Non-equilibrium Critical States.

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ABSTRACT

Microscopic mechanisms of relaxation in steady and transient non-equilibrium states of a liquid close to its critical point are considered. The type of relaxation is different for slowly and for rapidly changing conditions. For slowly varying states, the relaxation may be described in terms of the correlation radius of critical fluctuations playing the role of a local characteristic. We suggest a universal form of the heat current in those systems. A rapid and large perturbation of a critical liquid triggers a non-equilibrium state with a sequential relaxation on increasing length-scales. A step away from criticality generates a free field with strong and decaying correlations in initial state, while a step towards criticality initiates the increase of fluctuations and of their correlation at the large scale edge of the critical range.

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1. INTRODUCTION

The unusual properties of the critical state of matter are determined by a hierarchical system of strongly interacting long-range fluctuations. Other strongly interacting systems are known, including hydrodynamic turbulence, and quantum vacuum (the arena of elementary particles physics); at present, our knowledge of this systems is insufficient even to classify them

as belonging to same universality class. So far, the equilibrium critical state is the only case of strong interaction in which the discovery of scale invariance allowed one to understand the system behavior. One hopes to get a deeper insight into mechanisms of strong interaction by studying non-equilibrium critical systems in the presence of energy currents in real or/and configuration space. Our objective is to discuss some of non-equilibrium states of a near-critical liquid.

An important feature of critical fluctuations, best revealed by the renormalization group theory [1,2], is their self-consistency. This self-consistency is unidirectional in the length-scale dimension: conditions for fluctuation motions at a large length scale are determined by average characteristics of smaller scale fluctuations. This results, at equilibrium, in scale invariance of the fluctuation picture at all large length scales. In a more general treatment, the fluctuations on each length scale may be seen as sub-systems of the large hierarchical system described by corresponding degrees of freedom. A perturbation of equilibrium may change the self-consistency of the hierarchical system, creating non-equilibrium transient or steady characterized by energy currents between subsystems. As will be shown below, the character of the system kinetic depends on the characteristic time of perturbation relative to the relaxation time of fluctuations at the correlation radius length scale. In an inhomogeneous critical steady state with temperature and/or other parameters gradients, the energy exchange between scales takes the form of heat transfer in real space; the physical mechanism of this enhancement of the usual phonon heat transfer is the diffusion of critical fluctuations. The opposite limit is a non-equilibrium caused by a rapid change of thermodynamic conditions that triggers the appearance or disappearance of a wide range of critical fluctuations.

2. ENERGY TRANSPORT IN STEADY NEAR-CRITICAL STATES.

The length-scale decomposition [1,2,3] of the fluctuating order parameter field $\varphi(\mathbf{r})$ allows one to analyze the equilibrium and non-equilibrium properties of the system. The fluctuating field is treated as a superposition of fluctuations on sequentially increasing length-scales $a \sim r_0$, na, n^2a, n^3a ... . At each length-scale R, the fluctuating field is a system of relatively independent wave pockets of size R, and constructed from a minimal set of Fourier-harmonics. The critical fluctuations range from a microscopic (usually atomic $r_0 \sim 10^{-7}$cm) length-scale up to the length scale of the correlation radius $r_c >> r_0$. In liquid-gas critical point and in critical solutions, the order parameter is a conserving quantity, and the relaxation time of fluctuations increases with scale, ranging from microscopic times $\theta(r_0) \sim 10^{-12}$-$10^{-13}$ s up to the relaxation time $\theta(r_c)$. Both r_c and $\theta(r_c)$ increase as the system nears the critical temperature T_c. At equilibrium, the correlation radius yields the power law $r_c = r_0 \varepsilon^{-\nu}$, where $\varepsilon = (T-T_c)/T_c$ is the reduced temperature, and $\nu \approx 2/3$ is the critical exponent of the correlation radius. The relaxation time at a length-scale r depends on the scale as $\theta(r) = \theta(r_0)\varepsilon^{-(3\nu+z)}$, where z is the viscosity critical exponent. Recently, the ZENO experiment[4] has set a benchmark $\varepsilon \sim 10^{-7}$-10^{-8}, $r_c \sim 1$-10 mm, and $\theta(r_c) \sim 10^1$-10^3 s; then, the critical range is about fifteen orders of magnitude range of relaxation times . This was achieved, and is only possible, under microgravity conditions.

The fluctuations on a given length-scale may be treated as a subsystem of the hierarchical system. This subsystem is characterized by the probability distribution function (PDF) of wave pocket amplitude, and in particular by the mean square amplitude $\langle \varphi_R^2 \rangle$, the second moment of this PDF. At equilibrium, these characteristics are described by the scaling theory[1,2]; the most

important predi ctions are the universal non-Gaussian form of PDF (this prediction was never directly tested by experiment) and the power law for $<\varphi_R^2>\sim R^{-(1+\eta)}$ (confirmed by scattering experiments).

For quasistatic changes of temperature and other thermodynamic parameters, fluctuations in the critical range substantially change only at the large scale boundary of the hierarchy, at $R\sim r_c$. One can say that, in the first approximation, the size of the critical range is the main changing characteristic. Because of short relaxation times of smaller scale fluctuations, this remains true for characteristic times of changes greater than the relaxation time on correlation radius scale, and in particular in steady and near-steady states. Then, in spatially inhomogeneous states with not too large gradients ($d\, r_c /r \ll 1$), the correlation radius as a function of position and time becomes a "local" characteristic $r_c(\mathbf{r},t)$ of the critical liquid when slow in time and slow varying in space changes of thermodynamic parameters perturb the thermodynamic equilibrium in the liquid.

In a steady state with a correlation radius gradient (resulting, for example, from temperature inhomogenuity), the diffusion of fluctuations of the largest length scale results in an enhanced heat conductivity, and other effects; an extensive review of transport coefficient enhancement see [5]. Because of a large lifetime of those fluctuations, they diffuse like particles in liquid. To estimate the additional heat transfer, one takes into account the diffusion coefficient $D\sim 1/(\eta R)$ of these "particles". Here, η is the viscosity at the correlation radius scale, that coincide with the macroscopic viscosity. The equilibrium "particle" number density of correlation radius sized "particles" is $n_f \sim 1/r_c^{\,3}$. For given correlation radius gradient grad r_c , the

length l at which this concentration vanish is determined by the condition $dr_c = l \text{ grad } r_c \sim r_c$. The "particle number" current is $J = D_n \text{ grad } n_f \sim (D/ r_c^{\ 4}) \text{ grad } r_c$. This is equivalent to a flow $J\, r_c^{\ 3}$ of the critical component, with excess energy density $dE = c_p d\varepsilon$, c_p being the heat capacity at constant pressure. Usually, the correlation radius gradient is caused by the temperature gradient: $\text{grad } r_c = d\, r_c/d\varepsilon \text{ grad}(T/T_c)$, so that the relations takes the more familiar form of the heat transfer equation

$$J = -\Lambda \text{ grad } T, \quad \Lambda \sim c_p / (\eta r_c). \qquad \mathbf{1}$$

The heat conductivity is enhanced by the diffusion mechanism, the heat diffusivity $D_T = \Lambda / c_p \sim 1/\eta r_c$. Those relations (first derived in 1969-see [6]) are confirmed in the dynamic renormalization group based on mode-coupling theory and using the 4-D expansion.

From the above arguments, we suggest the critical heat current of the form

$$J = -\Lambda_r \nabla r_c, \qquad \mathbf{2}$$

with Λ_r being, close to the critical point, a singular power function of the distance to the critical point. This form gives a unified description of energy transfer enhancement in steady and slowly relaxing transient states with temperature, and/or with density and pressure gradients.

Near a wall, the fluctuations are altered by the liquid-wall interactions[7]. A fluctuation boundary layer of the correlation radius thickness exists even in equilibrium. From the above arguments, one expects that the layer with modified fluctuation characteristics will have the thermal resistivity different from the bulk one. This effect may explain some of delays in relaxation reported by microgravity researchers, it becomes significant very close to the critical point, and needs to be experimentally tested.

3. RAPID PARAMETER CHANGES AND HOMOGENEOUS NON-EQUILIBRIUM STATES.

In this section we consider, following ref. 8 and 9, a near-critical transient state that can not be described only in terms of a "local" correlation radius. Near T_c, a relatively small sudden temperature change may strongly perturb the equilibrium on a wide range of scales, triggering a macroscopically homogeneous violation of local equilibrium. The fluctuations on the atomic length scale r_0 play the role of a "thermal bath" for the rest of the degrees of freedom. At times t >> $\theta(r_0)$ (for room temperatures and atomic scale $r_0 \sim 10^{-7}$ cm, $t(r_0) \sim 10^{-12}$ sec) one characterizes this "thermal bath" by a time-dependent temperature T(t). This is the temperature measured by devices thermally coupled to the liquid. In the case considered here, the time t_{ch} of the rapid temperature change dT is large when compared to $\theta(r_0)$, but it is negligibly small when compared to t®, and we may consider a sharp temperature step at t=0.

One represents the order parameter field f(**r**,t) as a sum of Fourier-harmonics

$$\phi(\mathrm{r},t) = \sum_{\mathrm{k}=0}^{\mathrm{k}_\lambda} \phi_{\mathrm{k}}\, e^{-i\mathrm{kr}} \; ; \qquad \mathbf{3}$$

$\varphi(\mathbf{r},t)$ is a semi-macroscopic, real field ($\varphi_k=\varphi_{-k}^*$). The variable cut-off length $\lambda=1/k_l$ is introduced in (3) following the Wilson-Kadanoff renormalization group (RG) method[1,2]. The probability $W_{eq,l}(f)D\varphi$® to find the equilibrium system in an element $D\varphi$ of the configuration space defines the effective Hamiltonian H_λ [1,2]:

$$W_{eq,\lambda}(\phi)D\phi = e^{\frac{F_\lambda - H_\lambda(\phi)}{k_b T_c}} D\phi, \quad F_\lambda = -k_b T_c \ln \int e^{-\frac{H_\lambda}{k_b T_c}} D\phi,$$
$$H_\lambda = -F_{reg} - k_b T_c \ln \sum_{(\phi(r))} e^{-\frac{H^{(mic)}}{k_b T_c}}, \quad F_{reg} = F - F_\lambda. \qquad \mathbf{4}$$

Here and below, the subscripts $_{fin}$ and $_{in}$ label the characteristics of the final and the initial (t<0) states of the system. In the definition (6), $H^{(mic)}$ is the microscopic Hamiltonian of the system, k_b is the Boltzmann constant, F is the equilibrium free energy of the system, F_λ and F_{reg} are the singular and the regular parts of the free energy respectively[2]. The sum in (4) is over all states of the system with φ(r) a given function. The field φ(r) defined by (3) represents only a small fraction of the degrees of freedom of the system. Most of the degrees of freedom belong to small length scales r<λ. The effective Hamiltonian $H_\lambda(\varphi,e)$ is defined as an average over these small scale degrees of freedom. Up to a regular function of ε, $H_\lambda(\varphi,e)$ is the free energy of the system in the equilibrium state with a given configuration of the large scale field φ(r).

In the simple standard model (model B of ref. 10) the fluctuation kinetics of a conserved scalar order parameter field φ(**r**,t) is described by the Langevin equation of a general form

$$\frac{\partial \phi}{\partial t} = -\Delta \Gamma_\lambda \left(-\frac{\delta H_\lambda}{\delta \phi} + f_{\lambda,ext}\right). \qquad \mathbf{5}$$

The extraneous random force f_{ext}(**r**,t) models the interaction of the order parameter with small-scale degrees of freedom of the system. The kinetic operator Γ_λ and the effective Hamiltonian H_λ are dependent on the cut-off length λ. The dynamic renormalization group (DRG) gives a method to find the changes in the equation (5) when λ is increased from an old value λ_1 to a new

value λ_2; an essential condition of applicability of the method is the thermal equilibrium at length-scales $\lambda<\lambda_2$. In DRG, G_λ and H_λ are completely determined by the equilibrium on scales $R<\lambda$. The calculation below comes from this observation. The scales $R>\lambda$ are then not in equilibrium state, and exchange energy with smaller scales.

One has to study separately a step towards the critical point ($r_{c,fin}>>r_{c,in}$) in which a new range of strongly interacting fluctuations appear, and a step away from the critical point ($r_{c,fin}<<r_{c,in}$) where a large range of critical fluctuations disappears. Following the dynamic RG method[10,2], we introduce a variable scale $\lambda >> r_0$. The assumption is that at times $t \sim \theta(\lambda)$ the fluctuations on length scales $r< \lambda$ have approached the new equilibrium. The form of Langevin equation (5) is determined by the effective Hamiltonian $H_\lambda(f)$ and the kinetic operator G_λ (generalized mobility). One obtains H_λ and G_λ by taking an average over the fluctuations on scales $r<\lambda$ which are in the final equilibrium state. The forms of H_λ , G_λ, and thus of the equation (5) coincides then with that for fluctuations in the final equilibrium state; the initial conditions for the range $r>\lambda$ are defined by the initial (at $t<0$) state of the system.

Consider first a temperature step away from the critical point[8], so that $r_{c,fin}<<r_{c,in}$. Most important are changes in the fluctuation picture in the range of scales $r_{c,fin}<r<r_{c,in}$; we chose the length λ in this range. At $t > \theta(l) > \theta(r_{fin})$ the scales $r < \lambda$ have approached the new equilibrium characterized by the new correlation radius r_{fin}, and the RG calculation at $t>\theta(r_{fin})$ gives H_λ as a free field Hamiltonian [1,2]

$$H_\lambda = \sum_{k<k_\lambda} H_k \quad , \qquad H_k = \frac{1}{2\chi_{fin}}|\phi_k|^2 . \qquad \mathbf{6}$$

Here, $\chi_{fin}\sim\chi(\varepsilon_{fin})\sim\varepsilon_{fin}^{-\nu(2-\eta)}$ is the susceptibility of the system in the final state (the isothermal compressibility for the liquid-gas system). For the time-dependent average $M_{k(t)}=<|\varphi_k(t)|^2>$ one obtains

$$M_k(t) = (M_{k,in} - M_{k,fin})e^{-\frac{2t}{\tau_k}} + M_{k,fin}, \quad M_{k,in} = <|\phi_k|^2>_{in}, \quad M_{k,fin} = 2k_b T_c \chi_{fin}; \quad \tau_k = \frac{1}{D_{fin}k^2}. \qquad \mathbf{7}$$

The diffusion coefficient D_{fin} is scale-independent at the large length scales λ with $k<1/\lambda<<1/r_{c,fin}$.

The rapid increase of the temperature requires more energy than a slow heating. The effective Hamiltonian $H_\lambda(\varphi)$ is by definition (6) the free energy of the system in a state with given φ_k, $k<1/\lambda$. The entropy in this state may be written as $S_\lambda=-\partial H/\partial T=(1/T_c)<H_k>(\partial\ln\chi/\partial\varepsilon)$. The contribution of a single harmonic φ_k to the entropy is $s_k=(1/T_c)<H_k>(\partial\ln\chi/\partial\varepsilon)$. The single harmonic internal energy U_k is (according to the thermodynamic formula U=F+TS) $U_k=<H_k>+T_c s_k$. Let the initial state be at the critical point $\varepsilon_{in}=0$, and $<|\varphi_k|^2>_{in}\sim k^{-2+\eta}$. In the final equilibrium state one finds $<|\varphi_k|^2>_{fin}\sim\chi(\varepsilon_{fin})$, $k<<1/r_{c,fin}$. Summing up the contributions from all large-scale harmonics, one obtains the excess energy U_{stor} stored at $t\sim\theta(r_{c,fin})$:

$$U_{stor}(0) = \frac{V}{2}\frac{\partial\ln\chi_{fin}}{\partial\varepsilon}\frac{1}{\chi_{fin}}\int_0^{1/\lambda} <|\phi_k|>_{in}^2 \frac{d^3k}{(2\pi)^3} \approx Nk_b T_c \varepsilon_{fin}^{3\nu-1}. \qquad \mathbf{8}$$

Here $\lambda\sim r_{c,fin}$, and $N\sim V/r_0^3$ is the number of molecules in the system. At $t>\theta(r_l)$ the stored energy

is gradually converted into heat. The released heat $Q(t)=U_{stor}(0)-U_{stor}(t)$ as a function of time is

$$Q(t) = \frac{V}{2}\frac{\partial \ln \chi}{\partial \varepsilon_{fin}}\frac{1}{\chi_{fin}}\int_0^{k_\lambda}[<|\phi_k(0)|^2> - <|\phi_k(t)|^2>]\frac{d^3k}{(2\pi)^3} \propto U_{stor}(0)[1-(\frac{\tau(r_{c,fin})}{t})^{\frac{1+\eta}{2}}]. \qquad \mathbf{9}$$

In a system adiabatically insulated at $t>\theta(r_{fin})$, the time-dependent temperature yields the relation $dQ=C_v dT=CT_c d\varepsilon(t)$, with $C_v \sim \varepsilon^{3n-2}$ being the heat capacity at constant volume. The approach of the temperature to equilibrium follows now from the form (6) of the heat release. For $t>\theta(r_{c,fin})$ one obtains

$$\varepsilon(t)-\varepsilon_{fin} \sim \varepsilon_{fin}[\tau(r_{c,fin})/t]^{\zeta_+}, \quad \zeta_+ = (1+\eta)/2. \qquad \mathbf{10}$$

Let us now consider a step toward the critical point[9]: $\varepsilon_{in} >> \varepsilon_{fin}$. In contrast to the above case, the harmonics φ_k in the range $r_{c,in}<1/k<r_{c,fin}$ strongly correlate in the final state, and the problem cannot be reduced to that of a single harmonic. The suggested scenario is sequential equilibration: at a given time t, the fluctuations on small scales up to a time-dependent equilibration length scale $\lambda_{eq}(t)$ will equilibrate while the harmonics φ_k with $k<1/\lambda_{eq}$ will retain the initial magnitudes. These magnitudes are small compared to the final ones, and may be neglected. The statistics and the kinetics of the fluctuations on scales $r<\lambda_{eq}(t)$ yield then the equilibrium scaling relations [1,2,6]: on a scale $\lambda<\lambda_{eq}(t)$ the relaxation time is $\theta(\lambda)\sim\lambda^2/D(\lambda)\sim\lambda^{3+z/n}$, where z is the critical exponent for the viscosity[5,10]. The time dependence of λ_{eq} is controlled by the condition that $\theta(R\ )<t$ for $r<\lambda_{eq}(t)$, and $\theta(R\ )>t$ for $r>\lambda_{eq}(t)$. The scale $\lambda_{eq}(t)$ has then the equilibration time $\theta(\lambda_{eq}(t))\sim t$; this relation gives the scaling law for $\lambda_{eq}(t)$

$$\lambda_{eq}(t) = r_{in}\,[t/\tau(r_{in})]^{p}, \;\; p = \frac{\nu}{3\nu + z}. \qquad \textbf{11}$$

The theoretical values (see ref. 5) $\nu \cong 0.630$ and $z \cong 0.063$ give $p \cong 0.32$.

The sequential "cooling" of large scale fluctuations is accompanied by the release of heat Q(t), transferred to smaller scales and through the small scale "heat bath" to the thermostat. The scaling formula for the entropy $S(\lambda_{eq})$ of fluctuations on scales $r<\lambda_{eq}$ is $S_c - S(\lambda_{eq}) \sim (\lambda_{eq}/r_0)^{(1-3\nu)/\nu}$. The energy conservation law dQ=TdS results in

$$Q(t) \;=\; T_c\,[S(t) - S(\theta(r_{in}))], \quad Q_{fin} - Q(t) \;\propto\; Q_{fin}\,[\theta(r_{c,in})/t\,]^{(3\nu-1)/(3\nu+z)}, \;\; t > \theta(r_{c,in}), \qquad \textbf{12}$$

where $Q_{fin} \sim T_c \varepsilon_{in}^{3\nu-1}$ is the total amount of heat released.

Consider now a system that is adiabatically insulated during relaxation. At $t>t_1$, the heat Q(t) transferred from the large scales to the smaller ones having $R<\lambda_{eq}$ will result in an increase in the temperature T(t). A rapid cooling results then in a temperature minimum. The heat capacity $C_v(t_1)$ of the cooling at a time scale t_1 is a fraction x, $0<x<1$, of the equilibrium heat capacity C_v because the rapid cooling leaves the large scale fluctuations unchanged; from the scaling arguments one writes $C_v \cong A\varepsilon^{3\nu-2} = A(r_c/r_0)^{(2-3\nu)/\nu}$, $C_v(t_1) \cong xA(\lambda_{eq}(t_1)/r_0)^{(2-3\nu)/\nu}$. The conserved internal energy of the adiabatically insulated system is $U_{fin} = U_{in} - DU$, $DU = C_v(t_1)(T_{in} - T_1) \cong C_v(t_1)T_c(\varepsilon_{in} - \varepsilon_1)$. The quasistatic cooling characterized by the same decrease DU of the internal energy determines the final equilibrium state and the difference $\varepsilon_{in} - \varepsilon_{fin} \sim x(\varepsilon_{in} - \varepsilon_1)$, where $\varepsilon_1 = (T_1 - T_c)/T_c$ and T_1 is the temperature at the insulation time $t=t_1$. To arrive at $\varepsilon_{fin} << \varepsilon_{in}$, the temperature T_1 must be below T_c so that $\varepsilon_1<0$, $|\varepsilon_1| \sim \varepsilon_{in}$. The phase separation at $\varepsilon(t)<0$ is avoided

if at any time the critical nucleus has the size $R_c(t)>\lambda_{eq}(t)$. The time-dependent heat capacity of the system is $C_v(t)\sim xA[\lambda_{eq}(t)/r_0]$, with $\lambda_{eq}(t)$ given by formula (9). The thermodynamic relation $dQ(t)=C_v(t)dT=C_v(t)T_c d\varepsilon(t)$ leads then to the scaling law for the reduced temperature

$$\varepsilon(t) \propto \varepsilon_1[\theta(r_{c,in})/t]^{\zeta_-}, \quad \zeta_- = 1/(3\nu + z). \qquad \textbf{13}$$

The critical exponent $\zeta_-=1/(3n+z)$ differs from ζ_+ given by (7). Using the approximate theoretical values for the critical exponents (see ref. 5), one obtains for the liquid-gas and for the binary mixtures critical points ζ_+»0.517 and ζ_-»0.512. Both exponents are surprisingly close to each other and to the mean-field value 1/2.

In a general case, the near-critical system may simultaneously have slowly relaxing regions and rapidly relaxing parts. Then, the diffusion of fluctuations will lead to an interesting situation not yet studied.

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