Lindemann criterion and connection with quantality parameter

Corrections 10/07/17

insert also in the book

The original Lindemann criterion (Lindemann (1910)) compares the atomic fluctuation amplitude $\langle \Delta r^2 \rangle^{1/2}$ with the lattice constant a of a crystal. If this ratio, which is defined as the disorder parameter ΔL, reaches a certain value, fluctuations cannot increase without damaging or destroying the crystal lattice. The results of experiments and simulations show that the critical value for Δ_L for simple solids is in the range of 0.10 to 0.15, relatively independent of the type of substance, the nature of the interaction potential, and the crystal structure (Bilgram (1987); Löwen, H. (1994); Stillinger (1995)). Applications of this criterion to an inhomogeneous finite system like a protein in its native state (aperiodic crystal, Schrödinger, E. (1944)) requires evaluation of the generalized Lindemann parameter (Stillinger and Stillinger (1990))

$$\Delta_L = \frac{\sqrt{\sum_i \langle r_i^2 \rangle / N}}{a'}, \qquad (1)$$

$$\Delta \quad \longrightarrow \quad \sqrt{\langle \Delta r_i^2 \rangle / N}$$

or

where N is the number of atoms and a' the most probable non-bonded near-neighbor distance, $\mathbf{r}_i$ is the position of atom i, $\Delta r_i^2 = (\mathbf{r}_i - \langle r_i^2 \rangle)$, and $\langle \rangle$ denotes configurational averages at the conditions of measurement or simulations (e.g. biological, in which case $T \approx 310$ K, PH$\approx$ 7, etc.[1]). The dynamics as a function of the distance from the geometric center of the protein is characterized by defining a interior (int) Lindemann parameter,

$$\Delta_L^{int}(r_{cut}) = \frac{\sqrt{\sum_{i, r_i < r_{cut}} \langle r_i^2 \rangle / N}}{a'}, \qquad (2)$$

$$\Delta \quad \langle \Delta r_i^2 \rangle$$

which is obtained by averaging over the atoms that are within a chosen cutoff distance, r_{cut}, from the center of mass of the protein.

Simulations and experimental data for a number of proteins, in particular Barnase, Myoglobin, Crambin and Ribonuclease A indicate 0.14 as the critical value distinguishing between solid–like and liquid–like behaviour, and $r_{cut} \approx 6$ Å. As can be seen from Table 1, the interior of a protein is solid–like ($\Delta_L < 0.14$), while its surface is liquid–like ($\Delta_L > 0.14$) under physiological conditions. The beginning of thermal denaturation in the simulations appears to be related to the melting of its interior (i.e. $\Delta_L^{int} > 0.14$), so that the entire protein becomes liquid–like. This

Lindemann ("disorder") parameter for a nucleus

Making use of the harmonic oscillator approximation for the single–particle potential (c.f. Fig 2-22 Bohr and Mottelson (1969)), one can write (cf. Eq. (2-130) of

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[1]Fluctuations, classical (thermal) or quantal imply a probabilistic description. While one can only predict the odds for a given outcome of an experiment, probabilities themselves evolve in a deterministic fashion.

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is also the situation of the denatured state of a protein under physiological conditions (see e.g. Rösner et al (2017)).

	$\Delta_L(\Delta_L^{int}(6\text{ Å}))(300\text{ K})$			
	MD simulations			X–ray data
Proteins	Barnase	Myoglobin	Crambin	Ribonuclease A
all atoms	0.21(0.12)	0.16(0.11)	0.16(0.09)	0.16(0.12)
backbone atoms only	0.16(0.10)	0.12(0.09)	0.12(0.08)	0.13(0.10)
side–chain atoms only	0.25(0.14)	0.18(0.12)	0.19(0.10)	0.19(0.13)

Table 1: The heavy–atom $\Delta_L(\Delta_L^{int})$ value, for four proteins at 300 K. After Zhou et al. (1999).

the above reference),

$$\sum_{k=1}^{A}\langle r_k^2\rangle = \frac{\hbar}{M\omega_0}\sum_{k=1}^{A}\left(N_k + \frac{3}{2}\right) = \frac{3}{5}AR^2 \qquad (3)$$

where $A = N + Z$ is the nuclear mass number, while the nuclear radius $R = r_0 A^{1/3}$, with $r_0 = 1.2$ fm. It is of notice that N_k is the oscillator principal quantum number associated with the state k (c.f. Fig. 2-23 Bohr and Mottelson (1969)).

The average internucleon distance can be determined from the relation (Brink, D. and Broglia (2005), App. C)

$$a' = \left(\frac{V}{A}\right)^{1/3} = \left(\frac{\frac{4\pi}{3}R^3}{A}\right)^{1/3} = \left(\frac{4\pi}{3}\right)^{1/3} \times 1.2\text{ fm} \approx 2\text{ fm} \qquad (4)$$

Thus,

$$\Delta_L = \frac{\sqrt{\frac{3}{5}}R}{2\text{ fm}} \approx 2.3, \quad (A \approx 120). \qquad (5)$$

$\frac{0.69\,a_0}{2\,fm} \approx 0.35.$

While it is difficult to compare crystal, aperiodic finite crystal and atomic nuclei, arguably, the above value indicates that a nucleus is liquid–like. More precisely, it is made out of a non–Newtonian fluid, which reacts elastically to sudden solicitations, and plastically to strain. In any case, one expects from $\Delta_L \approx 2/3$ that the nucleon mean free path is long, larger than nuclear dimensions.

0.35

$(\gtrsim 10^{-21}\text{s}),$ long lasting

$(\lesssim 10^{-22}\text{s}),$

Quantality parameter

a_0

In quantum mechanics, the zero–point kinetic energy, $\sim \hbar^2/Ma_0^2$, involved in the localization of a particle within a volume of radius a implies that in the lowest energy state the particles may be delocalized because the potential energy gain of the single classical configuration of fixed particles which minimize $\mathcal{V}$ is overwhelmed by the quantal kinetic energy. Such delocalized quantal fluids provide the basis for discussing the state of electrons in atoms, and metals, of the he atoms in the ground state of atomic nuclei, a non–newtonian quantum fluid.

associated with

of He liquids (both fermionic ^{3}He and bosonic ^{4}He), and the state of nucleons in the ground state

the mean-field (HF) solution,

$\sim \hbar^2/Ma_0^2$

constituents		$M^{a)}$	a(cm)	v_0(eV)	K	phase($T=0$)
^{3}He		3	2.9(-8)	8.6(-4)	0.19	liquid
^{4}He		4	2.9(-8)	8.6(-4)	0.14	liquid
H_2		2	3.3(-8)	32(-4)	0.06	solid
^{20}Ne		20	3.1(-8)	31(-4)	0.007	solid
nucleons	bare	1	9(-14)	$100(+6)^{b)}$	0.4	liquid
	ind.	1	60(-14)	0.5(+6)	2.0	liquid

Table 2: Quantality parameter. After Mottelson (1998).[a)] units of nucleon mass, [b)] nuclear $^1S_0$ NN–Argonne potential v_{14}.

The relative magnitude of the quantal kinetic energy of the localized state compared with the potential energy can be qualitatively characterized by the quantality parameter (Mottelson (1998))

$$K = \frac{\hbar^2}{Ma^2}\frac{1}{|v_0|},$$ (6)

where M is the mass of the individual particles, while v_0 and a measure the strength of the attraction and the range corresponding to the minimum of the potential, respectively. When K is small, quantal effects are small and the lowest state of the system is expected to have a crystalline structure, while for sufficiently large values of K, the system will remain a quantum fluid even in its ground state.

The values of the force parameters and the resulting quantality parameters for several condensed matter systems are collected in Table 2. For nuclei we have two sets. One associated with the bare NN–interaction ($^1S_0$ channel),

$$a_0 \approx 1 \text{ fm}; \quad v_0 = -100 \text{ MeV},$$ (7)

and another with the induced pairing interaction

$$a_0 \approx R(= 1.2A^{1/3} \text{ fm}) \quad v_0 = -0.5 \text{ MeV}.$$ (8)

It is seen that the transition between quantum liquid and crystalline solid occurs at $K \approx 0.1$ (between He and H_2). Thus nuclei are expected to display a (non–Newtonian) quantum liquid structure.

In keeping with the fact that K is of the order of 1 in the nuclear case, it is likely that mean field theory is applicable to the description of the nucleons in the ground state of the system. The marked variation of the binding energy per particle as a function of mass number $A = N+Z$ for specific values of N and Z (magic numbers), testifies to the fact that nucleons display, in states lying close to the Fermi energy, a long mean free path as compared with nuclear dimensions ($R \approx 1.2A^{1/3}$ fm $\approx 6-7$ fm).

The results discussed above, namely that $K \ll 1$ implies localization, that is fixed relations between the constituents, and thus spontaneous symmetry breaking,

while $K \gtrsim 0.14$ implies delocalization and thus homogeneity, is an example of the fact that while potential energy always prefer spatial arrangements, fluctuations, classical or quantal, favour symmetry.

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