first 6 terms. We start from the expression given in (5.2), and get

$$\begin{aligned}
\sum_{x\in\mathcal{L}\setminus\{0\}} \frac{\operatorname{erfc}(|x|/2\alpha^{1/2})}{|x|} &\leq 92\operatorname{erfc}\left(\frac{1}{2\alpha^{1/2}}\right) + 12\pi\int_{3-\sqrt{3}}^{\infty} t\operatorname{erfc}\left(\frac{t}{2\alpha^{1/2}}\right) dt \\
&\leq 92\operatorname{erfc}\left(\frac{1}{2\alpha^{1/2}}\right) + 48\pi\alpha\operatorname{erfc}\left(\frac{3-\sqrt{3}}{2\alpha^{1/2}}\right) \\
&\leq (92 + 48\pi\alpha)\operatorname{erfc}\left(\frac{1}{2\alpha^{1/2}}\right) =: Y_\alpha\,.
\end{aligned}$$

In estimating the second term we used the relation

$$\operatorname{erfc}(x) = \frac{2}{\pi^{1/2}} \int_x^\infty e^{-t^2} dt = \frac{2}{\pi^{1/2}} e^{-x^2} \int_0^\infty e^{-2xs} e^{-s^2} ds \le \frac{1}{\pi^{1/2}} \frac{e^{-x^2}}{x}$$

before computing the integral.

Comparing with (2.4) and (5.2) we get

$$G_0 \le X_\alpha + Y_\alpha - 4\pi\alpha - \frac{1}{(\alpha\pi)^{1/2}} .$$

Since $G_{\mathrm{LR}}(x) \ge -X_\alpha$ and $G_{\mathrm{SR}}(x) \ge -4\pi\alpha$, the thesis is proven provided that we can find α such that

$$2X_\alpha + Y_\alpha - \frac{1}{(\alpha\pi)^{1/2}}$$

is negative. By evaluating these terms numerically one can see that for $\alpha = 0.05$ this expression is approximately -1.13. $\square$

We finally show that there are lattices for which G_0 is positive.

Lemma 5.6. *If $|\Omega_{\mathcal{L}}| = 1$ and there is a vector $k \in \mathcal{L}_0^*$ with $|k| \le 2$, then $G_0 \ge 0$.*

Proof. It is clear from (5.2) that

$$G_0 \ge G_{\mathrm{LR}}(0) - 4\pi\alpha - \frac{1}{(\alpha\pi)^{1/2}} .$$

The sum of the two negative terms is maximal for $\alpha = 1/4\pi$, and it equals -3. The thesis is proven if, for this value of α, we can show that $G_{\mathrm{LR}}(0) > 3$. Indeed, for $x = 0$ all terms in the series defining G_{LR} are positive, and it suffices to consider the two largest ones, which correspond to the vectors $\pm k$. We need

$$\frac{8\pi e^{-|k|^2/4\pi}}{|k|^2} > 3 .$$

This is clearly a monotone function, and diverges for $|k| \to 0$, hence there is an interval $(0, k_0)$ of values where the condition is satisfied. One can then check that $k_0 > 2$ (a more precise estimate gives $k_0 \simeq 2.33$). $\square$

Proof of Corollary 2.2. The equality of the expectation value with G_0 follows from Theorem 2.1. The dependence of G_0 on the lattice follows from Lemma 5.5 and Lemma 5.6. $\square$

Acknowledgements. This work has been supported by the DFG priority research program No. 1095, "Analysis, Modeling and Simulation of Multiscale Problems". We also thank Herbert Spohn for helpful comments.

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