

Van der Waals, Casimir, and Lifshitz forces in soft matter

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Abstract. E M Lifshitz's theory of fluctuation molecular forces (*Zh. Eksp. Teor. Fiz.*, Vol. 29, p. 94, 1955 [*Sov. Phys. JETP*, Vol. 2, 73, 1956]) and related problems are introduced from a historical perspective. Applications of the theory to soft matter physics are discussed, together with some new predictions (for example, the stability of smectic or cholesteric liquid crystal films).

Keywords: long-range forces, dispersion interactions, fluctuation forces, liquid crystals

1. Introduction

Because this work is based on E M Lifshitz's famous paper [1] in the *Zhurnal Eksperimental'noi i Teoreticheskoi Fiziki* [Journal of Experimental and Theoretical Physics (JETP)], a few words are in order on the historical background of fluctuation molecular forces. In the vast literature on this topic, which includes original, review (e.g., *JETP* publications [2–5]), and monograph sources, a range of definitions for these forces can be found, including such terms as molecular, dispersion, van der Waals, and Casimir forces. Also included in this type of interaction can be the so-called Kesome forces. As the multiplicity of names already suggests, the phenomenon under review is complex and multifaceted. In what follows, we use the term Lifshitz forces for brevity, having in mind that the retarded van der Waals forces calculated by London [6] or the nonretarded forces discovered by Casimir and Polder [7] are special cases of a general formula derived in Lifshitz's 1955 work [1].

The rest of the paper is arranged as follows. Section 2 presents basic historical facts and publications preceding Lifshitz's work and outlines the current research areas that apply the ideas of Ref. [1] to the fields of study that are apparently too remote from these ideas and which range from biology to nanomechanics and cosmology. Section 3 illustrates the role of long-range Lifshitz forces in determining the structural characteristics of simple liquids and liquid crystals. In Section 4, we calculate how the Lifshitz forces contribute to the chemical potential of a smectic film, a contribution which significantly affects the stability of smectic films of various thicknesses. Section 5 concludes by summarizing 50 years of ongoing (and still actively continuing) research initiated by Lifshitz's paper [1].

2. Brief history of molecular attraction forces

Noting the title of Lifshitz's work [1], *The theory of molecular forces between solids*, attraction forces between neutral molecules seem to provide a natural starting point for the background of the subject. Van der Waals was the first to suggest (based on his analysis of thermodynamic data on liquids and gases) that there are attractive forces between uncharged molecules or atoms. He made this statement in his doctoral dissertation in 1873 at Leiden University, but it took more than half a century before F London [6], in 1930, was able to use nonrelativistic quantum mechanics, already a well-developed theory at that time, to explain the origin of these forces (interaction of dipole moment fluctuations) and to show that they behave as $1/R^7$ with the intermolecular distance R .

The next major step, which took another 18 years, was the recognition by Casimir and Polder in 1948 [7] that at sufficiently large distances of a few microns, the retardation of electromagnetic interactions that transfer force from one fluctuating dipole to another should be added to the picture, with the result that the intermolecular forces decay as $1/R^8$, i.e., faster than in the London analysis. Interestingly, in another 1948 paper by Casimir [8], the attraction forces of this intermolecular nature were calculated for two ideally conducting parallel macroscopic plates separated by a

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distance d , and it was found that the attraction force between the plates behaves as $1/d^4$. For a quite long period of time (about thirty years), this paper attracted little or no attention and was viewed as just a small appendix to Casimir's and Polder's much more important joint paper [7]. However, later (and to a large extent due to Lifshitz's work [1], according to which Casimir's result follows as a special case of the general Lifshitz formula) it became clear that Casimir's work [8] describes the fundamental properties of the quantum physics entity that is known as the vacuum but which formally contains the infinite energy of quantum fluctuations.

The modern history of fluctuation forces begins with Lifshitz's work [1], in which interaction forces were calculated for arbitrary temperatures T for arbitrary macroscopic bodies characterized by frequency-dependent dielectric constants $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ and having arbitrary thicknesses (which automatically allows retardation effects). Technically, the necessary requirement for calculating interaction forces was to find the fluctuation-averaged Maxwell stress tensor in the vacuum.

We quote the expression for the Lifshitz force obtained in Ref. [1]:

$$F = \frac{\hbar}{2\pi^2 c^3} \operatorname{Re} \int_0^\infty dp d\omega p^2 \omega^3 \coth \frac{\hbar\omega}{2T} \times \left\{ \left[\frac{(s_1 + p)(s_2 + p)}{(s_1 - p)(s_2 - p)} \exp\left(\frac{2ip\omega d}{c}\right) - 1 \right]^{-1} + \left[\frac{(s_1 + \epsilon_1 p)(s_2 + \epsilon_2 p)}{(s_1 - \epsilon_1 p)(s_2 - \epsilon_2 p)} \exp\left(-\frac{2ip\omega d}{c}\right) - 1 \right]^{-1} \right\}, \quad (1)$$

where $s_1 = (\epsilon_1 - 1 + p^2)^{1/2}$ and $s_2 = (\epsilon_2 - 1 + p^2)^{1/2}$. Other equivalent forms can be found in multiple reviews on long-range fluctuation forces and in theoretical physics texts.

In the short-distance limit $d \ll \lambda_0$, where λ_0 is the wavelength at which the absorption is significant, the Lifshitz formula takes a very compact and elegant form,

$$F = \frac{\hbar\bar{\omega}}{8\pi^2 d^3}, \quad (2)$$

where

$$\bar{\omega} = \int_0^\infty dx \frac{(\epsilon_1(ix) - 1)(\epsilon_2(ix) - 1)}{(\epsilon_1(ix) + 1)(\epsilon_2(ix) + 1)}. \quad (3)$$

From Eqn (1), London's result for the interaction force between neutral molecules or atoms is readily obtained by assuming that both interacting bodies consist of a sufficiently dilute gas (which implies a near-unity dielectric constant). Expanding the dielectric constant difference in the Lifshitz formula and using the relation

$$\epsilon(ix) = 1 + \frac{2}{\pi} \int_0^\infty d\omega \frac{\omega \operatorname{Im} \epsilon(\omega)}{\omega^2 + x^2} \quad (4)$$

(notably, Lifshitz's work featured Matsubara frequencies, even though it was published a year before Matsubara came up with his techniques), it is straightforward to obtain London's $U \propto 1/r^6$ formula for the interaction energy $U(r)$ of atoms and molecules.

In a similar way, the opposite limit case $d \gg \lambda_0$ leads to the Casimir formula for the interaction force between two ideal

metallic plates at zero temperature,

$$F = \frac{\pi^2 \hbar c}{240 d^4}, \quad (5)$$

and the dilute gas approach described above yields the Casimir–Polder formula for the interaction energy of two widely separated atoms or molecules (i.e., when the retardation of electromagnetic fluctuations is important):

$$U(r) = -\frac{23\hbar c}{4\pi r^7} \alpha_1 \alpha_2, \quad (6)$$

where α_1 and α_2 are the molecular (or atomic) static polarizabilities.

There was a belief after Ref. [1] was published and its predictions were successfully tested for the first time [9–11] that no conceptually new approach was needed to extend its results to the case of a nonvacuum slit (for example, filled with some liquid)—an extension of obvious importance for realistic applications. This was the problem addressed by I E Dzyaloshinskii and L P Pitaevskii, who were then I E Lifshitz's postgraduate students; the problem proved to be much more challenging than originally expected. Most probably, indeed, the task cannot be solved at all by simply averaging fluctuating fields in a frequency-dispersive absorbing medium. The way out taken by the duo was a totally different, quantum-field-theoretical method based on a diagram (Matsubara) technique with Green's functions of an imaginary discrete frequency—a development that allowed directly calculating the Maxwell stress tensor in a medium. It can be argued that papers [12, 13] on this subject brought the theory of the Lifshitz fluctuation forces to completion. What was left was to apply the theory to specific problems and to appropriately modify it to include dynamic effects, anisotropy, thermal fluctuations, nonequilibrium effects, etc. Sections 3 and 4 give some illustrative examples of this.

3. Contribution of long-range Lifshitz forces to the structure factors of simple liquids and gases

In all of the work mentioned in Sections 1 and 2, we discussed precisely the interaction force between macroscopic bodies or (in the dilute gas limit) between individual atoms or molecules. Measuring such forces and interactions requires either specially designed (self-made) instruments (for example, those that were used in the early studies [9–11]) or much more complex and much more accurate (by a fraction of a percent) but still purpose-tailored ones [14]. However, current large-scale instruments (such as research reactors, synchrotrons, and other accelerators) do not measure interaction forces between macroscopic bodies but are used in extremely high-cost experiments designed to measure the structure factor $S(q)$. The structure factor provides important information about the density correlation function $\langle \rho(r)\rho(0) \rangle$ of the system under study, which, when Fourier transformed, gives exactly the structure factor

$$S(q) = \frac{1}{\langle \rho \rangle} \int d^3(\mathbf{r}-\mathbf{r}') \exp(i\mathbf{q}(\mathbf{r}-\mathbf{r}')) \langle \delta\rho(\mathbf{r}) \delta\rho(\mathbf{r}') \rangle. \quad (7)$$

In elucidating the role of long-range Lifshitz forces in determining the physical properties of condensed media, it is natural first to see how these forces contribute to the structure

factor. This question was investigated in Ref. [15] for isotropic liquids and in Refs [16, 17] for nematic liquid crystals.

The results in Refs [15–17] are derived from the fact that the structure factor $S(q)$ can be expressed in a simple way in terms of the second variation $\phi(\mathbf{q})$ of the system free energy,

$$S(q) = \frac{T}{\langle \rho \rangle \phi(\mathbf{q})}. \quad (8)$$

The theory developed by Dzyaloshinskii and Pitaevskii [12], in turn, provides an exact expression for the first variation of the free energy,

$$\Delta F = -\frac{T}{4\pi} \sum_{m=0}^{\infty} \int d^3\mathbf{r} D_{ii}(\mathbf{r}, \mathbf{r}', \omega_m) \delta\Pi(\mathbf{r}, i\omega_m), \quad (9)$$

where $\omega_m = 2\pi mT$ is the Matsubara frequency, the function $\delta\Pi$ describing the polarization of the medium reduces to the dielectric constant, and D_{ii} is the Green's function of a long-wavelength electromagnetic field, which obeys the Maxwell equations:

$$\left[\epsilon(r_1, i\omega_m) \omega_m^2 \delta_{ij} - \delta_{ij} \frac{\partial^2}{\partial r_p^2} + \frac{\partial^2}{\partial r_i \partial r_j} \right] D_{js}(\mathbf{r}_1, \mathbf{r}_2; \omega_m) = -4\pi \delta(\mathbf{r}_1 - \mathbf{r}_2) \delta_{is}. \quad (10)$$

Thus, the required second variation of the free energy is obtained by just calculating the first variation of the Green's function of the long-wavelength field. Cumbersome but conceptually straightforward calculations [15] yield the final expression

$$\phi(\mathbf{q}) = \frac{T}{2(2\pi)^3} \sum_{m=0}^{\infty} \omega_m^4 \int d^3\mathbf{p} D_{is}(\mathbf{p}) D_{is}(\mathbf{p} - \mathbf{q}) \left(\frac{\partial \epsilon}{\partial \rho} \right)^2. \quad (11)$$

In deriving Eqn (11), the following assumptions are made:

- the identity

$$\delta\epsilon(i\omega_m, r) \equiv \frac{\partial \epsilon(i\omega_m)}{\partial \rho} \delta\rho(r)$$

holds;

- density fluctuations are classic in nature;
 - electromagnetic fluctuations are quantum in nature.
- The last two conditions are satisfied if

$$\hbar q s \ll k_B T \ll \hbar q c,$$

where s is the speed of sound, c is the speed of light, and K_B is the Boltzmann constant.

In the limit $1 \ll \lambda_0 q$, when the retardation of the electromagnetic fluctuations is of little importance (here, as above, λ_0 is the wavelength at which the absorption is significant, typically in the infrared range), we have $\phi(q) \propto q^3$. For $q\lambda_0 \ll 1$ (retardation is important), $\phi(q) \propto q^4 \ln 1/(q\lambda_0)$. Both expressions are nonanalytic functions of wave vectors—a fact which is not unexpected (because of the long range) and gives hope for the experimental observation of such contributions against the background of the Ornstein–Zernike analytic dependence

$$\phi = A + Bq^2$$

characteristic of short-range forces. While the estimates obtained in Ref. [15] are quite optimistic, there is as yet no unique identification available for these long-range corrections. The presumed reason is that electromagnetic quantum fluctuations, even though by no means small, are difficult to measure through classical density fluctuations involved in the definition of the structure factor. On the other hand, in the neighborhood of the critical point, the only region where density fluctuations are not small, the order parameter fluctuations lead to a variety of other effects, thus creating a background on which the contribution from the long-range Lifshitz forces is difficult to discern.

Nematic liquid crystals [18] show better promise in this respect. In these, fluctuations of the dielectric constant are expressed in terms of the fluctuations of the director \mathbf{n} , which are of a soft (Goldstone) nature wherever the nematic phase exists and hence are easier to excite than the hard density fluctuations. The orientation ordering in nematic, smectic, and cholesteric liquid crystals are shown schematically in Fig. 1.

Theoretical calculations in Refs [16, 17] led to the following (somewhat counterintuitive) conclusions regard-

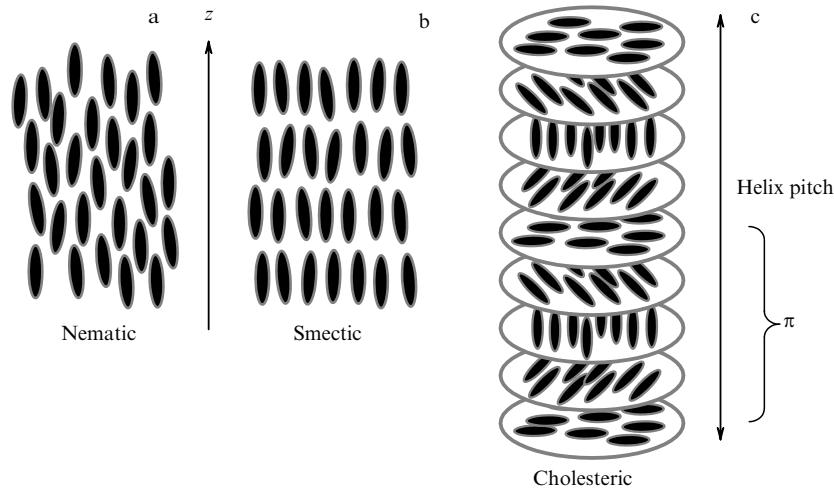


Figure 1. Orientation ordering in (a) nematic, (b) smectic, and (c) cholesteric liquid crystals constructed from rodlike molecules.

ing the long-wavelength contributions to the orientation elasticity of a nematic liquid crystal.

- The local contribution in the region where the retardation of electromagnetic interactions is of importance is expressed as

$$\delta F = \frac{1}{2} \int d^3r [8L(\text{div } \mathbf{n})^2 - 8L(\mathbf{n} \text{ rot } \mathbf{n})^2 + 8L(\mathbf{n} \times \text{rot } \mathbf{n})^2], \quad (12)$$

where

$$L = \frac{\hbar}{48c} \int_0^\infty \frac{\epsilon_a^2(i\omega)}{\epsilon^{3/2}(i\omega)} \omega d\omega, \quad (13)$$

and ϵ_a and ϵ are the respective anisotropic and isotropic parts of the dielectric constant. Interestingly, this result leads to a prediction that the uniform texture of the director is unstable if the long-range forces contribute sufficiently. This would spontaneously break the chiral symmetry of the nematic liquid crystal (as is the case of a phase transition in the recently discovered liquid crystal systems composed of banana-like molecules [19]).

- In the case of negligible retardation, the long-range forces lead to a complicated and nonlocal orientation elasticity,

$$\begin{aligned} \delta F = & \frac{M}{2\pi^2} \int d^3r d^3r' \left[24 \frac{(\mathbf{n}(\mathbf{r})\mathbf{n}(\mathbf{r}'))^2}{|\mathbf{r} - \mathbf{r}'|^6} \right. \\ & + \frac{8}{|\mathbf{r} - \mathbf{r}'|^4} \frac{\partial}{\partial x_i} (n_i(\mathbf{r}) n_l(\mathbf{r})) \frac{\partial}{\partial x'_k} (n_k(\mathbf{r}') n_l(\mathbf{r}')) \\ & \left. - \frac{3}{|\mathbf{r} - \mathbf{r}'|^2} \frac{\partial^2}{\partial x_i \partial x_k} (n_i(\mathbf{r}) n_l(\mathbf{r})) \frac{\partial^2}{\partial x'_k \partial x'_m} (n_k(\mathbf{r}') n_m(\mathbf{r}')) \right], \end{aligned} \quad (14)$$

where

$$M = \frac{\hbar\pi^2}{256} \int \frac{\epsilon_a^2(i\omega)}{\epsilon^2(i\omega)} d\omega.$$

4. Lifshitz forces in modulated systems

The effects of long-range fluctuation forces were considered in Sections 2 and 3 for a medium assumed to be continuous, which allowed neglecting microscopic inhomogeneities on the atomic or molecular scales of the order of a due to the inequality $\lambda_0 \gg a$ for the characteristic wavelengths of macroscopic fluctuations. However, the world of liquid crystals presents examples of systems (so-called cholesteric liquid crystals [18] or numerous polar and chiral smectic phases [20]) (Fig. 2) in which these inhomogeneities (for example, the pitch of the orientation spiral in cholesteric liquid crystals) are of the order of λ_0 . In these cases, if such a liquid-crystal film has a thickness d , its chemical potential $\delta\mu(d)$ can be nonmonotonic as a function of d .

It is shown in Ref. [21] that the chemical potential of a thin ($d < \lambda_0$) cholesteric film contains a long-wavelength contribution that decreases very slowly with the film thickness,

$$\delta\mu(d) \propto \frac{q_0^2}{d}, \quad (15)$$

where q_0 is the wave vector of the cholesteric spiral. Interestingly, the sign of this contribution is independent of the sign (chirality) of the cholesteric spiral itself.

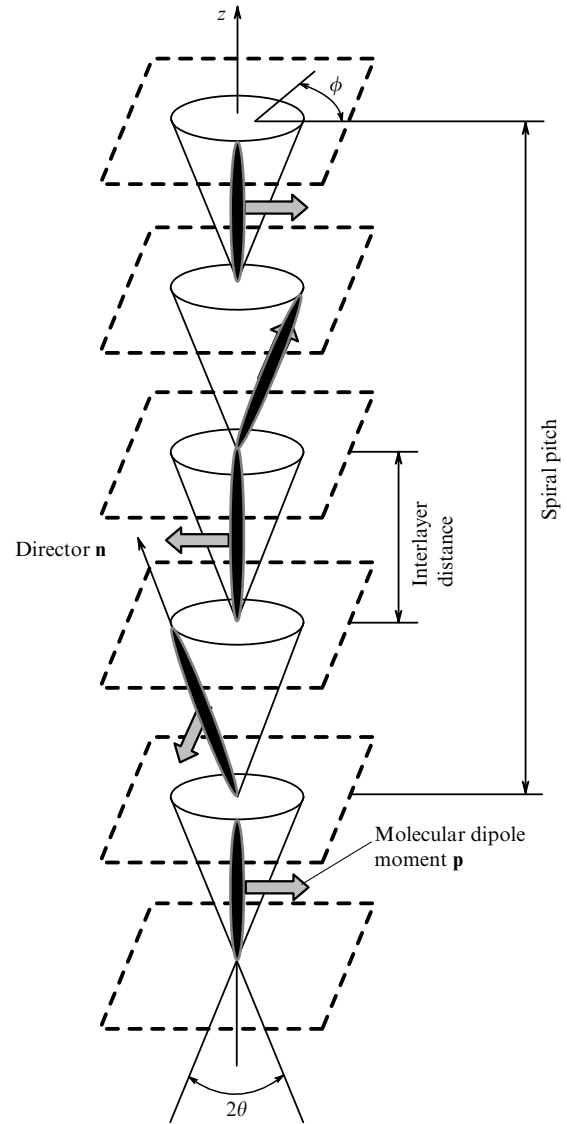


Figure 2. Orientational and translational order in polar and chiral smectic phases. Shown are a conical (with respect to the smectic axis) spiral structure and the direction of the dipole polarization.

For thick ($d > \lambda_0$) films with their dielectric constant tensor modulated (as in a cholesteric liquid crystal), the long-range contribution becomes oscillating:

$$\delta\mu(d) \propto \frac{1}{d^4} \cos(2q_0 d). \quad (16)$$

This has very important stability implications for the film. Namely, whenever the chemical potential becomes negative in a certain thickness range, a film of this thickness becomes unstable and produces a sequence of discrete phase transitions as the thickness is varied (or, equivalently, the film of a modulated liquid crystal becomes an intermittent sequence of those states that wet the substrate and those that do not).

5. Conclusion

This paper shows that Lifshitz's theory can adequately describe a wide range of fluctuation phenomena in condensed matter physics. Lifshitz's theory is also important for

elucidating the mechanisms by which large-period structures form in frustrated systems with competing short-range and long-range interactions. This is of fundamental importance not only for the physics of liquid crystals but also in other areas of condensed matter physics, in particular, in the study of superconductivity and of magnetic and polar structures. The results of such studies are important in solving semi-applied problems in nanomechanics and biophysics and fundamental problems in gravitation and cosmology [22], as well as in understanding the yet unexplored properties of the vacuum. It would take us beyond our scope to give even a brief list of these problems. Examples of the effects associated with long-range forces are usefully and abundantly illustrated in [23]. Biologically, of high importance are the manifestations of Lifshitz forces in cell membranes (see, e.g., review [23]). The same forces are basically responsible for a variety of interesting effects due to the aggregation of the condensed dispersions of deoxyribonucleic acid (DNA) and gold nanoparticles (see the recent review [24] and many references therein).

Importantly, Lifshitz's theory is not a monument to be worshipped. Current advances in experimental techniques for measuring and in theoretical approaches to describing the dielectric characteristics of real materials (see, e.g., Refs [25, 26]) have brought to the fore new conceptual problems in the physics of fluctuation forces. It turns out that a reliable agreement between experimental data and Lifshitz's theory can be achieved by using a plasma model to describe the dielectric constants of the materials involved. The Drude model, while widely used and useful, often turns out to be of no use in this particular context.

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References

1. Lifshitz E M *Sov. Phys. JETP* **2** 73 (1956); *Zh. Eksp. Teor. Fiz.* **29** 94 (1955)
2. Barash Yu S, Ginzburg V L *Sov. Phys. Usp.* **18** 305 (1975); *Usp. Fiz. Nauk* **116** 5 (1975)
3. Barash Yu S, Ginzburg V L *Sov. Phys. Usp.* **27** 467 (1984); *Usp. Fiz. Nauk* **143** 345 (1984)
4. Mostepanenko V M, Trunov N N *Sov. Phys. Usp.* **31** 965 (1988); *Usp. Fiz. Nauk* **156** 385 (1988)
5. Volokitin A I, Persson B N J *Phys. Usp.* **50** 879 (2007); *Usp. Fiz. Nauk* **177** 921 (2007)
6. London F Z *Phys.* **63** 245 (1930)
7. Casimir H B G, Polder D *Phys. Rev.* **73** 360 (1948)
8. Casimir H B G *Proc. Kon. Ned. Akad. Wet.* **51** 793 (1948)
9. Deryagin B V, Abrikosova I I *Sov. Phys. JETP* **3** 819 (1957); *Zh. Eksp. Teor. Fiz.* **30** 993 (1956)
10. Abrikosova I I *Sov. Phys. JETP* **6** 615 (1958); *Zh. Eksp. Teor. Fiz.* **33** 799 (1957)
11. Derjaguin B V, Abrikosova I I, Lifshitz E M *Phys. Usp.* **58** (9) (2015) DOI: 10.3367/UFNe.0185.201509i.0981; *Usp. Fiz. Nauk* **185** 981 (2015); *Usp. Fiz. Nauk* **64** 493 (1958)
12. Dzyaloshinskii I E, Pitaevskii L P *Sov. Phys. JETP* **9** 1282 (1959); *Zh. Eksp. Teor. Fiz.* **36** 1797 (1959)
13. Dzyaloshinskii I E, Lifshitz E M, Pitaevskii L P *Sov. Phys. Usp.* **4** 153 (1961); *Usp. Fiz. Nauk* **73** 381 (1961)
14. Capasso F et al. *IEEE J. Selected Topics Quantum Electron.* **13** 400 (2007)
15. Kemoklidze M P, Pitaevskii L P *Sov. Phys. JETP* **32** 1183 (1971); *Zh. Eksp. Teor. Fiz.* **59** 2187 (1970)
16. Dzyaloshinskii I E, Dmitriev S G, Kats E I *JETP Lett.* **19** 305 (1974); *Pis'ma Zh. Eksp. Teor. Fiz.* **19** 586 (1974)
17. Dzyaloshinskii I E, Dmitriev S G, Kats E I *Sov. Phys. JETP* **41** 1167 (1975); *Zh. Eksp. Teor. Fiz.* **68** 2335 (1975)
18. de Gennes P G, Prost J *The Physics of Liquid Crystals* (Oxford: Clarendon Press, 1993)
19. Mandle R J et al. *Phys. Chem. Chem. Phys.* **16** 6907 (2014)
20. Dolganov P V, Kats E I *Liquid Cryst. Rev.* **1** 127 (2014)
21. Dzyaloshinskii I E, Kats E I *J. Phys. Condens. Matter* **16** 5659 (2004)
22. Volovik G E *The Universe in a Helium Droplet* (Oxford: Clarendon Press, 2003)
23. Meunier J, Langevin D, Boccaro N (Eds) *Physics of Amphiphilic Layers. Proc. of the Workshop, Les Houches, France, February 10–19, 1987* (Springer Proc. in Physics, Vol. 21) (Berlin: Springer-Verlag, 1987)
24. Yevdokimov Yu M et al. *Russ. Chem. Rev.* **84** 27 (2015); *Usp. Khim.* **84** 27 (2015)
25. Chang C-C et al. *Phys. Rev. B* **85** 165443 (2012)
26. Banishev A A et al. *Phys. Rev. B* **88** 155410 (2013)