

Possibility of existence of gauge phase transitions in the schematic model of a classical liquid

E. M. Iolin

Physics Institute, Latvian Academy of Sciences

(Submitted 23 February 1990)

Zh. Eksp. Teor. Fiz. **98**, 908–918 (September 1990)

The Dirac constraint technique is used to analyze the properties of the relaxation model of a liquid. It is shown that the fluidity of a liquid can be described as a manifestation of gauge invariance. A phenomenological Hamiltonian describing a shear phase transition is constructed. It is shown that this transition is of first order and constitutes the onset of a new gauge quantity in the low-temperature phase. Some experimental consequences of the phase transition are discussed.

1. INTRODUCTION

A tremendous number of studies of structural phase transitions (PT) in crystals have been made in the past few decades (see, e.g., Refs. 1 and 2). The description of these (PT) reduces theoretically in many cases to a model of transverse optical modes that are as a rule soft. The question is: is a similar phase transition possible in liquids? Of course, one cannot simply use the Landau Hamiltonian to describe such a PT in a liquid, in view of its fluidity, i.e., lack of elasticity with respect to shear. For PT in a crystal, the soft mode is "frozen," but the displacement in it has a fully defined value. The shear coordinate in a liquid, however, has no direct physical meaning.

An attempt is made below to construct a phenomenological description of a shear PT in a liquid. The liquid is first described, following Leontovich³ and Rytov,⁴ as a system of relaxing tensors interacting with the shear. This model is analyzed by the Dirac constraint model. Dirac weak constraints are usually used for nondissipative systems. It is shown in the present paper that Dirac constraints can be used also for dissipative systems by doubling the dimensionality of phase space through introduction of additional fictitious Dirac-constraint variables. It is found, in particular, that the fluidity of a liquid can be explained as a manifestation of a certain gauge invariance. This approach is used next to formulate the Hamiltonian F of the PT. The harmonic part of F leads at the PT temperature to mode instability in a wide range of momenta \mathbf{q} , and not only at $\mathbf{q} = 0$ as in the usual PT theory. As to the anharmonic terms in F , they vanish at $T = T_c$. A consistent allowance of such a weak anharmonicity leads to an effective polynomial Hamiltonian. Its analysis shows that the PT is of first order. The phase transition is described by a variable $\psi_{\alpha\beta}^1$. For $\tau < 0$ ($\tau = (T - T_c)/T_c$) the modulus of the equilibrium value of $\psi_{\alpha\beta}^1$ becomes infinite, while a change of $|\psi_{\alpha\beta}^1|$ by a finite amount and an arbitrary change of the phase of $\psi_{\alpha\beta}^1$ does not change the state of the system. The PT constitutes in fact the onset of this distinctive gauge symmetry.

2. GENERAL FORMULATION

2.1. According to Leontovich's theory,³ as developed by Rytov⁴ and used mainly to describe depolarizing scattering of light (see, incidentally, Ref. 5), a liquid is characterized by an isotropic-dilatation tensor $u_{\xi\xi}$, by a shear tensor $\tilde{u}_{\alpha\beta}$, by relaxing scalars $\varphi_{\xi\xi}$, and second-rank zero-trace tensors $\tilde{\varphi}_{\alpha\beta}$ ($\text{Sp } \tilde{\varphi} = 0$).

The potential and kinetic parts F_p and F_k of the free energy and the dissipation function ψ_{LR} are given by the expressions

$$F_{LR} = F_p + F_k,$$

$$F_p = \int d^3r \left[\frac{1}{2} \varphi_{\xi\xi}^2 + \frac{1}{2} (\tilde{\varphi}_{\alpha\beta} + N\tilde{u}_{\alpha\beta})^2 + L\varphi_{\xi\xi} u_{\alpha\alpha} + \frac{1}{2} K u_{\alpha\alpha}^2 \right], \quad (1)$$

$$F_k = \int d^3r \left[\frac{\rho_0}{2} \dot{u}_{\alpha\alpha}^2 + \frac{M}{2} (\dot{\tilde{\varphi}}_{\alpha\beta})^2 \right],$$

$$\psi_{LR} = \int d^3r \left[\frac{\tau^s}{2} (\dot{\varphi}_{\xi\xi})^2 + \frac{\tau^a}{2} (\dot{\tilde{\varphi}}_{\alpha\beta})^2 \right], \quad (2)$$

where

$$\tilde{u}_{\alpha\beta} = \frac{1}{2} \left(\frac{\partial u_{\alpha}}{\partial r_{\beta}} + \frac{\partial u_{\beta}}{\partial r_{\alpha}} - \frac{2}{3} \delta_{\alpha\beta} \text{div } \mathbf{u} \right),$$

$$u_{\alpha\alpha} = \text{div } \mathbf{u}, \quad \tilde{\varphi}_{\alpha\beta} = \tilde{\varphi}_{\beta\alpha}, \quad (3)$$

ρ_0 is the density; $u_{\alpha}(r)$ is the displacement component at the point \mathbf{r} of the liquid, N and L are respectively the interaction constants of the shear $\tilde{u}_{\alpha\beta}$ with $\tilde{\varphi}_{\alpha\beta}$ and of $\text{div } \mathbf{u}$ with $\varphi_{\xi\xi}$; K is the hydrostatic compression modulus; τ^s and τ^a are the relaxation times. Compared with Refs. 3 and 4, we have added in (2) a term describing the contribution of the kinetic energy $\tilde{\varphi}_{\alpha\beta}$ of the anisotropic fluctuations, and the corresponding mass density M .

The equations of motion have the usual form

$$\rho_0 \ddot{u}_{\alpha}(\mathbf{r}) = -\delta F_p / \delta u_{\alpha}(\mathbf{r}),$$

$$\tau^s \dot{\varphi}_{\xi\xi}(\mathbf{r}) = -\delta F_p / \delta \varphi_{\xi\xi}(\mathbf{r}),$$

$$M \ddot{\tilde{\varphi}}_{\alpha\beta}(\mathbf{r}) = -\delta F_p / \delta \tilde{\varphi}_{\alpha\beta}(\mathbf{r}) - \tau^a \dot{\tilde{\varphi}}_{\alpha\beta}(\mathbf{r}). \quad (4)$$

It follows from (4) that the high-frequency shear modulus $\mu = N^2$. In the $\omega\tau \ll 1$ regime the shear and bulk viscosities are respectively $\eta_s \propto \mu\tau^a$ and $\eta_0 \propto L^2\tau^s$. The isotropic and anisotropic parts V_i and V_a of the interaction with the external electric field \mathbf{E} are given by

$$V_i = \int d^3r (A\varphi_{\xi\xi} + B \text{div } \mathbf{u})^2 E^2, \quad (5)$$

$$V_a = \int d^3r C (\tilde{\varphi}_{\alpha\beta} + N\tilde{u}_{\alpha\beta}) E_{\alpha} E_{\beta}, \quad (6)$$

where A , B , and C are the corresponding constants. It must be emphasized that the presence of the factor $\tilde{\varphi}_{\alpha\beta} + N\tilde{u}_{\alpha\beta}$ in (6) is rigorously mandatory. If, say, we use $\tilde{\varphi}_{\alpha\beta} + L_1\tilde{u}_{\alpha\beta}$, where $L_1 \neq N$, we get for the correlator $\langle V_a(0) V_a(t) \rangle = \infty$;

this would mean, for example, the presence of purely elastic depolarized scattering of light with an infinitely large cross section, which is of course absurd. The mechanism that ensures the presence of $\tilde{\varphi}_{\alpha\beta} + N\tilde{u}_{\alpha\beta}$, in (1), notwithstanding, e.g., the variation of the parameters themselves with temperature, remains unclear.

2.2. To answer this question, we consider⁶ the symmetry of (1). The expression for F_p is invariant to motions $\tilde{\varphi}_{\alpha\beta} \rightarrow \tilde{\varphi}_{\alpha\beta} + \delta\tilde{\varphi}_{\alpha\beta}$ and $\tilde{u}_{\alpha\beta} \rightarrow \tilde{u}_{\alpha\beta} + \delta\tilde{u}_{\alpha\beta}$ such that

$$\delta\tilde{\varphi}_{\alpha\beta} + N\delta\tilde{u}_{\alpha\beta} = 0. \quad (7)$$

The free energy of the liquid does not change for shear deformation in the form of a transverse wave. Recognizing the arbitrary dependence of $\delta\tilde{\varphi}_{\alpha\beta}$ and $\delta\tilde{u}_{\alpha\beta}$ on the spatial coordinates, we can regard the motion (7) as a gauge transformation that does not alter the state of the liquid. To take the gauge into account it is natural then to use the additional weak constraint (see the Appendix for details)

$$P_\alpha(\mathbf{r}) \equiv (\delta_{\alpha\beta} - \nabla_\alpha \nabla_\beta / \Delta) p_\beta(\mathbf{r}) + \frac{1}{2} N \nabla_\beta (\delta_{\alpha\gamma} - \nabla_\alpha \nabla_\gamma / \Delta) \tilde{p}_{\beta\gamma}(\mathbf{r}), \quad (8)$$

$$P_\alpha(\mathbf{r}) \approx 0.$$

Here $p_\alpha(\mathbf{r})$ and $\tilde{p}_{\beta\gamma}(\mathbf{r})$ are conjugate momenta that ensure a displacement of the variables u_α and $\tilde{\varphi}_{\beta\gamma}$ at the point \mathbf{r} of the liquid. According to Dirac,⁷ the weak coupling means that physical meaning is possessed only by values of V that satisfy, after setting up the Poisson brackets and taking (8) into account, the relation

$$[V, P_\alpha(\mathbf{r})] \approx 0. \quad (9)$$

Of course, the Hamiltonian F should satisfy the weak equality $[F, P_\alpha(\mathbf{r})] \approx 0$. Simple calculations show that $[F_{LR}, P_\alpha] = 0$. It follows from (9) that the quantities $\tilde{\varphi}_{\alpha\beta}$, $\tilde{u}_{\alpha\beta}$, and $\tilde{\varphi}_{\alpha\beta} + L_1 \tilde{u}_{\alpha\beta}$ taken separately have no meaning if $L_1 \neq N$, but a physical meaning is possessed by the quantity $\tilde{\varphi}_{\alpha\beta} + N\tilde{u}_{\alpha\beta}$,

$$[\tilde{\varphi}_{\alpha\beta} + N\tilde{u}_{\alpha\beta}, P_\gamma] = 0.$$

Correspondingly, the divergence of the correlators $\langle \tilde{\varphi}_{\alpha\beta}^2 \rangle = \langle \tilde{u}_{\alpha\beta}^2 \rangle = \infty$ leads to no experimental consequences whatever and does not preclude the use of the quadratic Hamiltonian (1).

One might question the extent to which weak Dirac constraint (8), (9) can be applied to the system (4) in which relaxation terms play an important role. The weak Dirac constraint is usually employed in nondissipative field theory. Let us show that a weak Dirac constraint can be used in our dissipative system. To and use next Dirac constraints in the resultant Hamilton function. Many methods of formally describing dissipation in the framework of Lagrange and Hamilton functions have been published. We shall use the simple method of Ref. 8. To simplify the equations we omit the here-inessential tensor indices of $\tilde{u}_{\alpha\beta}$ and $\tilde{\varphi}_{\alpha\beta}$. The Leontovich–Rytov equations take the schematic form

$$\rho_0 \ddot{u} = -N(\varphi + Nu), \quad (10)$$

$$M\dot{\varphi} = -(\varphi + Nu) - \tau^a \dot{\varphi}.$$

According to Ref. 8 to recast the equations $\ddot{q}_\nu = f_\nu(q, \dot{q}, t)$, $\nu = 1, 2, \dots, n$ in Lagrange form we must introduce also n supplementary purely fictitious variables q_{n+1}, \dots, q_{2n} . In

this case the Lagrangian L_f takes the form

$$L_f = \sum_{\nu=1}^n \dot{q}_\nu \dot{q}_{n+\nu} + f_\nu q_{n+\nu}. \quad (11)$$

To obtain Eqs. (10) for our situation we introduce the fictitious variables q_3 and q_4 , find (11), and then obtain by the usual rules the Hamiltonian

$$H_f = p_u p_s + p_\varphi p_4 + \frac{\tau^a}{M} p_4 q_4 + \left(\frac{N}{\rho_0} q_3 + \frac{1}{M} q_4 \right) (\varphi + Nu), \quad (12)$$

where p_u, p_φ, p_3 , and p_4 are the momenta respectively conjugate to the variables u, φ, q_3 , and q_4 . From (12) follow Eqs. (10) and also the equations of motion for the fictitious coordinates

$$\ddot{q}_3 = -N \left(\frac{N}{\rho_0} q_3 + \frac{1}{M} q_4 \right),$$

$$\ddot{q}_4 = - \left(\frac{N}{\rho_0} q_3 + \frac{1}{M} q_4 \right) + \frac{\tau^a}{M} \dot{q}_4. \quad (13)$$

Note that q_3 and q_4 do not attenuate but increase exponentially with time. This raises no difficulties in our case, since q_3 and q_4 are fictitious quantities. It should be noted that on the whole unusual dependences on the time and on other variables occur almost always in the Lagrangian or Hamiltonian descriptions of dissipative systems. For example, the equation $\dot{x} = \gamma x$ can be obtained by using the Lagrangian

$$L_2 = \frac{1}{2} \dot{x}^2 \exp(-\gamma t).$$

Let us return to the question of the Dirac constraint. The Hamiltonian H_f is compatible with the weak constraint

$$P_f = p_u - N p_\varphi \approx 0, \quad [P_f, H_f] = 0. \quad (14)$$

Introduction of the constraint (14) produces in the right-hand sides of (10) an arbitrary function $\lambda(t)$, for by virtue of (14) we can add to H_f the quantity $\lambda(t) P_f$. The appearance of the quantity $\lambda(t)$ in (10) is quite natural, since $[\varphi, P_f] \neq 0$ and $[u, P_f] \neq 0$, i.e., the quantities φ and u are not observables but depend on the gauge. As to the quantity $\varphi + Nu$, its equations of motion do not depend on $\lambda(t)$, since $[\varphi + Nu, P_f] = 0$, and the corresponding dispersion equation coincides in the limit $M \rightarrow 0$ with those obtained in Refs. 3 and 4.

The presence of the weak constraint (14) in the Leontovich–Rytov model was first demonstrated by us in Ref. 6. It was assumed there, however, that this constraint is conserved only approximately, and it is violated by dissipation. Expression (14) makes it possible to apply a weak Dirac constraint to systems with dissipation, and actually dissipation does not disrupt the weak constraint. One cannot exclude the possibility of this approach being useful for the analysis of a larger group of problems than in the present paper.

It is known from experiments on depolarized scattering of light that the spectrum of the correlator of the anisotropic characteristics of the liquid does not contain $\delta(\omega)$ at the frequency $\omega = 0$. We can satisfy this condition phenomenologically by assuming V_a to be proportional to a Poisson bracket of several $Q_{\alpha\beta}$ with free energy F :

$$V_a \propto \int d^3r [Q_{\alpha\beta}, F] E_\alpha E_\beta. \quad (15)$$

Putting, for example $Q_{\alpha\beta} = \tilde{p}_{\alpha\beta}$ and $F = F_{LR}$, we obtain for V_a Eq. (6). Equation (15) is more general than (6). In fact, allowance for anharmonicity in F can cause the minimum of F to be reached at certain stationary time-independent values $\tilde{q}_{\alpha\beta} + N\tilde{u}_{\alpha\beta}$. According to (6) this would lead to a peak $\delta(\omega)$ in the spectrum of the depolarized light scattering. This scattering can be eliminated with the aid of weak Dirac constraints. Indeed, assume a trajectory in coordinate space, with q and p respectively the coordinate along it and the conjugate momentum. If the Hamiltonian satisfies the condition $\partial F/\partial q = 0$, we can incontrovertibly a weak constraint $p \approx 0$, $[p, F] = 0$ such that q becomes unobservable.

The "inertial" variables can thus be eliminated. The interaction with the remaining ones can be represented, without loss of generality, in the form (15), which will be used from now on. The stationary time-independent quantities occur in the phase transition. It will be shown later, however, that the phase transition acquires a new symmetry property—gauge invariance, which guarantees the absence of purely elastic scattering by these static quantities $\tilde{q}_{\alpha\beta} + N\tilde{u}_{\alpha\beta}$.

2.3. We now describe the phase transition. Assume that that it accompanied by instability of transverse waves. We denote by $\psi_{\alpha\beta}^\perp$ that part of

$$\psi_{\alpha\beta} \equiv \tilde{q}_{\alpha\beta} + N\tilde{u}_{\alpha\beta}, \quad (16)$$

which corresponds to the transverse waves (see the Appendix). Assume that the harmonic part of the free energy (with the kinetic energy subtracted) is

$$F_{ih} = \tau \int K_2(\mathbf{r}_1 - \mathbf{r}_2) \psi_{\alpha\beta}^\perp(\mathbf{r}_1) \psi_{\alpha\beta}^\perp(\mathbf{r}_2) d^3r_1 d^3r_2, \quad (17)$$

where T_c is the PT temperature.

In the Leontovich–Rytov theory we have $K_2(\mathbf{r}) \propto \delta(\mathbf{r})$. Expression (17) is a formal generalization of (1). Assume that the kernel $K_2(\mathbf{r}) = 0$ at $r > R_{K_2}$ (R_{K_2} is of the order of the interatomic distances) and that the eigenvalues of the kernel $K_2(\mathbf{r})$ are positive. Let us make expression (17) clear. Recall the description of PT in crystals. We introduce first the free-energy part F_1

$$F_1 = \frac{1}{2} \sum_i \tau u^2(\mathbf{R}_i),$$

where $\mathbf{u}(\mathbf{R}_i)$, is the displacement in the i th cell. F_1 corresponds to mode instability in a wide momentum range. The next step is to introduce (without the factor τ) into F the term

$$F_2 = \sum_{i,j}' f_{\alpha\beta}(\mathbf{R}_i - \mathbf{R}_j) u_\alpha(\mathbf{R}_i) u_\beta(\mathbf{R}_j),$$

which describes the interaction between cells, with $f_{\alpha\beta} \neq 0$ as $\tau \rightarrow 0$. This causes dispersion of the soft modes to appear in $F = F_1 + F_2$ and one of these modes freezes as $\tau \rightarrow +0$.

We consider now a PT in a liquid. We take a point \mathbf{r} and a small region of size $\sim R_{K_2}$ surrounding it. The free energy of this small drop can be written, by analogy with the crystals and with Ref. 4, in the form (17). What is now the interaction $V(\mathbf{r}_1 - \mathbf{r}_2)$ between drops centered about \mathbf{r}_1 and \mathbf{r}_2 ? According to (6) and (15) the interaction between anisotropic fluctuations is of the form

$$V_{12} \sim \int f(\mathbf{r}_1 - \mathbf{r}_2) \frac{\delta F}{\delta \psi_{\alpha\beta}^\perp(\mathbf{r}_1)} \frac{\delta F}{\delta \psi_{\alpha\beta}^\perp(\mathbf{r}_2)} d^3r_1 d^3r_2 \\ \sim \tau^2 \int f(\mathbf{r}_1 - \mathbf{r}_2) \psi_{\alpha\beta}^\perp(\mathbf{r}_1) \psi_{\alpha\beta}^\perp(\mathbf{r}_2) d^3r_1 d^3r_2,$$

where f is the corresponding weighting function: for PT we have $V_{12} \propto \tau$, i.e., V is negligibly small. All modes with momenta $q \lesssim R_{K_2}^{-1}$, are therefore softened in a liquid as $\tau \rightarrow +0$, and not only one of them as in a crystal. Since $|\psi^\perp| \propto \tau^{-1/2}$, anharmonicity of order n also makes a negligibly small contribution $\propto (\delta F/\delta \psi^\perp)^n \propto \tau^{n/2}$ to F . What is substantial, however, is the interaction between the local densities \tilde{F} of the free energy.

Let us consider in greater detail the case of anharmonicity

$$F_{iah} = \int \tilde{F}(1) \tilde{F}(2) K_i[(1) - (2)] d(1) d(2) \quad (18)$$

with bare F_{ih} (17). We omit for simplicity the tensor and other subscripts. How is $F = F_{ih} + F_{iah}$ to be calculated if F_{iah} is itself dependent on F ? We divide F_{iah} into $R \gg 1$ parts and "include" them in succession. In each step, an arbitrarily small part of F_{iah} is included as $R \rightarrow \infty$, so that to calculate the free-energy density \tilde{F} we can use the value of F obtained in the preceding step:

$$0) \tilde{F}(1) = F_0(1) = \tau \psi^\perp(1) \int K_i[(1) - (2)] \psi^\perp(2) d(2),$$

$$1) \tilde{F}(1) = F_0(1) + R^{-1} F_0(1) \int K_i[(1) - (2)] F_0(2) d(2) \\ = F_1(1),$$

$$2) \tilde{F}(1) = F_2(1) = F_1(1) + R^{-1} F_1(1)$$

$$\times \int K_i[(1) - (2)] F_1(2) d(2), \dots$$

Changing to the continuous variable, we obtain in the n th approximation:

$$\frac{\partial F_n(1)}{\partial n} = \frac{1}{R} \int K_i[(1) - (2)] F_n(1) F_n(2) d(2). \quad (19)$$

Any acceptable analysis of the nonlinear equation (19) can be made in the case $R_{K_4} \gg R_{K_2}$ (where R_{K_1} and R_{K_2} are the "action" radii of the kernels of the anharmonic and harmonic parts of F , respectively). The radius R_{K_2} is comparable with the dimension of the short-range order regions. Averaging $F_n(\mathbf{r})$ over a region of size $\sim R_{K_1}$, denoting by V the volume of the liquid and by \tilde{F}_n the averaged value of F_n , and neglecting the fluctuations, we obtain in the mean-field approximation an expression for the effective Hamiltonian F_e

$$\frac{\partial \tilde{F}_n}{\partial n} = \frac{1}{R} (\tilde{F}_n)^2 \int K_i(2) d2, \quad (20) \\ F_e = \tilde{F}_R = \left\{ V \left[\tau \int \psi^\perp(1) \psi^\perp(2) K_i[(1) - (2)] d(1) d(2) \right] \right. \\ \left. - \int K_i(1) d(1) \right\}^{-1}.$$

We emphasize that the effective Hamiltonian (29) is a nonlinear functional of ψ^\perp . In the paraphase ($\tau < 0$) the minimum of F_e corresponds to the small quantities $|\psi^\perp|$. When $|\psi^\perp|$ is increased, a situation in which the denominator of F_e reverses sign becomes in principle possible. Such a transi-

tion, however, calls for overcoming an infinitely high barrier and we shall not consider it. In the condensate phase ($\tau < 0$) the minimum of F_e

$$F_e \sim - \left(\int K_i(1) d1 \right)^{-1}$$

corresponds to $|\psi^\perp| = \infty$. In this case F_c is independent of ψ^\perp in an overwhelming part of the F_c phase space; as a result, turns out to be a redundant variable and for $\tau < 0$ we can use the gauge [see (A6) below]

$$Q_\alpha \equiv \nabla_\beta (\delta_{\alpha\tau} - \nabla_\alpha \nabla_\tau / \Delta) \tilde{p}_{\beta\tau}(\mathbf{r}) \approx 0. \quad (21)$$

The weak coupling (21) ensures the absence of elastic scattering by the static quantities $|\psi^\perp| = \infty$. It is customary in field theory to postulate from the outset a gauge symmetry, although it can also be spontaneously violated. In our case the phase transition, which can be arbitrarily called a gauge transition, leads to the appearance of symmetry of (21) in a condensate. If $\tau < 0$ there is no correlation between the phases $\psi_{\alpha\beta}^\perp(\mathbf{r}_1)$ and $\psi_{\alpha\beta}^\perp(\mathbf{r}_2)$ at $|\mathbf{r}_1 - \mathbf{r}_2| > R_{K_2}$. Since $\delta F / \delta \psi_{\alpha\beta}^\perp = 0$, out of all the harmonic and anharmonic interactions in a condensate, only the interaction between the free-energy densities turns out to be substantial.

3. CONSEQUENCES OF PHASE TRANSITION

A transition from a phase with gauge symmetry (21) to the paraphase is of first order, with a transition heat $\propto K_4^{-1}$. The interaction with anisotropic external fields $\propto [Q_{\alpha\beta}, F]$ is equal to zero in the condensate phase. In the paraphase this interaction leads to anisotropic-field scattering intensity

$$J_I \sim \langle (\delta F / \delta \psi_{\alpha\beta}^\perp)^2 \rangle \propto \tau.$$

In experiments on depolarized scattering of light, one of the attributes of the discussed phase transition might be a kink on the plot of the scattering intensity J_1 against temperature.

Dilatational fluctuations of the density $\rho(q)$ as functions of the momentum q can interact with the shear part F_e of the free energy. The corresponding part of the Hamiltonian is of the form:

$$\mathcal{H} = \sum_{\mathbf{q}} S_0^{-1}(\mathbf{q}) |\rho(\mathbf{q})|^2 + S_1^{-1}(\mathbf{q}) |\rho(\mathbf{q})|^2 F_e / V, \quad S_0^{-1} \sim K. \quad (22)$$

Here $S_0(\mathbf{q})$ is a structure factor, while $S_1(\mathbf{q})$ is an analogous quantity indicative of the interaction of F_e / V with $|\rho(\mathbf{q})|^2$.

The intensity of scattering by dilatational fluctuations of the density is given by

$$I(\mathbf{q}) \sim [S_0^{-1}(\mathbf{q}) + S_1^{-1}(\mathbf{q}) F_e / V]^{-1}. \quad (23)$$

The discontinuity of F_e at $\tau = 0$ leads to a discontinuity of the scattering intensity in the PT. Fourth-order anharmonicity in solids corresponds usually to an increase of the elasticity with increase of temperature. In our case this corresponds qualitatively to a positive $S_1(\mathbf{q})$ and to a jumplike decrease of $I(q)$ on going from the condensate to the paraphase.

Let us discuss the anomalies of the dissipative properties. A theory of dynamic phenomena in PT in the mean-field approximation is usually developed under the assumption that the parameters of the dissipative function ψ are indepen-

dent of temperature. In our case the expression for ψ should be compatible with the fluidity requirement on the liquid. Let us show that this leads in the paraphase to the relation (25)

$$\psi = \int d^3r \frac{\tau^{\alpha\perp}}{2} (\dot{\tilde{\varphi}}_{\alpha\beta}^\perp)^2 \quad (24)$$

$$\tau^{\alpha\perp} = \tau \tau^{\alpha c}, \quad \tau > 0, \quad (25)$$

where $\tau^{\alpha c}$ is finite as $\tau \rightarrow +0$; $\tilde{\varphi}_{\alpha\beta}^\perp$ and $\tilde{u}_{\alpha\beta}^\perp$ are the parts of $\tilde{\varphi}_{\alpha\beta}$ and $\tilde{u}_{\alpha\beta}$ corresponding to transverse waves [see (A2)]. Starting from (8), (12), (14), (17), and (24), we write down the equations of motion for the physical quantities. Changing to Fourier expansions in the momentum and frequency

$$\psi_{\alpha\beta}(\mathbf{r}) = (2\pi)^{-3} \int \psi_{\alpha\beta}(\mathbf{q}, \omega) \exp(i\mathbf{q}\mathbf{r} - i\omega t) d^3q d\omega, \quad (26)$$

$$K_2(\mathbf{r}) = (2\pi)^{-3} \int K_2(\mathbf{q}) \exp(i\mathbf{q}\mathbf{r}) d^3q$$

and neglecting the contribution of the kinetic energy of the anisotropic fluctuations ($M \rightarrow 0$), we obtain the dispersion equations of the longitudinal (27) and transverse (28) waves

$$\rho_0 \omega^2 = (K - L^2) q^2 + L^2 q^2 \frac{(-i\omega \tau^s)}{(1 - i\omega \tau^s)}, \quad (27)$$

$$\rho_0 \omega^2 = N^2 q^2 K_2(q) \tau \frac{-i\omega \tau^{\alpha c}}{2\tau K_2(q) - i\omega \tau^{\alpha c}}. \quad (28)$$

Since the phase transition takes place on transverse waves, Eq. (27) has no singularities as $\tau \rightarrow +0$ (Eq. (27) contains for simplicity only the interaction of $u_{\xi\xi}$ with isotropic fluctuations $\varphi_{\alpha\alpha}$). Assume that $\tau^{\alpha\perp}$ is finite as $\tau \rightarrow +0$. Then for any arbitrarily low frequency ω there exists a value $|\tau| < \omega \tau^{\alpha\perp} / K_2(q)$ such that the propagation of a transverse wave of frequency ω goes over into the solid-state regime, i.e., there will be no fluidity for $\tau \rightarrow +0$. We must therefore stipulate $\tau^{\alpha\perp} \sim \tau^\alpha$, where $\alpha \geq 1$. If $\alpha > 1$, we have at any frequency, not necessarily a low one, for a transverse wave and sufficiently small $\tau > 0$

$$\rho_0 \omega^2 = -\frac{1}{2} N^2 q^2 i\omega \tau^{\alpha\perp},$$

i.e., we would have a viscous-flow regime. This is incorrect, since a transition into the solid-state regime should take place at high frequencies. It must therefore be assumed that $\alpha = 1$. The dispersion relation for transverse waves takes the form

$$\rho_0 \omega^2 = N^2 q^2 K_2(q) \tau \frac{-i\omega \tau^{\alpha c}}{2K_2(q) - i\omega \tau^{\alpha c}}. \quad (29)$$

The transition $\omega \tau^{\alpha c} \sim 2K_2(q)$ from the solid-state regime to viscous flow is independent of τ , and the high-frequency shear modulus, and the viscosity are proportional to τ . Since the dissipative function is not negative, expressions (24) and (25) are not valid at $\tau < 0$. For $\tau < 0$ the quantity $\tilde{\varphi}_{\alpha\beta}^\perp$ becomes a gauge function and makes no contribution to the dissipative function. At small but finite M , there is always an immediate vicinity of the point $\tau = 0$ in which the approximation $M = 0$ is apparently invalid. An analysis of this situation is outside the scope of the present paper.

Note also a certain similarity property of F . It can be

seen from (17) and (18) that the substitution $\psi_{\alpha\beta}^{\perp} \equiv \Phi_{\alpha\beta} |\tau|^{-1/2}$ leads to $F = F(\Phi)$, i.e., the temperature dependences of all the quantities at $|\tau| \ll 1$ can be obtained by changing over to $\Phi_{\alpha\beta}$. It must be borne in-mind, however, that such a similarity transformation works only within the limits of a definite sign of τ ; a continuous transition from $\tau > 0$ to $\tau < 0$ is impossible.

4. BRIEF DISCUSSION OF THE EXPERIMENTAL SITUATION

Many, frequently contradictory, experimental data have been published (see, e.g., Refs. 9–14) on PT in liquid metals. Let us consider the relatively well studied PT in liquid rubidium and cesium. According to Refs. 13 and 14, in liquid cesium at 580 K and 930 K and in liquid rubidium at 550–600 K and 920 K the temperature dependences of the viscosity η and of the density ρ_0 have weak anomalies in the form of kinks. It is difficult, unfortunately, to compare these experimental data with (16)–(29), since it is known that η and ρ_0 are determined in liquids primarily by the activation energy of formation of cavities for the ion hopping, and by the frequency of the hops.¹⁵ The calculation of these quantities, is, of course, not the subject of our study.

The experimental data^{11,12} on neutron scattering by liquid rubidium and cesium point to the existence, in the same temperature ranges, of a shift (but in a narrow temperature interval) of the position of the maximum of the structure factor $S(q)$, and a jumplike change of the derivative $\partial S(q, T)/\partial T$ at $T \approx T_c$. Let us show that these results agree qualitatively with the calculations of the present paper. The neutrons are scattered by density fluctuations $\Delta\rho$. Assume a medium with uniform density ρ_0 , in which a small displacement $\mathbf{u}(\mathbf{r})$ takes place. It follows from the continuity equation that this leads to the density change:

$$\Delta\rho \approx -\rho_0 \operatorname{div} \mathbf{u} + \rho_0 (\operatorname{div} \mathbf{u})^2 + \rho_0 (\mathbf{u} \nabla) \operatorname{div} \mathbf{u}. \quad (30)$$

The first term of (30) describes the intensity $S_{\parallel}(q)$ of scattering by dilatational excitations $u_{\xi\xi}$. It follows from (23) that $S(q)$ undergoes a jump—as a rule, a decrease—on going from the condensate to the paraphase. The temperature dependence of the shear part of the free energy F_c at $\tau > 0$ can also lead to a jump of the derivative $\partial S_{\parallel}(q, T)/\partial T$ as $\tau \rightarrow +0$. The contributions of the longitudinal waves to the second and third terms of (30) are small, introduce no qualitatively new effects, and can be neglected.

Let us consider the contribution of the combined action of transverse \mathbf{u}_{\perp} and longitudinal \mathbf{u}_{\parallel} waves [the last term of (30)] to the scattering intensity $S_{\parallel\perp}(q)$. Simple calculation yields

$$S_{\parallel\perp}(q) = \frac{V_0}{(2\pi)^3} \int d^3 q_1 |\mathbf{u}_{\perp}(\mathbf{q}_1) \mathbf{q}|^2 S_0(\mathbf{q}-\mathbf{q}_1), \quad (31)$$

where V_0 is the volume per atom of the liquid. Recognizing that at $t > 0$

$$u_{\perp}(q) \propto \frac{\tau}{Nq} \psi^{\perp}(q) \propto \frac{\delta F}{\delta \psi^{\perp}(q)},$$

we get

$$S_{\parallel\perp}(q) = g \frac{V_0}{(2\pi)^3} \int d^3 q_1 \frac{q^2}{q_1^2} \left(1 - \frac{(\mathbf{q} \cdot \mathbf{q}_1)^2}{q^2 q_1^2} \right) \frac{\tau}{N} S_0(\mathbf{q}-\mathbf{q}_1), \quad (32)$$

where g is a numerical constant that cannot be determined

within the framework of the phenomenological description. There occurs therefore in the paraphase an additional scattering $S_{\parallel\perp}(q)$ whose intensity is proportional to $\sim \tau$. There is no such scattering in the condensate phase. At $\tau = 0$ a jump takes place in the derivative $\partial S_{\parallel\perp}(q, T)/\partial T$. The presence of $S_{\parallel\perp}(q)$ is by itself peculiar to a liquid. In a crystal, for example, $S_0(\mathbf{q})$ consists of spikes $\delta(\mathbf{q} - \mathbf{H})$, where H is the reciprocal-lattice vector. In this case,

$$S_{\parallel\perp}(\mathbf{q}) \propto [\mathbf{q} \cdot \mathbf{u}_{\perp}(\mathbf{q} + \mathbf{H})]^2.$$

What is peculiar to the liquid is the temperature dependence $S_{\parallel\perp}(q) \propto \tau$.

Further studies of PT in a liquid and, in particular, a detailed measurement of the temperature dependences of $S(q)$, of the energy spectrum $S(q, \omega)$, and of the heat capacity and heat of the transition, as well as of the acoustic properties, are desirable.

APPENDIX

The Hamiltonian (1) corresponds to Poisson brackets of the displacements, tensors, and conjugate momenta:

$$\begin{aligned} [u_{\alpha}(\mathbf{r}), p_{\beta}(\mathbf{r}')] &= \delta_{\alpha\beta} \delta(\mathbf{r}-\mathbf{r}'), \quad [u_{\alpha}(\mathbf{r}), u_{\beta}(\mathbf{r}')] = 0, \\ [\tilde{\varphi}_{\alpha\beta}^{(a)}(\mathbf{r}), \tilde{p}_{\alpha'\beta'}^{(b)}(\mathbf{r}')] &= \delta_{\alpha\beta}^{a'\beta'} \delta_{ab} \delta(\mathbf{r}-\mathbf{r}'), \\ \delta_{\alpha\beta}^{a'\beta'} &= \delta_{\alpha\alpha'} \delta_{\beta\beta'} + \delta_{\alpha\beta'} \delta_{\beta\alpha'} - \frac{2}{3} \delta_{\alpha\alpha'} \delta_{\beta\beta'}, \\ \left[\varphi_{\xi\xi}^{(a)}(\mathbf{r}), \frac{1}{3} p_{\eta\eta}^{(b)}(\mathbf{r}') \right] &= \delta_{ab} \delta(\mathbf{r}-\mathbf{r}'), \\ [\varphi_{\xi\xi}^{(a)}(\mathbf{r}), \tilde{p}_{\alpha'\beta'}^{(b)}(\mathbf{r}')] &= 0, \\ [p_{\alpha\beta}^{(a)}(\mathbf{r}), \tilde{p}_{\alpha'\beta'}^{(b)}(\mathbf{r}')] &= 0, \quad [\tilde{p}_{\alpha\beta}^{(a)}(\mathbf{r}), p_{\gamma}(\mathbf{r}')] = 0, \\ [p_{\alpha}(\mathbf{r}), p_{\beta}(\mathbf{r}')] &= 0. \end{aligned} \quad (A1)$$

In other words, u_{α} , $\tilde{\varphi}_{\alpha\beta}^{(a)}$, $\varphi_{\xi\xi}^{(a)}$ and the conjugate momenta P_{α} , $\tilde{p}_{\alpha\beta}^{(a)}$, $1/3 p_{\eta\eta}^{(a)}$ are pair-wise independent variables. Note that $p_{\alpha}(\mathbf{r})$ is the real momentum density of the liquid particles, then Eq. (A1) is not met, and instead

$$[p_{\alpha}(\mathbf{r}), p_{\beta}(\mathbf{r}')] = \delta(\mathbf{r}-\mathbf{r}') e_{\alpha\beta\gamma} \operatorname{rot}_{\gamma} \mathbf{p} + \dots$$

By analogy with field theory, we assume (A1) to be valid), i.e., that the momenta commute with one another. This is not contradictory in the scope of the Leontovich–Rytov model. We consider a system in which there are several relaxing tensors $\tilde{\varphi}_{\alpha\beta}^{(a)}$ ($S p \tilde{\varphi}^{(a)} = 0$, a is the number of the tensor) and several PT that occur at temperatures T_{ca} , respectively. Assume by analogy with a solid, that an instability to transverse wave is present in the PT. That part of the free energy F which is of interest to us is expressed in terms of quantities $\psi_{\alpha\beta}^{(a)\perp}$ corresponding to transverse waves

$$\begin{aligned} \psi_{\alpha\beta}^{(a)} &= \tilde{\varphi}_{\alpha\beta}^{(a)} + N_{\alpha} \tilde{u}_{\alpha\beta}, \\ \psi_{\alpha\beta}^{(a)\perp} &= \nabla_{\alpha} \nabla_{\gamma} / \Delta (\delta_{\beta\gamma} - \nabla_{\beta} \nabla_{\gamma} / \Delta) \psi_{\gamma\delta}^{(a)} + \alpha \neq \beta. \end{aligned} \quad (A2)$$

In the quadratic approximation we have

$$\begin{aligned} F = \int d^3 r \left\{ \frac{1}{2} \rho_0 \dot{u}_{\alpha}^2 + \frac{1}{2} \sum_a \tau_a (\psi_{\alpha\beta}^{(a)\perp})^2 + \frac{1}{2} K (u_{\xi\xi})^2 \right. \\ \left. + \frac{1}{2} (\varphi_{\xi\xi}^{(a)})^2 + L u_{\xi\xi} \varphi_{\alpha\alpha} \right\}, \\ \tau_a = (T - T_{ca}) / T_{ca}, \end{aligned} \quad (A3)$$

where N_a is the interaction constant. The fluidity condition—the weak coupling (8)—is realized in the form of the relation

$$P_\alpha(\mathbf{r}) \approx 0, \\ P_\alpha(\mathbf{r}) \equiv (\delta_{\alpha\beta} - \nabla_\alpha \nabla_\beta / \Delta) p_\beta(\mathbf{r}) \\ + \frac{1}{2} \sum_a N_a \nabla_\beta (\delta_{\alpha\gamma} - \nabla_\alpha \nabla_\gamma / \Delta) \tilde{p}_{\beta\gamma}^{(a)}(\mathbf{r}). \quad (\text{A4})$$

Let a PT take place at $a = 0$. There appears therefore at $\tau_0 < 0$, besides (A4), a new gauge condition (A5)

$$(\delta_{\alpha\beta} - \nabla_\alpha \nabla_\beta / \Delta) p_\beta(\mathbf{r}) + \frac{1}{2} \sum_a' N_a \nabla_\beta (\delta_{\alpha\gamma} - \nabla_\alpha \nabla_\gamma / \Delta) \tilde{p}_{\beta\gamma}^{(a)}(\mathbf{r}) \approx 0. \quad (\text{A5})$$

The prime on the summation sign means absence of a term with $a = 0$. For $\tau_0 < 0$ we have thus the conditions (A5) and (A6)

$$Q_\alpha \equiv \nabla_\beta (\delta_{\alpha\gamma} - \nabla_\alpha \nabla_\gamma / \Delta) \tilde{p}_{\beta\gamma}^{(0)}(\mathbf{r}) \approx 0. \quad (\text{A6})$$

At $\tau_0 < 0$ the displacement $u_\alpha(\mathbf{r})$ does not interact effectively with $\psi_{\mu\nu}^{(0)\perp}$.

Assume that we continue to cool the liquid. The interactions of u_α with $\psi_{\mu\nu}^{(a)\perp}$ ($a = 0, 1, \dots$) will then be “turned off” in succession. If the number of such tensors is finite below a certain temperature, either the liquid ultimately freezes into a crystal or glass, or we arrive at the condition

$$(\delta_{\alpha\beta} - \nabla_\alpha \nabla_\beta / \Delta) p_\beta(\mathbf{r}) \approx 0. \quad (\text{A7})$$

Obviously, (A7) is not compatible with any transverse shear motions $\tilde{u}_{\alpha\beta}^\perp$, i.e. the system contains only longitudinal exci-

tations with finite speed of sound. According to the Landau criterion this corresponds in principle to superfluidity. Taking into account the schematic character of the model, the statement (A7) can hardly be taken too seriously. If, however, the number of tensors $\tilde{\varphi}_{\alpha\beta}^{(a)}$ below a certain temperature is infinite, we have a condensation point T^{ca} near a certain temperature T_m at which an infinite number of relaxing tensors is produced. One cannot exclude the possibility of identifying T_m with the melting temperature.

¹ A. Z. Petviashvili and V. L. Pokrovskii, *Fluctuation Theory of Phase Transitions* [in Russian], Nauka, 1982.

² S.-K. Ma, *Modern Theory of Critical Phenomena*, Benjamin-Cummings, 1976.

³ M. Leontovich, *J. Phys. (USSR)*, **4**, No. 16, 499 (1941).

⁴ S. M. Rytov, *Zh. Eksp. Teor. Fiz.* **58**, 2154 (1970) [*Sov. Phys. JETP* **31**, 1163 (1971)].

⁵ E. M. Iolin, V. V. Kozlov, G. L. Antokol'skii, and V. S. Baranov, *ibid.*, **74**, 1415 (1978) [**47**, 741 (1978)].

⁶ E. M. Iolin, *Abstracts, All-Union Conf. on Magnetic Resonance in Condensed Media (Physical Aspect)*, Kazan', 1984, Part 1, p. 172.

⁷ P. A. M. Dirac, *Lectures on Quantum Mechanics*, Academic, 1964.

⁸ A. S. Galiullin, *Analytic Dynamics* [in Russian], Vysshaya Shkola, Moscow, 1989, p. 254.

⁹ *Izv. Vyssh. Ucheb. Zaved., Chernaya metallurgiya*, No. 5–7 (1985).

¹⁰ N. A. Vatolin, E. A. Pastukhov, and V. N. Sermyagin, *Doklady Akad. Nauk SSSR* **222**, 641 (1975).

¹¹ Yu. I. Sharykin, P. Glazkov, S. N. Skovorod'ko *et al.*, *ibid.* **244**, No. 1, 78 (1979) [**24**, 34 (1979)].

¹² A. Yu Astapkovich, E. M. Iolin, E. N. Kozlov *et al.*, *ibid.* **283**, 73 (1982) [*sic*].

¹³ V. A. Fomin, *Author's Abstract of Candidate's Dissertation, High-Temp. Inst. USSR Acad. Sci.*, 1966.

¹⁴ S. N. Skovorod'ko, *Author's Abstract of Candidate's Dissertation, High-Temp. Inst., USSR Acad. Sci.*, 1980.

¹⁵ V. G. Bar'yakhtar, L. E. Mikhailova, A. G. Il'inskii *et al.*, *Zh. Eksp. Teor. Fiz.* **95**, 1404 (1989) [*Sov. Phys. JETP* **68**, 811 (1989)].

Translated by J. G. Adashko